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## Clays, Zeolites and Related Structures in Catalysis

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## Chapter 1

### Clay and clay minerals in catalysis

#### 1.1. Introduction, clay and clay minerals

Clays and/or clay based materials are well suited for the eco-friendly (green) chemistry. The main advantages of clays and clay minerals are that they are abundant, cheap, non-corrosive, recyclable, recoverable and environmentally friendly. Moreover, they have abilities to promote numerous organic conversions under solvent-free conditions and they can be recycled without a significant loss of activity, because they can be easily separated from the reaction mixture.

Clays occur in rocks of any type as a sedimentary, igneous or metamorphic.<sup>1</sup> Moreover they are also dispersed in atmospheric aerosols<sup>2</sup> and suspended in the water of rivers, lakes, seas, oceans etc.<sup>3</sup> Over the years, efforts have been made to unify the definition of clay and clay minerals by several nomenclature committees, such as AIPEA (Association Pour l'Étude des Argiles) and CMS (Clay Mineral Society). However, the definition is still inconsistent and the professionals or the branches interested in clay science try to create their own definition the most suitable for the exact field (e.g. geologist, mineralogist, petrologist, sedimentologist, etc.).<sup>3,4</sup>



The joint nomenclature committees (JNCs) of the AIPEA and CMS in 1995 defined term clay as “...a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with (sic) dried or fired”.<sup>5</sup> Origin of the clays or clay minerals are not mentioned in their definitions, thus, these materials may be also synthetic.

Silicates with layered structure (phyllosilicates) are main component of the clays. Moreover, clays may contain other minerals (crystalline or amorphous  $\text{SiO}_2$ , zeolites and/or oxides and hydroxides of iron and aluminum, etc.) and organic matters, which may or may not affect the plasticity, hardness, and other features of the clays upon drying or firing. Minerals presented in the clays can be divided to the two main groups according the AIPEA and CMS<sup>5</sup>:

- i) Clay minerals, these include all phyllosilicates and other minerals from allophane group or hydroxides, oxides, and oxyhydroxides which give plasticity to the clays after drying or firing. Clay minerals are only presented in minority in the clays.
- ii) Associated minerals, these may be presented in clays, but do not belongs to the mentioned above.

Impurities in the clays are very hard to detect because of their low content and may be associated to their instability as a catalysts and catalysts supports. However, some minerals such as iron and copper oxides are catalytically active.<sup>6,7</sup> Classification scheme for clay minerals and phyllosilicates could be found for example in B. K. G. Theng (2019).<sup>8</sup>



Clay minerals may adopt variety of particle (crystal) shapes and not only in different species but also within specie (e.g. halloysite particles may adopt cylindrical, spheroidal, and platy (tabular) forms.<sup>9-18</sup> Among the basic coordination polyhedra, from which the structures of phyllosilicates are built, include tetrahedra  $[\text{MO}_4]^{m-}$  and octahedra  $[\text{NO}_6]^{n-}$ . The central cations of tetrahedra (T) are designated as M, and in addition to the most common  $\text{Si}^{4+}$ , they can also be, for example,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ge}^{4+}$ . The central cations of octahedrons are designated as N and may be  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Li}^{+}$ , etc. In phyllosilicates, some octahedron anions appear not only as  $\text{O}^{2-}$  but also  $\text{OH}^{-}$  or  $\text{F}^{-}$ .<sup>15,19</sup>

Linkage between adjoining tetrahedra occurs through corner sharing such that the basal oxygens are approximately coplanar, forming an open hexagonal network, while the apical oxygens point in the same direction. On the contrary octahedral sheet consists of linked aluminum or magnesium octahedra in which the central cations,  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$ , are coordinated, and equidistant, to six hydroxyl anions. Combination of two types of sheet in equal proportions gives rise to the 1:1 (T-O) silicate layer type as in case of kaolinite (diocathedral) and serpentine (trioctahedral). More precisely, The 1:1 structure consists of the repetition of one tetrahedral and one octahedral sheet, while one octahedral sheet sandwiched between two inward-pointing tetrahedral sheets gives layer 2:1 (T-O-T) structure, as in case of pyrophyllite (dioctahedral) and talc (trioctahedral).<sup>8,20</sup>

Unit cell for the 1:1 layer structure includes six octahedral sites and four tetrahedral sites, on the contrary six octahedral sites and eight tetrahedral sites characterize the 2:1 lays unit cell. Structures with all the six octahedral sites occupied are



known as trioctahedral and structures with only four of these sites occupied are known as dioctahedral.<sup>20,21</sup>

Clay structure can be either electrically neutral or negatively charged<sup>22</sup>. Electrically neutral may be clay structure when

- i) the octahedral sheet contains trivalent cations in two octahedral sites ( $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) with vacancy in the third octahedron;
- ii) divalent cations (e.g.  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ) occupy all the octahedral sites;
- iii) The tetrahedral sheet contains  $\text{Si}^{4+}$  in all tetrahedra.<sup>22</sup>

On the contrary clay layer may be the negatively charged when

- i)  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$  are substituted by lower charge cations in octahedral sites;
- ii)  $\text{Al}^{3+}$  is substituted by  $\text{Si}^{4+}$  in tetrahedral sites;
- iii) Vacancies are presented in the structure.<sup>22</sup>

Three the most used phyllosilicates in organic catalysis are kaolinite, halloysite and chrysotile. These clays with other 2:1 type phyllosilicates may catalyze wide variety of organic conversions. Summarized organic conversions catalyzed by different clay may be found in.<sup>8</sup>

In advance of the discussion of the catalytic reactions themselves, selected representatives of phyllosilicates will be introduced in more detail. Activity of the clays and clay minerals is a consequence of their high surface area, chemical nature, local concentration effects (adsorption on the solid





surface lead to the increase of the reactant concentrations), and low dimensionality (molecules on the surface are more likely to meet).<sup>23</sup>

### *1:1 layer structure*

In the dioctahedral 1:1 structure (e.g. kaolinite, serpentine) each layer is about 0.7 nm thick and one surface of the layer consists completely of basal oxygen atoms, which are part of the tetrahedral sheet and second surface is composed mostly of OH groups from the octahedral.<sup>20</sup>

Generally minerals with 1:1 layer structure belongs to the kaolin group with a general composition  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Polytypes in the kaolin group are kaolinite, dickite and nacrite. Halloysite is a hydrated polymorph of kaolinite with curved layers. The predominance of  $\text{Al}^{3+}$  in octahedral sites is characteristic for the kaolin group.<sup>20</sup>

Kaolinite structure was the first structural interpretation from powder XRD (X-ray diffraction) pattern. It was estimated, that kaolinite belonged to the monoclinic *Cc* symmetry with  $d(001) = 1.43$  nm and is formed by two layer structure.<sup>24</sup> Afterwards Brindley and Robinson (1945 and 1946)<sup>25,26</sup> showed that monoclinic symmetry does not satisfy exactly the XRD pattern and the symmetry is most likely triclinic *C1*.

According the B. K. G. Theng (2019)<sup>8</sup> basal or  $d(001)$  spacing correspond to the repeat distance along the c-axis (0.713 nm), because kaolinite do not contain interlayer materials. Value 0.713 nm is also equal to the thickness of an individual layers which are stacked at each other with a translation of –



$a/3$ .<sup>27</sup> Layer structure of kaolinite is electrically neutral in ideal unit composition, however, in reality, many kaolinites carry a negative charge. This negative charge may be caused by presence of an alumino-silicate gel, which coats the surface<sup>28</sup> or by inclusion of mica and smectite layers in the particle.<sup>29-32</sup>

Predicted structure of kaolinite was confirmed by Hobbs et al. (1997)<sup>33</sup> who modelled the kaolinite structure by an all-atom ab initio energy minimization method. Bish (1993)<sup>34</sup> estimated that low temperature influence the interlayer separation but has little effect on tetrahedral and octahedral parameters by using a low-temperature neutron powder diffraction study. The single-crystal synchrotron data confirmed C1 symmetry and determined unit-cell parameters of the kaolinite:  $a = 0.5154(9)$  nm,  $b = 0.8942(4)$  nm,  $c = 0.7401(10)$  nm,  $\alpha = 91.69(9)^\circ$ ,  $\beta = 104.61(5)^\circ$ , and  $\gamma = 89.82(4)^\circ$ .<sup>35</sup> These results were successfully confirmed also by X-ray and neutron powder diffraction with slight variation of  $\beta$  angle value.<sup>36</sup>

Kaolin minerals has tendency to have poor structural order which is caused by a series of stacking faults or defects in the structure. These structural errors give a rise of the variety of disordered polytypes, which have significantly different XRD patterns (broad and asymmetrical peaks) compared with well-ordered kaolinite (sharp and narrow peaks).<sup>37-39</sup>

General formula for Dickite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and for the first time was introduced.<sup>40</sup> Crystal structure of dickite belongs to the monoclinic space group  $Cc$  and the cell parameters are:  $a = 0.5138(1)$  nm,  $b = 0.8918(2)$  nm,  $c = 1.4389(2)$  nm,  $\beta = 96.74(2)^\circ$ .<sup>41</sup> As well as the dickite the nacrite has the same space crystal structure group ( $Cc$ ) which is made up by



stacking six layers.<sup>42</sup> Parameters of the unit cell were estimated by Blount et al. (1969)<sup>43</sup>:  $a = 0.8906(2)$  nm,  $b = 0.5146(1)$  nm,  $c = 1.5664(3)$  nm, and  $\beta = 113.58(3)^\circ$ . There are two forms of nacrite the hydrated and dehydrated nacrite. The hydrated form contains one water molecule per  $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$  in the interlayer space and the basal distance is 0.842 nm.

Hydrated polytype of kaolinite with general formula  $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4 \times 2\text{H}_2\text{O}$  is known as halloysite. It was proven by Hofmann et al. (1934)<sup>44</sup> that the water is present in the interlayer space and the layer periodicity (basal spacing) is close to 1 nm.<sup>45</sup> When the thermal treatment is applied to the halloysite the interlayer water could be irreversibly removed.<sup>46</sup> The dehydration is starting at 70-100 °C and the whole structure is completely collapsed at 400 °C. The collapse is connected with decrease to 0.7 nm.<sup>47-49</sup>

Other group of 1:1 minerals is the serpentine group which contains the trioctahedral silicates. General formula of serpentine group is  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  and to the group belong Mg-rich minerals as lizardite, antigorite, and chrysotile.<sup>50</sup>

## *2:1 layer structure*

The tetrahedral sheets are inverted and 2/3 of the octahedral hydroxyl groups are substituted by tetrahedral apical oxygen atoms in the 2:1 layer structure.<sup>20</sup> In this case the layer surfaces consist of basal oxygen atoms (tetrahedral). The periodicity along the c-axis varies from different types of



phyllosilicates, e.g. 0.91-0.95 nm for talc and pyrophyllite, about 1.2 nm for smectite and vermiculite, and 1.40-1.45 nm for chlorite. The higher values are connected to the interlayer occupancy. Talc interlayer space is empty which corresponds to the lowest values.

The differences in the 2:1 phyllosilicates are in terms of charged layers. For example pyrophyllite and talc are electrically neutral (hence no charge-balancing cation is present in the interlayer space), but smectite, vermiculite, mica, and chlorite are negatively charged.<sup>27</sup>

Diocahedral 2:1 phyllosilicate which can be usually found in soils and sedimentary rocks is named illite.<sup>51</sup> Term “illite” can be also used as a group name for 2:1 minerals with a non-expandable layer and a wide variety of chemical compositions, which differs based on their genetic environments (hydrothermally altered igneous rocks, shales, and mudstones).<sup>52,53</sup> However, there is a lot of data which is in a good correlation a high-quality three-dimensional structure refinement for illite is still missing, but results suggest that cations are statistically distributed over all three octahedral sites.<sup>54,55</sup> Much more is discussed the stability of illite in natural environments, because the evidence of the metastability of illite was reported.<sup>57</sup>

Phyllosilicates with similar 2:1 structure to previous described but with a total (negative) layer charge 0.2-0.6 per half unit cell are smectites. Smectites could be divided to the diocahedral and triocahedral, when octahedral sheet may either be dominantly occupied by trivalent cations or divalent cations, respectively.<sup>27</sup>



There is a variety of cations which may occupy tetrahedral, octahedral, and interlayer sites in smectites. Tetrahedral sites are commonly occupied by  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ , and  $\text{Fe}^{3+}$  and octahedral sites could be occupied by  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Li}^+$ . Interlayer space is the most reactive part of the smectites and the cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) balance the negative layer charge and may be hydrated and exchangeable.<sup>27</sup> In the interlayer spaces could be also found water molecules which smectites contain in several forms.<sup>57</sup> Hydration of smectites could be divided to these pH-dependent modes<sup>27</sup>:

- (i) Interlayer hydration of internal surfaces,
  - a. hydration of interlayer cations,
  - b. interactions of clay surfaces with water molecules and interlayer cations,
  - c. water activity in the clay-water system,
- (ii) continuous hydration related to an unlimited adsorption of on internal and external surfaces,
- (iii) capillary condensation of free water in micropores.

The hydration process of the interlayer could be influenced by several features as variation of electrostatic surface potentials (caused by differences in layer charge location), hydration energy of the interlayer cation, water activity, water molecules polarization by interlayer cations, and size and morphology of smectite particles.<sup>58-65</sup> Inner sphere (the cation is firstly directly bounded to the surface and secondly to water molecules) and outer sphere (interlayered cation is completely surrounded by water molecules and may react with the clay mineral surface through its water ligands) hydration complexes can be formed in interlayer space.<sup>27</sup>



The most important phyllosilicates belonged to the group of trioctahedral smectites are hectorite, saponite, and saunconite and the most important members of the dioctahedral group of smectites are volkonskoite, nontronite, beidellite, and montmorillonite.<sup>66</sup> Montmorillonite is used very often in organic synthesis in the laboratory and as well in the industrial scale.<sup>66</sup>  $(M_y^+ \times nH_2O)(Al_{2-y}^{3+}Mg_y^{2+})Si_4^{4+}O_{10}(OH)_2$  is a general formula of montmorillonite.<sup>27</sup> The most of the reactions catalysed by montmorillonites make use of the acidic nature of cation-exchanged or acid-treated clays.<sup>67</sup>

Another phyllosilicate with 2:1 structure which is negatively charged is vermiculite. On the contrary to the montmorillonite the vermiculite is generally trioctahedral smectite which layers are separated by hydrated cations occupying the interlayer space.<sup>27</sup> Vermiculite may be found as macroscopic vermiculites which contains large particles and predominantly in trioctahedral structure. On the contrary the microcrystalline vermiculite may be found as trioctahedral and as well as dioctahedral.<sup>68</sup> Basal spacing of vermiculite as well as generally smectites is dependent on the nature of the inorganic counterions and the relative humidity of the atmosphere<sup>68</sup> and may be found in three hydration states:

- i) fully dehydrated (basal spacing 0.9-1.0 nm; zero sheets of water molecules),
- ii) partially hydrated (basal spacing (~1.2 nm; one sheet of water molecules),
- iii) fully hydrated (basal spacing 1.4-1.5 nm; two sheet of water molecules).



Same value of basal spacing (1.4 nm) as fully hydrated vermiculite has other 2:1 phyllosilicate group with trioctahedral layer structure, chlorites. Generally, chlorites may be divided to the four groups<sup>69</sup>:

- i) trioctahedral chlorites (the most frequent),
- ii) dioctahedral chlorites,
- iii) di-trioctahedral chlorites,
- iv) tri-dioctahedral chlorites.

Other types of phyllosilicates that are worth mentioning are allophane and imogolite, which are hydrous alumino-silicates of short-range order. They are nanosized and frequently coexist in the clay fraction of many soils, in particular those that have volcanic origin.<sup>27</sup> From the XRD studies is clearly evident that in many times the allophanes could be considered as amorphous. However, there are several studies that show that the allophane consists of hollow spherules (nanoballs) with an outer diameter ~5 nm and a wall thickness of 0.7–1.0 nm, thus the allophane are described as short-range order more often than.<sup>70,71</sup>

Layer structure of allophane has numerous defects (vacancies), but the layer structure of imogolite is essentially made up of a 1:1 type layer. The defects in allophane allow free water diffusion into and out of the intraspherule void space.<sup>72-76</sup>

The last but not least will be mentioned palygorskite and sepiolite which differ from other layer silicates. They have in structure a continuous two-dimensional tetrahedral sheet, but the continuous octahedral sheets are missing. They



structure is formed by ribbons (fibrous particle). Each ribbon is connected/linked to the next inversion of  $\text{SiO}_4$  tetrahedra along a set of Si-O bonds. Fibrous particles of sepiolite vary in length (10-5,000 nm), in width (10-30 nm), and in thickness (5-10 nm). Similar values could be determined for the palygorskite, however, the maximum length of the particles is shorter about 2,000 nm and on the opposite the minimum length is higher about 1,000 nm.<sup>8,27</sup> Under the ambient conditions of temperature and humidity in their structure is presented free (zeolitic) water and exchangeable counterions (Brigatti et al. 2013). Mild thermal treatment (<200 °C in air) results in zeolitic water removal from the structure.

Other literature should be consulted for more details, structure models and key references to the extensive literature, e.g. B. K. G. Theng (2019)<sup>8</sup>, M. F. Brigatti (2006)<sup>27</sup>, A. Swineford (1960)<sup>77</sup>, F. Bergaya and G. Lagaly (2013)<sup>78</sup>, and C. Weaver and L. D. Pollard (1973)<sup>79</sup>.





## 1.2. Clay activation and modification

Clays and clay minerals have ability to act as solid acids either in the Brønsted or Lewis sense, which is main reason why they are catalytic active.<sup>23</sup> Surface acidity of the clays may also be modified (in some case we may say controlled) by cation exchange, dehydration, heating, and wetting. For example dehydration may lead to highly acidic clay surface and preheated temperature may influence relative concentration of Brønsted and Lewis acid sites.

Acid activation could be performed by treating the clay with dilute solution of a mineral acid as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, etc. and the ultrasonic treatment and microwave irradiation may accelerate the acid activation of the clay.<sup>80</sup> Alternative acid activation of the clay may be done by passing a dilute aqueous suspension of the clay mineral through a H<sup>+</sup> exchange resin<sup>81,82</sup>, or hydronium ions for the exchange positions at the mineral surface may be estimated directly by conductometric or potentiometric titration with a suitable base<sup>83</sup>. Clay minerals vary in their resistance and stability to acid attack and in the rate of acid dissolution, which is influenced by the acid type and concentration, duration of the acid treatment, used temperature during treatment and as well by octahedral sheet composition, crystallinity, and particle size of the clay sample.<sup>8</sup>

Common practice in order to enhance and stabilize the surface acidity is usage of mineral acid solutions, which



introduce protons into the interlayer exchange sites.<sup>8</sup> Many clay-catalysed reactions are catalysed by using acid-activated smectites (e.g. K-catalysts). K-catalysts are commercially available and they are used in variety of clay-catalysed reactions as pure or after impregnation with certain metal salts.<sup>84-94</sup> Majority of the K-catalysts are created by montmorillonite, which is treated by HCl (in various concentrations) at 80 – 90 °C.<sup>95</sup> There are a number of used modifications, let's name calcination, ultrasonic treatment, or microwave irradiation.<sup>89,96-102</sup> Acid-activated clays (bentonite, kaolinite, montmorillonite, and palygorskite) have catalytic tradition in industry, e.g. Houdry process (crude oil is converted to high-octane gasoline.<sup>103,104</sup> In the mid 60's synthetic zeolites starting to replace the clays in petroleum industry. Nevertheless, clays and pillared interlayered clays still play key role in the petroleum refining industry.<sup>105</sup>

Acid-activated clays and pillared interlayered clays play significant role in other industry field as in decolourization of oils and fats, in biofuels production and in fine chemicals synthesis.<sup>100,106-120</sup> Pillared interlayered clays are very suitable for using in organic catalysis, because of their large surface area, pore volume, thermal stability, and high surface acidity. Moreover, pillared acid-activated clays have both microporosity and mesoporosity, which are dependent on the level of acid treatment and pillaring conditions.<sup>121,122</sup> More information can be found for example in the reviews by Figueras (1988),<sup>123</sup> Lambert and Poncelet (1997),<sup>124</sup> Ohtsuka (1997),<sup>125</sup> Klopogge (1998),<sup>126</sup> Gil et al. (2000, 2008, 2010, 2011),<sup>127-130</sup> Ding et al. (2001),<sup>115</sup> Cool and Vansant (2004),<sup>131</sup> Bergaya et al. (2006),<sup>132</sup> and Vicente et al. (2013).<sup>133</sup>



Other clay activation may be performed by thermal treatment. Temperature ranges significant for the changes in clay structure are four<sup>134-136</sup>:

- i) < -5 °C (part of the surface-associated water is frozen);
- ii) 25 °C (room temperature) – 300 °C (dehydration connected with water loss from external particle and interlayer surface);
- iii) < 400 °C (dihydroxylation connected with water loss form condensation of two structural hydroxyl groups);
- iv) 600 – 900 °C (structural decomposition and recrystallization).

For example, in the last range (600 – 900 °C) transformation of kaolinite to metakaolinite occurs<sup>137</sup> and/or formation of Al<sup>IV</sup> was observed for montmorillonite.<sup>138</sup> Freezing has also very good influence on increased surface acidity (partial removal of water molecules associated with interlayer counterions by freezing), however, temperature below zero is not so often used for the clay-catalysed organic reactions.<sup>136</sup>

To reduce the time of the thermal treatment is very useful microwave irradiation, which allows heat the reactants directly.<sup>139-141</sup> Moreover, usage of the microwave irradiation leads to the decrease of solvent amount in the reaction or to the solvent free conditions, which is eco-friendly and can be placed into green chemistry.<sup>89,90,142-144</sup> Changes induced by microwaves treatment are similar to them induced by thermal treatment.<sup>140</sup> For example to induce same changes in sepiolite (same value of specific surface area) was needed a



few minutes of microwave treatment and two days of thermal treatment.<sup>102</sup>

Other way to minimize or cancelation of the amount of solvents is usage of ultrasonic activation. Ultrasonic activation does not affect the structure of the clays, but affect the particle size. For example low-frequency ultrasound irradiation applies to montmorillonite lead to the decrease of the average particle diameter. On the other hand use of ultrasound to palygorskite in suspension lead to the particle aggregation.<sup>145</sup>

Clays can be organically modified (named as organoclays) for example by intercalation of quaternary ammonium cations into smectites.<sup>146-148</sup> However, this modification leads to worse thermal stability. Organoclays treated with mineral acids could be used as catalysts of organic reactions. Without mineral acids treatment the organoclays may be successfully used as absorbent of hydrophobic organic contaminants and,<sup>148-152</sup> phase-transfer and triphase catalysts<sup>92,142,153-161</sup>

Other clay modification which is often used is organic modification, which can be divided to the two part: i) intercalation of cationic organic compounds and ii) surface grafting of organosilanes (silylation) and other organic species.<sup>8,162</sup> It has been proven that full and partial occupancy of the interlayer space by organic surfactants or cations promotes catalytic activity.<sup>153,161</sup> Surface hydroxyl density, functionality, and structure of the silane coupling agent, solvent polarity, and reaction temperature are the major feature of the grafting success.<sup>162</sup>



### *Brønsted acidity*

Transfer of a proton from the silicate surface (“solid acid”) to the adsorbed organic species (“base”) is the basic mechanism of the catalytic reaction induced by clays.<sup>67,84,90,163-165</sup> The variety of the clay catalysed organic reaction involving the Brønsted acids is very wide<sup>92</sup> and some of the reaction could be found in Chapter 1.3.

From the studies performed on smectites was proven that Brønsted acid sites essentially arise from the dissociation of water molecules, which are associated with exchangeable cations and the acidity is positively correlated with the ionic potential of the counterion.<sup>166-171</sup>

Water content of the clays is connected to the proton-donating capacity of clay minerals. When water is < 5 wt.% the increase in dissociation of the residual water is observed.<sup>172</sup> When Frenkel (1974)<sup>173</sup> studied the  $\text{Al}^{3+}$  montmorillonite he found out that the surface acidity and concentration of acid sites of dry samples are appreciably larger than for the wet ones. As well as dehydrated (no water content) kaolinite has a very high surface acidity, e.g. kaolinite heated up to 50 °C can mediate the double-bond isomerization of 1-pristene to 2-pristene, while kaolinite heated up to 150 °C is able to catalyse the hydrogen transfer to obtain pristane.<sup>174</sup>

The heating of the clays, e.g. montmorillonite, at more than 200 °C leads to the decrease of the number of the Brønsted acid sites, but the Lewis acidity may actually.<sup>80,92,175,176</sup> As well as the decrease of cracking activity and increase of Lewis acidity was observed after heating montmorillonite at 400 °C



by Mishra and Parida.<sup>177</sup> After calcination above 400 °C all interlayer cation-coordinated water is removed and remains of Brønsted acidity could be explained by the presence of structural hydroxyl groups on planar and edge surface<sup>164</sup>, or by re-adsorption of water to incompletely coordinated ions (e.g.  $\text{Al}^{3+}$  ions).<sup>178</sup>

Dehydration can be easily catalysed by solid acid of low strength, but for the catalysis of alkane (hydrocarbon) cracking the catalyst with very strong Brønsted sites must be used. When the used solid catalyst has acid strength between -16 (strong) and +0.82 (low) the catalyst is capable of catalysis of variety reactions, as isomerization, etc.<sup>179,180</sup>

When the high acid strength is need in the reaction the increase of the reaction temperature may be the solution. However, the reaction may be accompanied with other side reaction and the catalyst may be rapidly deactivated.<sup>8</sup>

### *Lewis acidity*

Ions and molecules which allows accepting pair of electrons from a base acts as an electron-pair donor (Lewis acidity). In the clay catalysis it can be said that Lewis acids are surface sites capable of accepting an electron from a suitable electron donor.<sup>164,181-183</sup> As was already mentioned Lewis acidity can arise from heating up to the point of dehydroxylation, but in general, Lewis acid sites are connected with ferric ions within the layer structure, and under-coordinated aluminium exposed at clay particle edges.<sup>8</sup>



The presence of the Lewis acid sites is connected to the ability of clay minerals to promote oxidation of adsorbed organic molecules, and interlayer complex formation with arenes and substituted arenes mostly followed by their dimerization, oligomerization, and polymerization.<sup>84,92,184</sup> For example, sodium exchanged montmorillonite was successfully used in catalysis of conversion of triphenylamine to N,N,N',N'-tetraphenylbenzidine. The reaction process can be described by electron transfer to structural ferric ions, which lead to creation of the triphenylamine radical cation followed by dimerization, deprotonation, and the benzidine rearrangement.<sup>185</sup> Other explanation could be that the conversion occurs by direct coupling of two radical cations with the benzene rings in the para position, which was continued by proton elimination.<sup>185</sup> Similar process is involved in the oxidation of diaminomaleonitrile and tetrathiafulvalene, when structural Fe<sup>3+</sup> in montmorillonite play key role in the reaction.<sup>186,187</sup>

The oxidation of the hydrocortison in aqueous media in the presence of palygorskite/sepiolite can be described similarly. However, sepiolite is less active than palygorskite, because they have similar layer structure, but sepiolite contains less iron ions in the structure.<sup>188</sup>

Acid treated montmorillonite, exchanged with various polyvalent cations, can catalyse the Brønsted acid conversion of  $\alpha$ -pinene to camphene as well as the Lewis acid rearrangement of camphene hydrochloride to isobornyl chloride.<sup>176</sup> Brønsted and Lewis acidity may operate competitively during the high temperature transformation of limonene in the presence of Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, and H<sup>+</sup>/Al<sup>3+</sup> montmorillonites.<sup>189</sup> Maximum of Lewis acidity was observed



after heating up to 300 °C, on the contrary the maximum of the Brønsted acidity was obtained after thermal treatment at 150 °C. There was also observed the synergy between Brønsted and Lewis acidities which was responsible for the high efficiency of Fe<sup>3+</sup> and Zn<sup>2+</sup> K10 montmorillonites in catalysis of acylation of aromatic ethers with acetic anhydride (Friedel-Crafts reaction).<sup>190</sup>

Since the Brønsted and Lewis acidity may coexist, the determination which one is dominant during the reaction is very difficult.





### 1.3. Organic catalysis

Clays and clay minerals have ability to catalyse many reactions, because bring the reactants together in an environment of reduced dimensionality, increase reaction rates, yields, and product selectivity. Reactions as isomerization (rearrangement into a new molecule/compound with same number and type of atoms but with differing in bonding arrangements), dimerization (two structurally identical compounds, monomers, are combined through covalent bonding or other bonding modes), oligomerization (3-50 monomers are combined into one molecule), and polymerization (converting of the monomer, or mixture of monomers into a large chain-like or network molecule) can be successfully catalysed in the presence of the clays such as acid activated K10 montmorillonite. The reactions may running in the proton-rich mesopores and interlayers, which lead to shape-selectivity and dimensionally confined transformations.<sup>67,85,164,191-194</sup>

In isomerization and dimerization of organic species in the presence of the clay minerals in some cases the reaction is Brønsted acid catalysis, but more often the reaction involves carbocation intermediates. Dimerization can be mediated by electron transfer from the adsorbed monomer to the metal ion (acting as Lewis site) to yield the corresponding radical-cation under certain conditions and over transition metal-exchanged smectites, e.g. conversion of triphenylamine to N,N,N',N'-tetraphenylbenzidine.<sup>195</sup>



Both, Brønsted and Lewis acid sites may be involved in catalysis of polymerization in the presence of clays. Generally, the reaction concern radical-cation intermediates, which are generated by electron transfer from monomer to the exchangeable counterion. Chemical initiators or ionizing radiation can be introduced to the reaction when monomers do not polymerize spontaneously. In the case of polymerization of hydroxyethyl methacrylate, there is no need to involve something more to the reaction, because the reaction is running spontaneously, when clay mineral contains octahedrally coordinated transition metal ions, as  $\text{Fe}^{2+}$ . In some cases the surface modification of the clays is needed.<sup>8</sup>

Clay minerals and their surface-modified forms have ability to catalyse the oxidation and reduction of organic compounds.<sup>87,91,92,196</sup> Transition metal ions (iron) occupying structural or interlayer exchange sites or associated with metal oxide pillars are very often involved in catalysis of redox reactions.<sup>197-199</sup> It was proven that clay minerals with ferrous iron are more effective in catalysis than their ferric iron-rich counterparts.<sup>200</sup>

Many studied reaction can be named after their respective discoverer(s) and they are generally called the *name reactions*. Name reactions are organic chemical conversions and clay minerals (especially montmorillonites) and their various surface-modified forms may play key role in mechanisms of many of them. For the detailed list of the name reactions, their mechanisms and other details we refer to the book J.J. Li (2006).<sup>201</sup> In the following, we focus on selected reactions in alphabetical order.



### *Alder-ene reaction*

Enophile is a compound containing a multiple bond ( $C=C$ ,  $C=O$ ,  $C=N$ ,  $N=N$ ) to an alkene bearing an allelic hydrogen (the ene). The Alder-ene reaction is also named ene reaction and deals with addition of an enophile. It was reported that K10 montmorillonite act as a Lewis acid catalyst for this reaction between dioxymalonate as the enophile and various lactones. As a product of the Alder-ene reaction in this case is obtained  $\gamma$ -lactones.<sup>202,203</sup>

Ordinary potter's clay modified by  $H_2PtCl_6$  was used for catalysis of the 2-furylhydrazone reduction. The reaction can be divided to these parts<sup>204</sup>:

- i) reducing of metal precursor with  $H_2$  gas to catalyse the reduction of 2-furylhydrazone to 2-methylene-2,3-dihydrofuran,
- ii) in the presence of clay supported- $Pt^0$  2-methylene-2,3-dihydrofuran is combined with an aldehyde to afford corresponding alcohol.

### *Baeyer-Villiger reactions*

The Baeyer-Villiger oxidation is the oxidative fission of a C-C bond adjacent to a carbonyl, which change ketones to esters and cyclic ketones to lactones. Triarylmethanes were synthesized via Baeyer-Villiger condensation of aromatic aldehydes under solvent-free conditions by using N,N-dimethylaniline in the presence of montmorillonite as catalysts.<sup>205</sup> Nitro group in the 2, 3, or 4 position on the aromatic ring serve as electron-withdrawing substituent.



Within 5 hours was isolated 96% of yield when 2-nitrobenzene was used as substrate. On the other hand, the yield decreases to 81% within 18 hours by using aldehydes having electron-donating substituents.<sup>205</sup>

Montmorillonite as catalysts was used also by Shanmugam and Varma (2001)<sup>206</sup> who were able to synthesize heteroaryldiarylmethane leuco bases by Baeyer-Villiger condensation of heterocyclic aldehydes with N,N-dimethylaniline at 100 °C. Modification of montmorillonite by  $\text{Sn}^{2+}$  as well as modification of palygorskite and mica (by  $\text{Sn}^{2+}$ ) may catalyse the Baeyer-Villiger oxidation of ketones with hydrogen peroxide to obtain the corresponding lactones or esters.<sup>207-209</sup>

Pillared clays contained different amounts of iron ions can also be successfully used as catalysts of Baeyer-Villiger oxidation of cyclohexanone to caprolactone from benzaldehyde and oxygen (as oxidant) at room temperature.<sup>210,211</sup> The yield suggested that there is a correlation between the Fe content (1-3 mmol/g clay) and accessible surface area of the pillared interlayered clays and catalytic activity.

Cyclohexanone may be converted to caprolactone also from benzonitrile (solvent) and hydrogen peroxide (oxidizing agent) in the presence of kaolinite grafted with Fe(III) picolinate and dipicolinate complexes.<sup>211,212</sup> Not only iron ions may be used for the clay modification, but also magnetic nanoparticles of  $\text{Fe}_3\text{O}_4$  were deposited into nanopores of an acid-treated montmorillonite. This way modified montmorillonite was able catalysed Baeyer-Villiger oxidation of many different cyclic and aromatic ketones in presence of hydrogen peroxide at



room temperature and as well under solvent-free conditions.<sup>213</sup>

### *Bamberger reaction*

Bamberger reaction or rather Bamberger rearrangement is able to convert (rearrange) N-phenylhydroxylamine to 4-aminophenol under homogeneous conditions. However, in the presence of K10 montmorillonite the same initial compound (N-phenylhydroxylamine) is converted to p-nitrosodiphenyl amine and moreover the whole reaction runs faster when montmorillonite is present. The change of the product is probably caused by the mesopore structure of the montmorillonite, which prevents the O-protonated form to lose its water.<sup>214</sup>

### *Baylis-Hillman reaction*

This reaction can be also found as Morita-Baylis-Hillman reaction and it is a C-C forming reaction. The reaction proceeds between a carbon electrophile and an alkene (containing electron-withdrawing group) in the presence of a tertiary amine catalyst. Clay minerals have ability for the transformation of the Baylis-Hillman adducts, but they are not active for the reaction *per se*.<sup>215-217</sup>

### *Beckmann reaction*

Beckmann reaction or rearrangement is able to rearrange an oxime to an amide or cyclic oxime to lactams. Acid activated



montmorillonite (commercially available KSF montmorillonite) promotes this rearrangement of various ketoximes.<sup>218</sup> Moreover, the reaction can be catalysed by K10 montmorillonite in the dry conditions under microwave irradiation.<sup>219</sup> Wide study was performed by Mitsudome et al. (2012)<sup>220</sup> who used  $Ti^{4+}$ -exchanged montmorillonite to catalyse the liquid phase Beckmann rearrangement of aromatic, aliphatic, and alicyclic ketoximes under mild reaction conditions (90 °C, benzonitrile). They also tested the separation of the catalyst by filtration and proved that catalyst can be easily separated and successfully reused, because it does not lose its activity.

### *Biginelli reaction*

Biginelli reaction, also named Biginelli pyrimidone synthesis, is an acid-catalysed multicomponent condensation. The reaction involves an aromatic aldehyde (e.g. benzaldehyde), ethyl acetoacetate, and urea. The product of the homogeneous reaction (refluxing of the components in ethanol with HCl as catalyst) is 3,4-dihydropyrimidin-2(1*H*)-one.<sup>221</sup> When using the KSF montmorillonite as catalyst there is no need of solvent in the reaction. Product 3,4-dihydropyrimidin-2(1*H*)-one can be obtained in 82% yield and with 98% selectivity by heating initial components at 137° for 48 hours as well without solvent presence and in the presence of KFS montmorillonite.<sup>222</sup> Similar improvements by using montmorillonite were observed by substituting different aromatic and aliphatic aldehydes for benzyl aldehyde and  $\beta$ -dicarbonyl compounds for ethyl acetoacetate.<sup>222</sup>



Dihydropyrimidones can be also prepared from different aldehydes, ethyl acetoacetate, and urea or thiourea in the presence of bentonitic clay and under infrared irradiation and free-solvent conditions.<sup>223</sup> In catalysis of dihydropyrimidones is also very effective acid-activated montmorillonite, Ti- or Al-pillared interlayered clays,<sup>224,225</sup> or montmorillonite supported by  $\text{ZnCl}_2$ ,  $\text{GaCl}_3$ ,  $\text{InCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{SmCl}_3$ , and  $\text{FeCl}_3$  reagents.<sup>226,227</sup>

### *Diels-Alder reaction*

Lewis acid-catalysed [4+2]-cycloaddition reaction between a diene (conjugated, can be either open-chain or cyclic and may contain variety of substituents) and alkene (substituted), termed the dienophile, to yield a cyclohexene (substituted) adduct is named Diels-Alder reaction. When in the Diels-Alder reaction imines are used as dienophile, the reaction is named aza-Diels-Alder reaction.

Diels-Alder reaction can be divided to the two types<sup>8</sup>:

- i) normal-demand reaction (the dienophile has an electron-withdrawing group conjugated to the alkene)
- ii) inverse-demand reaction (dienophile is conjugated to a group – amine, ether, or phenol – donator of electron)

Reaction of cyclopentadiene, cyclohexadiene, and furan with  $\alpha,\beta$ -unsaturated carbonyl compounds (as dienophiles) under free-solvent condition can be successfully catalysed by K10 montmorillonite.<sup>228,229</sup> Very good results were achieved with



cation-exchanged montmorillonites at room temperature and variety of organic solvents.<sup>230</sup>

The Diels-Alder reaction of 4,6-bis(4-methoxyphenyl)-pyran-2(H)-one and 4-(4-methoxyphenyl)-6-methyl-pyran-2(H)-one (as dienes) with naphthoquinone and N-phenylmaleimide (as dienophiles) was studied with using different clays ( $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Fe}^{3+}$  montmorillonites, bentonite, pyrophyllite and Filtrol-24).<sup>231,232</sup> From the comparison of the results show up that pyrophyllite was the least efficient and Filtrol-24 had highest activity. When activities of montmorillonites were compared the highest activity was determined for  $\text{Fe}^{3+}$  montmorillonite and the lowest for the  $\text{Al}^{3+}$  montmorillonite.

Only one product (4-vinylcyclohexene) was generated by Diles-Alder reaction (dimerization) of butadiene in the presence  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  montmorillonite.<sup>233</sup> For the reaction of the cyclopentadiene with methylvinyl ketone was showed that  $\text{Al}^{3+}$  montmorillonite is rather inactive and this can be explained by shielding of the interlayer  $\text{Al}^{3+}$  by coordinated water molecules, which apparently resist azeotropic removal with toluene, also the interlayer  $\text{Al}^{3+}$  may form a polyhydroxy complex.<sup>234,235</sup>

### *Ferrier reaction*

Lewis acid catalysed reaction which combine a nucleophilic substitution reaction with an allylic shift in a glycol (2,3-unsaturated glycoside) is named Ferrier (glycol allylic) reaction or more precisely rearrangement. At the beginning the K10 montmorillonite was used as a catalyst of glycosidation of various alcohols with 3,4-di-O-acetyl-L-





rhamnal and 3,4,6-tri-O-acetyl-D-glucal in dichloromethane, and the C-glycosidation of glycals.<sup>236,237</sup>

Montmorillonite and microwave irradiation were used as catalysts for solvent-free synthesis of unsaturated glycosides from tri-O-acetyl-D-glucal and an alcohol<sup>238,239</sup> find out that using silver-impregnated montmorillonite as catalyst of Ferrier rearrangement of 6-hydroxy glycals (in chloroform at 50 °C) can lead to the yield reach 80-85% of 1,6-anhydro disaccharides. Complete stereoselectivity was observed in Ferrier rearrangement of 3,4,6-tri-O-acetyl-D-glucal with benzyl alcohol to yield  $\alpha$ -glucoside in the presence of K10 and KSF montmorillonite supported dodecatungstophosphoric acid.<sup>240</sup>

### *Fischer glycosidation/glycosylation*

The acid-catalyzed synthesis of glycoside by reacting an aldose or ketose with an alcohol (Fischer glycosidatio/glycosylation) may be successfully catalysed by montmorillonite. K10 montmorillonite was able to increase yields of glycosidation of 1-O-acetyl-2,3-dideoxy-dl-pent-2-enopyrano-4-ulose with various alcohols<sup>241</sup> and KSF montmorillonite was very efficient in case of glycosilation of glucose with butanol and dodecanol.<sup>242</sup>

### *Fischer-Hepp reaction*

Conversion of an aromatic N-nitroso or nitrosamine to a carbon nitroso compound is known as Fischer-Hepp reaction or Fischer-Hepp rearrangement. Again using K10, KSF and/or



polyvalent cation-exchanges K10 montmorillonites leads to better results in case of Fischer-Hepp rearrangement of N-methyl-N-nitrosoaniline to N-methyl-4-nitrosoaniline. During the conversion N-methylaniline and aniline were also generated.<sup>243</sup>

### *Fischer indole synthesis*

Fischer indole synthesis means that indoles are generated during cyclization of arylhydrazones. Not only usage of the different montmorillonite as catalyst helps to promote the Fischer indole synthesis, but as well usage of microwave irradiation.<sup>244, 245</sup> For example reaction of phenylhydrazine with various ketones in the presence of KSF montmorillonite under the microwave irradiation is one pot synthesis of indoles.<sup>246</sup> Moreover, usage of KSF montmorillonite during the synthesis of cyclohexane-1,2-dione-1-phenylhydrazones to the corresponding 1-keto-1,2,3,4-tetrahydrocarbazoles under microwave irradiation may be performed under solvent-free conditions.<sup>247</sup>

### *Fischer-Tropsch synthesis*

Conversion of a mixture of carbon monoxide and hydrogen (synthesis gas; syngas) into liquid hydrocarbons is generally known as Fischer-Tropsch synthesis. To promote this synthesis is very often used pillared interlayered clays as alumina pillared montmorillonite<sup>248,249</sup>, ruthenium pillared montmorillonite<sup>250</sup>, ruthenium-alumina pillared interlayered clays<sup>251,249</sup>, iron oxide pillared montmorillonite<sup>252</sup>, alumina and cerium alumina pillared interlayered clays.<sup>253</sup> In all



mentioned cases, the pillared clays have better efficiency than same non-pillared clays. For example, 46% C<sub>5</sub>-C<sub>12</sub> selectivity was obtained by using an acid-activated montmorillonite loaded with cobalt (20 wt.%) and ruthenium (0.1 wt.%) and even higher selectivity (C<sub>5</sub>-C<sub>20</sub>) was observed with a cobalt-impregnated C/Al-pillared montmorillonite<sup>254</sup>.

### *Friedel-Crafts reaction*

Attachment of an acyl group (acylation) or an alkyl group (alkylation) to an aromatic ring in presence of Lewis acid catalyst is known as Friedel-Crafts reaction. In the first experiments with clay (Cu<sup>2+</sup> bentonite) which catalysed Friedel-Crafts alkylation (tert-butyl bromide with benzene) the ratio of the products (mono to di-alkylated) was influenced by the hydration status of the catalyst, when the water content increased the ratio decreased.<sup>255</sup>

Corresponding ketones can be obtained from acylation of toluene, benzene, and xylene with carboxylic acids and cation exchanged montmorillonites appear to be very effective in this reaction.<sup>256</sup> Cation exchanged montmorillonites were also successfully used in promotion of Friedel-Crafts reaction of alcohols, amines, phenols, and thiols with acetyl chloride and benzoyl chloride<sup>257</sup>, arenes with cholesterol to get arylocholestenes.<sup>258</sup>

Montmorillonites also influenced in positive way the selectivity for monoalkylated product.<sup>259</sup> Catalytic activity is mostly controlled by Lewis acidity (acid-treated montmorillonites heated at high temperatures ~500 °C). On the contrary the rate of alkylation (samples dried at ~100 °C)



is influenced by Brønsted acidity.<sup>260</sup> During the alkylation of anisole with various dienes in the presence of cation-exchanged K10 montmorillonites was found the Brønsted acidity may also positively influence diene polymerization as well as dealkylation, but the clay calcination may suppress both reactions.<sup>261</sup>

Almost 97% yield of 1-(4-methoxyphenyl)-1-dodecanone from the reaction of anisole with dodecanoic acid may be obtained when the reaction run in the presence of  $Ti^{4+}$  montmorillonite.<sup>262</sup> Claycic (K10 montmorillonite supported  $ZnCl_2$ ) used as the catalyst in Friedel-Crafts alkylation has very interesting features as synergic acceleration, reactivity inversion, and selectivity for isomer formation.<sup>263-268</sup> Probably reagent in claycic is dispersed in the mesopores of the acid-treated clay and thus is readily accessible to substrate. Due to this claycic is stronger Lewis acid catalyst than  $ZnCl_2$ .<sup>269</sup> This suggestion corresponds to the other observation and can be also connected to the high efficiency of pillared montmorillonites in Friedel-Crafts reactions.<sup>270-275</sup> Not only  $ZnCl_2$  but as well other chlorides (as  $SbCl_3$ ,  $FeCl_3$ ) have very positive influence on the Friedel-Crafts reactions.<sup>270,276</sup>

### *Friedländer synthesis*

The Friedländer (quinoline) synthesis is condensation of an aromatic 2-amino aldehyde/ketone with another aldehyde/ketone which contain a reactive  $\alpha$ -methylene group.<sup>201,277</sup> In the beginning the usage of the clay as catalyst was accompanied by usage of microwave irradiation, e.g. preparation of polycyclic quinoline derivatives.<sup>278</sup>



### *Fries reaction*

The conversion of phenolic esters (and lactams) into hydroxyl ketones is known as Fries rearrangement and can be successfully catalysed by used of clays, for example montmorillonite was used as catalyst in reaction of phenyl toluene-p-sulfonate to give 2- and 4-hydroxyphenyl-p-tolyl sulfones,<sup>279</sup> or cation (Na<sup>+</sup>, H<sup>+</sup>, Al<sup>3+</sup>) exchanged K10 montmorillonite promotes reaction of phenyl and naphthyl esters.<sup>280</sup>

K-series of montmorillonites as catalyst were studied by Bolognini et al. (2004)<sup>281</sup> in use in Fries rearrangement and the correlation between calcination temperature of clay and conversion was observed, conversion decreased with the temperature of calcination. Results also suggested that the catalytic activity is controlled by Brønsted acidity, which arises from the dissociation of water molecules associated with Al<sup>3+</sup> ions.

### *Heck reaction*

Heck reaction can be also named Mizoroki-Heck reaction and substituted alkene is prepared by palladium catalysed coupling of an unsaturated halide/triflate (such as an aryl, benzyl, and vinyl) with an alkene. Clays modified with palladium and other counterions were successfully used in Heck reaction, e.g. Pd<sup>2+</sup>/Cu<sup>2+</sup> K10 montmorillonite was used in reaction of aryl halides with acrylates to obtain (E)-cinnamates<sup>282</sup>, K10 montmorillonite intercalated by palladium chloride was used to synthesise trans-stilbenes from aryl halides and styrene<sup>142</sup>, sepiolite modified by PdCl<sub>2</sub> catalyse



reaction of halobenzenes with styrene<sup>283</sup>, and Pd<sup>0</sup> nanoparticles supported on an aminopropyl- functionalised clay promote reaction of iodo- and bromo-arenes with n-butyl acrylate and styrene.<sup>284</sup> Moreover incorporation of Pd<sup>0</sup> nanoparticles into the interlayer space of montmorillonite-chitosan complex gives reactants and as well as products access to the catalyst.<sup>285,286</sup>

### *Knoevenagel condensation*

Knoevenagel condensation is commonly catalysed by amines and serve to yield an  $\alpha,\beta$ -unsaturated ketone from a carbonyl compound by coupling it to an activated methylene compound followed by elimination of water.<sup>8</sup> Modified clays have ability to promote Knoevenagel condensation, e.g montmorillonite modified with silylpropylethylene diamine.<sup>287</sup> Not only modified clays are successful in Knoevenagel condensation, also the natural clays can be used completed with irradiation treatment (microwave, infrared). For example, natural bentonite (with high amount of montmorillonite) successfully catalysed the Knoevenagel condensation of aromatic aldehydes with diethyl malonate to yield benzyldenemalonate derivatives (under infrared irradiation<sup>288</sup>, KSF montmorillonite under solvent free conditions was able catalysed cross-aldol condensation of aromatic aldehydes with ketones (under microwave irradiation<sup>289</sup>, and others<sup>290,291</sup>).



### *Michael addition*

The conjugated addition of carbon nucleophile to an  $\alpha,\beta$ -unsaturated carbonyl compound is Michael addition. Very effective catalyst for the reaction of silyl ketene acetals to  $\alpha,\beta$ -unsaturated esters turned out to be  $\text{Al}^{3+}$  montmorillonite.<sup>292,293</sup> The Michael addition of imidazole to ethyl acrylate with the corresponding N-substituted imidazole as a product can be performed also under solvent free condition when  $\text{Li}^+$  and  $\text{Cs}^+$  exchanged montmorillonite is used under microwave or ultrasound treatment.<sup>294,295</sup>

Solvent free Michael addition can be also catalysed by commercially available clays (K10 and KSF montmorillonites), e.g. direct (one-pot) synthesis of 3-(furan-2-yl)-4H-chromen-4-ones from 1-(2-hydroxyphenyl) butane-1,3-diones and 2,5-dimethoxy-2,5-dihydrofuran through an alkoxyalkylation reaction<sup>296</sup>, solvent-free Michael addition of indoles (and pyrrole) to nitroolefins<sup>297,298</sup>, dry tandem addition-elimination of indoles with 3-formylindole to yield tri-indolylmethanes (Chakrabarty and Sarkar (2002), and reaction of aniline derivatives to cinnamaldehyde, followed by cyclization and oxidation to yield quinolines under microwave irradiation.<sup>299</sup>

### *Mukaiyama aldol reaction*

This reaction is described as condensation of silyl enol ethers and aldehydes with usage of Lewis acid catalyst.  $\text{Al}^{3+}$  montmorillonite can be used in condensation of 1-phenyl silyl enol ether with benzaldehyde to obtain corresponding adduct<sup>300,301</sup> or in reaction of silyl ketene acetals with carbonyl compounds.<sup>302</sup>



Modification of montmorillonite by  $\text{Sn}^{4+}$  was an excellent choice for the Mukaiyama aldol reaction of congested ketones with silicon enolates to obtain the corresponding silylated aldol products.<sup>303</sup>

### *Nicholas reaction*

The reaction of capture of a dicobalt hexacarbonyl-stabilized propargylic cation by a nucleophile to yield the propargylated (alkylated alkyne) product following oxidative demetallation is named Nicholas reaction. Use of clays as catalyst of the Nicholas reaction is very rare and only K10 montmorillonite is involved in the studied reactions. As one of the example could be mentioned the synthesis of 2-ethynyl-tetrahydrofuran from 6-(tetrahydro-2H-pyran-2-yloxy)hex-1-yn-3-ol which is accompanied with clay treatment in solution of the  $\text{Co}_2(\text{CO})_6$ -alkyne complex in dichloromethane, further filtering, and decomplexing the alkyne with ceric ammonium nitrate.<sup>304</sup>

### *Paal-Knorr synthesis*

The Paal-Knorr synthesis refers to the acid-catalyzed formation of pyrroles from dicarbonyl compounds and primary amines. Pyrroles and pyrazoles can be easily prepared under solvent-free conditions from primary amines or hydrazine, respectively, when K10 montmorillonite is used as the catalyst.<sup>305</sup> Usage of K10 montmorillonite complemented by microwave irradiation as catalyst of solvent-free synthesis of substituted pyrroles leads to the 100% selectivity.<sup>306</sup> When various cation exchanged montmorillonites in reaction of 2,5-hexanedione with amines





in dichloromethane to get the corresponding pyrrole derivatives were studied the yields decrease in the following order of the cation used for the montmorillonite modification  $\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{K}^{10}$ .<sup>307</sup>

### *Prins reaction*

Prins reaction or Prins cyclization is acid-catalysed addition/condensation of alkenes/alcohols with carbonyl compounds (formaldehyde). Various cation-exchanged montmorillonites acting as Brønsted acids was successfully used in reaction when styrene was added to paraformaldehyde or 1,3,5-trioxane (in toluene) to yield 4-aryl-1,3-dioxanes selectively.<sup>308</sup> Diastereoselectivity was also observed when KSF montmorillonite catalyses cyclization reaction of homoallylic alcohols with aldehydes to obtain 4-hydroxy-2,6-disubstituted tetrahydropyrans in high.<sup>309</sup> Timofeeva et al. (2015)<sup>310</sup> suggested that the cyclization reaction is controlled by the Brønsted acidity and as well as by the microporosity of the catalyst.

### *Sakurai allylation reaction*

This reaction can be found also as Hosomi-Sakurai allylation and it is an acid catalyzed addition of allylsilanes to electron deficient carbonyl compounds, such as aldehydes or ketones. Reaction between benzaldehyde and allyltrimethylsilane to get the trimethyl[(1-phenyl-3-butenyl)oxy]silane in 98% yield together with 1% of 4-phenyl-1-buten-4-ol, derived from the hydrolysis of the silane product was successfully catalyzed by  $\text{Cu}^{2+}$  montmorillonite as catalyst by Kawabata et al. (2005)<sup>311</sup>.



Work of Elizarov et al. (2016)<sup>312</sup> proves the montmorillonite which is supported by bismuth(III) salts is very effective in Hosomi-Sakurai allylation of aromatic aldehydes.

### *Sonogashira reaction*

The cross-coupling of organohalides with terminal alkynes catalysed by palladium/copper is known as Sonogashira reaction. Organopalladium clays (intercalated complexes of palladium with tridentate pincer bis-carbene ligands into K10 montmorillonite and bentonite) were used as catalysts in reaction of aryl halides with terminal acetylenes. Moreover, the used catalysts can be used repeatedly with stable activity.<sup>313</sup> Not only palladium and copper are used for the clay modification, but as well as nickel ion can be successfully used and the product may serve as very good catalyst in the Sonogashira reaction, e.g. aryl-sulfur coupling reaction of thiophenol with aryl iodide in the presence of K10 montmorillonite (when nickel ions are coordinated to the amine groups of 3-aminopropyl trimethoxysilane in K10 montmorillonite).<sup>314</sup>

### *Strecker reaction*

Strecker reaction or Strecker amino acid synthesis is condensation of an aldehyde and an amine to form  $\alpha$ -aminonitrile, which is then hydrolyzed to an amino acid.  $\alpha$ -aminonitriles in 85%–94% yields was obtained in reaction of aryl imines, formed in situ from aldehydes and amines, with trimethylsilyl cyanide in the presence of KSF montmorillonite.<sup>315</sup> Similarly, Sn-exchanged montmorillonite



is also very effective in catalysis of  $\alpha$ -aminonitriles, which was described by strong Brønsted acid.<sup>316,317</sup>

### *Suzuki reaction*

This reaction can be also found as Suzuki coupling reaction, or Suzuki-Miyaura reaction and is described as cross-coupling of boronic/organoboronic acid with organohalides, catalyzed by a palladium complex. Clays for the usage as catalyst in Suzuki reaction can be modified by palladium nanoparticles<sup>284</sup>, by  $\text{PdCl}_2$ <sup>283</sup>, or by  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  complex.<sup>318,319</sup> Very interesting approach was applied by Li et al. (2017)<sup>320</sup>, when  $\text{Pd}^{2+}$  (by cation exchange) was introduced into a montmorillonite complex with L-cystine to get an effective catalyst for the reaction.

### *Wacker reaction*

Other palladium catalysed reaction is the Wacker oxidation which is able to convert terminal alkenes to ketones in the presence of a copper salt (which play role as a co-catalyst) under aerobic conditions.  $\text{Pd}^{2+}$  exchanged montmorillonite serve as a catalyst of the transformation of terminal olefins to the corresponding methyl ketone. As the co-catalyst was used  $\text{CuCl}_2$  and N,N-dimethylacetamide as a solvent (heated at 80 °C).<sup>321</sup>



## 1.4. Natural processes

Mineral surfaces may play role in mineral-based heterogeneous catalysis (geocatalysis).<sup>322</sup> Geocatalysis in more restricted sense is understood the transformation of organic compounds in sediments and solis.<sup>323-328</sup>

The best known example of the geocatalytic reaction is the cracking of petroleum in the presence of clays and/or clay minerals. Generally the cracking of the petroleum/paraffin may be performed by either thermal or a catalytic mechanism.<sup>329-331</sup> The thermal process could be successfully replaced with improved efficiency by catalytic processes with solid acids, such as acid activated clays, pillared interlayered clays, and/or synthetic zeolites (see Chapter 2).<sup>332-337</sup> This replacement may lead up to the 1.7 times lower activation energy than value obtained for the usual thermal cracking.<sup>338</sup> Kaolinite still remains as the largest used catalyst and catalyst support in modern petroleum cracking.<sup>105,339</sup>

Efficiency of the catalysis could be increased by using zeolites as additive. For example, rectorite surface enhanced by 2-3  $\mu\text{m}$  particles of zeolite (ZSM-5) has appreciably higher yield of, and selectivity to, propylene<sup>340</sup> or zeolite-impregnated alumina pillared montmorillonite is highly efficient in cracking heavy vacuum gas oils.

These days is very important the cracking of the vegetable oils to yield biofuels. Klopogge et al. (2005)<sup>117</sup> described that



biofuels can be obtained by pillared interlayered clays which involve in  $\beta$ -scission and hydrogen transfer reactions, e.g. using a ruthenium-impregnated alumina pillared montmorillonite as catalyst is possible to convert waste cooking oil to biodiesel through the cracking of  $C_{15}$ - $C_{18}$ n-paraffins to light alkanes and iso-paraffins,<sup>341</sup> and/or using a nickel- or cobalt-impregnated natural clay to convert microalgae oil into diesel-grade hydrocarbons.<sup>342</sup> Catalytic cracking in the presence of bentonite produce branched and cyclic alkanes, on the contrary during the thermal cracking a high concentration of n-alkanes is produced.<sup>343</sup>

Although the addition of the zeolite enhanced the selectivity and yields of the reaction,<sup>340</sup> when the performance of two natural clays and their pillared derivatives in the catalytic cracking of polyethylene was compared with ultrastable Y zeolite the better results were obtained for the clay catalysed reaction.<sup>344</sup>

Very intensively was studied the hypothesis that the fatty acids are the precursors of n-paraffins in petroleum.<sup>345,346</sup> In the start the hypothesis was studied by heating the behenic acid ( $C_{21}H_{43}COOH$ ) with bentonite at 200 °C for 89 and 760 h in the absence and presence of water.<sup>347</sup> In the reaction without bentonite the hydrocarbons was not obtained, but in reaction with the bentonite hydrocarbons of three, four, or five carbon units were produced. Moreover, with the increasing time of heating the concentration of the saturated hydrocarbons increases and olefinic type decreases. Eisma and Jurg (1969)<sup>329</sup> repeat the testing with presence of kaolinite at different heating times and temperatures. Again the production of the hydrocarbons was confirmed and  $C_{21}$  n-alkane was major obtained compound and yield of low



molecular weight hydrocarbons decreased with increasing heating time. From the obtained results Eisma and Jurg (1969)<sup>329</sup> suggested that the process is initiated by decarboxylation of the fatty acid.

Systematic study of clay-catalyzed decarboxylation of behenic acid and subsequent cracking of the corresponding n-alkane product was performed by Johns and coworkers.<sup>348-351</sup> They as well as Eisma and Jurg (1969) confirmed that C<sub>21</sub> n-alkane is the major product of decarboxylation and moreover they find out that formation of minor amounts of C<sub>16</sub>-C<sub>20</sub> hydrocarbons (in case of using the Ca<sup>2+</sup> montmorillonite and temperature 260 °C) is consequence of decomposition of n-C<sub>21</sub> and presence of C<sub>18</sub>, C<sub>19</sub>, and C<sub>20</sub> paraffins is caused by subsequent cracking of C<sub>21</sub> n-alkane and equally originates from the initial behenic acid. The temperature of the reaction influences the reaction rate and as well as the kinetics of the reaction could be described by Arrhenius equation<sup>349,351</sup>:

$$k = Ae^{-E_a/RT}, \quad (1.1)$$

where  $k$  is the rate constant,  $A$  is the Arrhenius constant (so called frequency factor),  $E_a$  is the activation energy for the reaction,  $R$  is the universal gas constant and  $T$  is the absolute temperature (in Kelvin).

Calculated activation energy value for the not clay-catalysed thermal process is 244.3 kJ/mol, which is approximately two times higher than values for the clay-catalysed reaction, e.g. when SWy-1 montmorillonite is used the activation energy value is 111.3 kJ/mol.<sup>8</sup>



It should be mentioned that the rate of behenic acid decarboxylation at 250 °C could be appreciably enhanced by addition of hydrogen peroxide or strongly inhibited when surface of the clay catalyst is blocked by phosphatite.<sup>351</sup>

Kerogen and/or organic matter in sediment and soil in interaction with clay minerals can be used to hydrocarbon (petroleum) generation. Difficulties in these studies are caused by very intimate association between clay minerals and kerogen/organic matter so thus is very hard to distinguish if the effect of the clay is protective or catalytic.<sup>352</sup> Kerogen is a high molecular weight carbon-rich organic material contained in sedimentary rocks which is insoluble in water and common organic solvents. Various minerals (e.g. bentonite, kaolinite) have the positive effect on yields and in decreasing activation energy in the pyrolysis of kerogen.<sup>353</sup>

During the studies of pyrolysis with montmorillonite was proven that yields of the C<sub>1</sub>-C<sub>6</sub> (dominance C<sub>4</sub>-C<sub>6</sub> hydrocarbons) hydrocarbons were five times higher than were obtained during pyrolysis without montmorillonite<sup>354-358</sup>. Organic-rich modern sediments, six kerogens and several clays were used in hydrous and anhydrous pyrolysis study of diamondoids formation at 340 °C.<sup>359,360</sup> From the results was evident that the process can be inhibited by using calcite. On the other hand the K10 montmorillonite and acidic aluminosilicate (MS-25) have positive effect on the reaction and the reaction proceeds through cooperation between Brønsted and Lewis acid sites.

Generally from the experiments with mixtures of kerogens and different clay minerals could be stated that hydrocarbons adsorption rises as the specific surface area of the mineral



component increases. Moreover, montmorillonite can catalyse the formation of light hydrocarbons and aromatic compounds and illite and palygorskite stay relatively inactive as catalysts, but they can similarly retain the hydrocarbons formed during pyrolysis.<sup>8</sup>

### *Prebiotic organic reactions*

In addition to everything that has been said about the influence of clays to catalysis of organic reactions it has been proposed that clay minerals played an important role in chemical evolution and life's origin.<sup>361</sup> Clay minerals have ability to taking up and concentrating extraneous molecules, protecting them against ultraviolet/cosmic radiation, and allowing the adsorbed molecules to be transformed or polymerized. Moreover, clay minerals may promote synthesis of biomonomers from gaseous constituents as well as provide an environment in which such monomers can adopt a specific orientation, condense, and serve as templates for organic replication.<sup>362</sup> In such reason the clay minerals may have ability to mediate chemical evolution and prebiotic organic synthesis.<sup>194,363-368</sup>

Variety of study dealing with formation of amino acids<sup>369-371</sup>, polypeptides<sup>363,371</sup>, monosaccharides<sup>372</sup>, polysaccharides<sup>373</sup>, and nucleic acid bases<sup>374</sup>. Hashizume et al. (2018)<sup>375</sup> was published and proved that used clays in synthesis has positive influence on the obtained compounds.

Peptide bonds are thermodynamically unstable, prone to hydrolysis, and condensation of unsubstituted amino acids in water is energetically unfavourable.<sup>376,377</sup> However, heated





montmorillonite complex with glycine and  $\beta$ -alanine had ability to form a peptide bond.<sup>378</sup> High molecular weight polypeptides may be created by condensation of L-amino acids on the surface of kaolinite and temperature of the reaction may be below 100 °C.<sup>363</sup> Fuchida et al. (2014)<sup>379</sup> were able to synthesize diketopiperazine from glycine complex at 150 °C for 336 h under dry conditions and at presence of montmorillonite, when the montmorillonite was absent the glycine failed to oligomerize.

Repeated wetting, drying, and/or heating in the presence of clay catalyst may lead to the formation of oligopeptides from pristine amino acids. These processes may simulate the conditions of the cyclic wetting and evaporations of lagoons and rock pools.<sup>380</sup> Using this approach, short-chain oligoglycines were prepared in the presence of kaolinite and montmorillonite.<sup>381-383</sup> Alanine and glycine oligomers may be formed in the presence of various cation-exchanged bentonites, where  $\text{Cu}^{2+}$ -exchanged bentonites are very effective.<sup>384</sup> Study by Rimola et al. (2007)<sup>385</sup> suggests that synergy between the  $\text{Cu}^{2+}$ -glycine interaction and water, acting as a proton transfer agent, which lead to a significantly lower activation barrier for peptide bond formation. Among others divalent counterions ( $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ) can catalyse peptide chain elongation.<sup>386</sup>

Clays does not serve only as a support and catalyst of polypeptide formation, but may serve as discriminate between amino acid enantiomers due to the preferential adsorption of one optical isomer over other. The mechanism is not fully understood and described but this selective adsorption of amino acids and peptides by clay minerals may provide a clue to the origin of L-homochirality of amino acids



in proteins of living organisms.<sup>387</sup> For example, in the reaction of aspartic acid with kaolinite at 60 - 90 °C during different periods of time only small amount (3%) of the D-isomer polymerized in comparison to the L-isomer (25%) and to the racemic mixture (14%).<sup>388,389</sup> One hypothesis explain these diversity due to the preferential adsorption of the L-enantiomers to the edge surface of kaolinite particles, which may be enantiomorphous due to interlayer displacements and the presence of octahedral site vacancies.<sup>390,391</sup>

The most important biopolymer in the early life on Earth is ribonucleic acid (RNA),<sup>392</sup> which has ability to act as an enzyme (catalysts of the protein synthesis) and as a store house of genetic information.<sup>376</sup> Oligodeoxyribonucleotides with longer chains (than in case in the absent of montmorillonite) can be prepared in the presence of montmorillonite by condensation of thymidine monophosphate with cyanamide at neutral pH.<sup>393</sup> Kaolinite was also very successfully used in the formation of oligonucleotides by exposing adenosin monophosphate to UV radiation.<sup>394</sup>

These and many others experiments and studies prove that the clay and clay minerals has very big potential as the catalysts of the natural processes and played a key role in the prebiotic synthesis of bioorganic molecules.



## 1.5. Inorganic catalysis

Not only organic reaction can be successfully catalysed by clay and clay minerals, as well as they can be used in catalysis of a few inorganic reactions.

They can be involved in catalyse of the aquation of  $[\text{Cr}(\text{H}_2\text{O})_4\text{X}_2]^+$  to  $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$  ( $\text{X}=\text{halide}$ ) and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .<sup>395,396</sup> Usually the reaction of the Cr(III) is very slow (about weeks), however, usage of clay minerals or zeolites (see chapter 2) can accelerate the reaction and it can be performed in minutes or hours. Usually the clay minerals act mass base catalysts by elimination of the protons from the solution.<sup>396</sup>

Even more than Cr(III) complexes are Co(III) complexes. Surrey powder contains a high layer charge smectite, which as used to obtain high yield of Na or K tris-oxalatochromate(III) (3- to 4-fold) and tris-ethylenediamine chromium(III) chloride (1.5-fold) complexes.<sup>396</sup>

Also the presence of clay can positively influence the obtained yields (3-4 times higher) of complexes such as  $\text{K}_3[\text{Cr}\{(\text{COO})_2\}_3]$  from chromium(III) chloride and potassium hydrogen oxalate at room temperature.<sup>395</sup>



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## Chapter 2

### Zeolites and related structures in catalysis

#### 2.1. Introduction, zeolites

The first known mention of zeolites dates back to the end of the 18th century (1756), when a Swedish mineralogist Axel F. Cronstedt described minerals found in different localities (Lapland, Sweden and Iceland), which shared identical properties not yet found in other minerals. These properties also provided the basis for the name of zeolites itself (from the Greek words for *zeo* and *litos*, meaning boil and stone); because minerals during heating seemed to boil<sup>1</sup>. During the nineteenth century there were other references to minerals with properties similar to the above-mentioned zeolites and other descriptions of their properties. For example, that natural zeolite crystals (e.g. faujasite, chabazite) desorb water without apparent changes in transparency and morphology (A. Damour, 1857)<sup>2</sup>. That reversible dehydration is possible and water molecules are therefore simply contained in the structure and not chemically bound in aluminosilicate crystals, or that dehydrated zeolites are largely capable of absorbing gases such as ammonia, carbon dioxide or chloroform, and others (G. Friedel, 1896)<sup>3</sup>. Other authors deal with dehydrated forms of zeolites and the subsequent adsorption of molecules, until in 1932 the term "molecular sieve" was defined by J. W. McBain. Subsequent studies have



confirmed this theory that molecules spatially suitable are adsorbed in crystal of mineral, whereas for example branched structures do not pass through this "sieve" and remain unadsorbed<sup>4</sup>. Another discovery in the field of zeolites was ion-exchange in salt solution, e.g. potassium was exchanged for calcium, and that this phenomenon was reversible, e.g. in chabazite, (H. Eichhorn, 1858)<sup>5</sup>. The resolution of crystal structure of zeolite analcime (W. H. Taylor, 1930)<sup>6</sup> and sodalite (L. Pauling, 1930)<sup>7</sup> led to the definition of the main characteristics for zeolite structures.

- (a) 3D structure of zeolite is constructed by corner-sharing of tetrahedrons  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$
- (b) presence of so-called micropores, i.e. regular channels and/or cavities in one to three directions, up to 2 nm
- (c) the presence of  $[\text{AlO}_4]$  tetrahedrons brings to the structure a negative charge compensated by alkaline ions and alkaline earth ions located in micropores and easily ion-exchangeable for other cations
- (d) presence of water molecules in micropores and their easy reversible desorption under mild temperature conditions
- (e) chemical composition:  
 $(\text{M}^+)_a(\text{M}^{2+})_b[\text{Al}_{(a+2b)}\text{Si}_{n-(a+2b)}\text{O}_{2n}] \cdot m\text{H}_2\text{O}$

With regard to the following rules:

- (f) observe the Lowenstein rule, the Si/Al molar ratio is always  $\geq 1$ , i.e. two tetrahedrons with Al cannot adjacent





(g) moreover, the ratio  $O/(Si+Al) = 2$ , applies for tectosilicates which include zeolites<sup>8</sup>



## 2.2. Synthetic zeolites, introduction

Natural zeolites are of interest particularly from the theoretical point of view, for understanding their properties and structure. From a practical point of view the use of natural zeolites is minimal, deposits with a high content of zeolites and their application is considerably limited due to present impurities. However, they can be used for example as building materials, for separation and purification of wastewater, gases and the others.

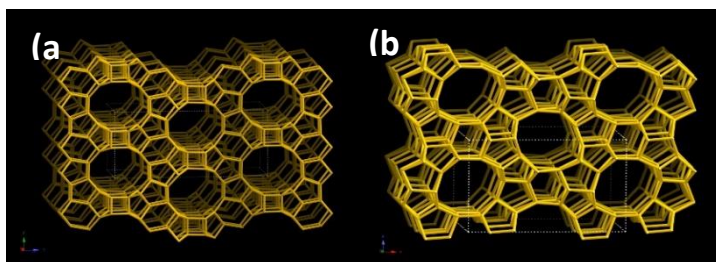
The first mention of the hydrothermal (170 °C) preparation of zeolite from a mixture of potassium silicate and sodium aluminate is dated to 1862<sup>9</sup>, a summary of further work until 1937 can be found e.g. in review<sup>10</sup>. However, sufficient analytical techniques, especially powder X-ray diffraction, have helped to identify the actual composition and structure of the resulting materials (hence another chapter will deal with analytical techniques).

Among the historical milestones in zeolite synthesis, can be mentioned the first preparation of naturally not occurred zeolites structures (P and Q), the 1940s; the use of such silicon and aluminium sources (sodium silicate and sodium aluminate) which allowed hydrothermal preparation at a more favourable temperature, 100 °C (zeolites A, B, C); zeolite X (a counterpart to natural faujasite), which found a wide range of applications in the future, was published in 1950<sup>11</sup>.



However, the real breakthrough was the use of organic hydroxides, which finally made it possible to achieve Si/Al molar ratios in large scale compared to the previously used purely inorganic medium, where the molar ratios of Si/Al were near 1. The quaternary ammonium ions present in the synthesis mixtures caused an absolute boom in the synthesis of zeolites. Among the most significant representatives certainly belong zeolite beta (with tetraethylammonium hydroxide as the reagent)<sup>12</sup> or zeolite **ZSM-5** (prepared with tetrapropylammonium hydroxide)<sup>13</sup>. For an illustration of these zeolites structure, see framework images in **Figure Z1**.

To date, 248 different zeolite structures are known. The classification of the individual structures is carried out using a three-digit code consisting of letters of the Latin alphabet. This classification has been managed by the International Zeolite Association (IZA) since 1973, which is internationally recognized by IUPAC. The database is available at address: <http://www.iza-structure.org/><sup>14</sup>.



**Figure Z1:** Images of zeolite structures: beta, framework type BEA (a) and **ZSM-5**, framework type **MFI** (b), viewed along [100] and [010], respectively<sup>14</sup>



Then there was a huge shift in the synthesis of zeolites. Besides zeolites with low Si/Al molar ratios near 1, on the contrary pure silicate structures were prepared, i.e. without the presence of aluminium atoms in the structure (as the central atoms). New structures were synthesized, with different channel systems both in size and orientation, etc.

Zeolites can be prepared under different conditions, with different ratios of the components (resulting in different Si/Al molar ratio), with different organic hydroxides or salts, at different temperatures, etc. Thus, we can switch from one type of zeolite to another. By these changes we can achieve the same structures differing only by the Si/Al molar ratio or, on the contrary, by a small change we can get another type of framework, i.e. different type of zeolite<sup>15</sup>.

Another important change in the structure of zeolites is the possibility to replace the central atom (Si, Al) with another atom, thus the so-called isomorphically substituted framework of the zeolite is achieved. Examples are microporous aluminophosphates (AlPOs)<sup>16</sup>, which can completely isomorphically replace silicon in the framework, alternating tetrahedrons with trivalent Al and pentavalent P oxides to form a neutral framework; and their compositional alternatives, i.e. metallo-alluminophosphates (MeAPOs), where the trivalent Al is replaced by divalent metals such as Mg or Co to obtain a negative framework charge; silico-aluminophosphates (SAPOs), replacement of some P atoms by Si to form a negative charge of the framework; metallo-silico-alumino-phosphates (MeAPSOs)<sup>17</sup>. If there is charge in the framework, then the ion-exchange and catalytic properties are similar to aluminosilicate structures.



In this regard, an isomorphic substitution of silicon in aluminosilicates for other elements of the fourth group of the Periodic Table, i.e., those that are preferably tetravalent, is possible, similarly the substitution of aluminium for the element of the third group. And these substitutions occurred in the case of germanium<sup>18</sup>, tin<sup>19</sup> or titanium<sup>20</sup> and an element of the third group as gallium<sup>18</sup> and boron<sup>21</sup>.



## 2.3. Synthesis of zeolites

In view of the above, it should be noted that although we know about the individual effects in zeolite synthesis, a prediction of the conditions for obtaining the desired resultant structure is limited. It is known that by the hydrothermal “classical” way we only obtain a fraction of the possible structures<sup>22</sup>.

The synthesis of zeolites can be carried out in an acidic, neutral or alkaline environment in a hydrothermal manner at temperatures of 100-200 °C and autogenous pressure. The most perfect zeolite crystals were prepared in an acidic environment (the fluoride method), but its use is limited to laboratory syntheses. Industrial syntheses are carried out in an alkaline environment at pH = 10-13. Because the silica dissolves at pH above 10.5, hydroxides are evident mineralizing agents. The alumina source is dissolved in the hydroxide medium before adding to the synthesis mixture to achieve good homogeneity and solubility, since after mixing with the silica source no further dissolution occurs. It is important in the case of the gel form of the synthesis mixture that all the components are fully homogeneous (dissolved) before the initial crystallization occurs. The synthesis of zeolites in alkaline medium at high pH values results predominantly in zeolites with lower Si/Al molar ratios, while at lower pH values high silicate zeolites are formed. During synthesis, the pH of the reaction mixture generally increases, due to the gradual condensation of silicate ions to form  $\equiv\text{Si-O-Si}\equiv$  bonds, releasing hydroxide ions into solution. As an



alternative procedure of synthesis, a fluoride method in a weakly acidic medium (pH around 5) has been proposed which allows the synthesis of zeolites with a high Si/Al molar ratio. At these pH values, the solubility of the silicate particles increases to form hexafluorosilicate anions. Moreover, this method provides advantages such as i) defect-free structure, ii) allows direct synthesis of ammonium forms of zeolites allowing to obtain zeolite directly in the H-form after calcination, and iii) organic templates are not as easily degradable as at high pH.

Furthermore, it was shown that the success of the synthesis also depends on the method of preparation of the reaction mixture, such as temperature, order of the added components, aging of the reaction mixture before the actual synthesis, seeding, purity of the reactants, stirring during the synthesis and others.

Typical synthesis using usual heating takes from several hours to several months. At the beginning, gel precursors (sources of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) are transformed into initial nuclei, from which crystals start to grow and the period of crystallization begins. Thus, the first change in the amorphous phase is the initial ordering of precursors without a noticeable indication of the resulting framework. In the next step, nucleation, a state of suitable arrangement is reached, and a time of crystals growth occurs. Generally and simply, nucleation occurs as a result of homogeneous nucleation from solution or by the presence of others crystals, for example by seeding with crystals of the same type of previously prepared zeolite<sup>23</sup>.



In addition to conventional heating, microwave synthesis has proven to be very promising, among other things, to shorten the total synthesis time (nucleation and crystal growth) to several hours<sup>24</sup>.

Stirring also affects the crystallization of zeolites. Stirring particularly results in homogenization of the reaction mixture, and can influence the crystallization time, size and uniformity of resulted crystals. Under stirring, smaller crystals are formed as opposed to static synthesis; at other times, stirring is undesirable as additional unwanted phases are formed.

Subsequent separation of crystals from the solution is performed primarily by filtration; for very small crystals, centrifugation can be used, especially in a laboratory scale.

From the point of view of the composition of the reaction mixture, the Si/Al molar ratio determines the resulting composition of the zeolite framework, moreover cases are known where just changing this ratio, while maintaining all other synthesis parameters, lead to the preparation of another zeolite (e.g. Beta to **ZSM-12**, ferrierite to **MCM-22**).

In general, the given product has a smaller Si/Al molar ratio than was in the initial gel composition. This is due to the solubility of silica, with increasing concentration of OH<sup>-</sup> ions and higher alkalinity of the mixture, the lower Si/Al molar ratio is in the resulted product. To achieve zeolites with Si/Al molar ratios higher than 5, it is usually necessary to use instead of inorganic cations an organic one. Large molecules of organic agents allow the filling of cages and pores with less amount than would be necessary in the case of hydrated





inorganic cations, which supports the occurrence of less Al in the final product.

Water amount in the reaction mixture affects the rate of the synthesis, for example, the synthesis of large zeolite crystals takes place in very dilute reaction mixtures. The amount of water used in large-scale zeolite syntheses is minimized to increase the yield of the synthesis while forming a stirrable mixture and to facilitate mass transfer in the synthesis mixture. Increasing the concentration of hydroxide anions accelerates the transport of silicate particles in solution, thereby reducing the time required to crystallize the zeolite. The presence of cations often has a controlling influence on the formation of a given structure. This effect is more noticeable with organic cations, which in addition have an influence on the aluminium concentration in the zeolite framework. In some syntheses, inorganic and organic cations are used simultaneously. Most of the syntheses are carried out in an aqueous medium, but the synthesis of zeolites occurring in an organic medium has also been described<sup>23,25</sup>.

For the zeolite synthesis itself, it is necessary to use some source of silicon and aluminium, more precisely  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , respectively. Imagine that under certain temperatures, pressures and other conditions such as pH, it is created/reshaped the original grouping into another. But how to achieve such three-dimensional diversity?

Mentioned organic molecules offer one possible influence. So, what is their role? The name itself (organic additives, templates, structure directing agents) offers an easy answer, although their role is not always so clear.



Organic additives are not only the mentioned quaternary ammonium salts/cations, but hundreds of molecules tested, amines, diamines, oxygenates (i.e. alcohols, ethers, esters etc.), quaternary phosphonium salts, phosphazenes, etc.<sup>26</sup>.

In the first approaching, organic and inorganic cations can be understood as compensating for the negative charge of the framework. Thus, this influences interaction and incorporation of aluminium ions as carriers of negative charge ( $\text{AlO}_4^-$ ) into the structure. Therefore, (larger) organic cation size, opposite to an inorganic one, can be understood as a parameter affecting the (less) amount of Al in the resulting structure. I.e. inorganic cations cause Si/Al molar ratio around 1, while organic ones allow ratios higher up to the purely silica form.

The main role of structure directing agents in zeolite synthesis is the formation of zeolite, which would otherwise not occur in their absence. The role of organic additives can be divided to three main conceptions. The first one can be approached using the size and proportions of the molecules, the role as a filler and subsequent replacement lead to the creation of an empty space (VOID FILLER). This is an example of less specificity, so several types of molecules can act as fillers for a given type of zeolite. The second approach takes the molecule as a true TEMPLATE, i.e. the zeolite structure is formed with respect to the size and shape of the organic molecule itself (size and shape reproduction). In fact, it was shown that the concept of template applies to a limited group of structures. Therefore, rather than the idea of the real template, concept of the STRUCTURE DIRECTING AGENT (SDA) is preferable in the case of zeolite nucleation and crystallization. In such cases, the molecules are specific (well-



fitting molecules) and form one type or small group of structurally similar frameworks.

Sometimes cations can act as a "gel modifier", affecting the chemistry of the gel and the formation of different precursors.

Background of SDA specificity next to the other parameters is fundamental. On the other hand, it is obvious that size and shape are significant to the nature of the resulting product. The hydrophobicity and rigidity of the molecule also play a role, i.e. a rigid, bulky and relatively short C-chain with adequate hydrophobicity demonstrates to be the best SDA (strong hydrophobicity of SDA makes the zeolite crystallization difficult). The optimal C/N<sup>+</sup> molar ratio in molecule of organic directing agent was calculated to be 11-15 for the formation of high silicate zeolites. Thus, SDA is effective when the non-bonding interactions (i.e. van der Waals) are maximal and the dimension of SDA is in accordance with the resulting pores. In other words, the interaction of solvated cations with silica species has a key effect on the crystallization product and is the basis for the role of structure directing agents.

Simply said, the background around specificity of SDA leads to the conclusion that it does not play such an important role in zeolite synthesis, it is part of a complex process and cannot be elevated to other parameters such as composition of the synthesis mixture, temperature, crystallization time and others. The molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in the reaction mixture, which also indicates the charge density of the framework, is at least similarly substantial. According to Oswald's rule, crystal formation takes place through a series of transient



crystallographic phases before the formation of a final thermodynamically stable structure<sup>27</sup>, that is, crystallization takes place under clearly defined conditions and does not depend on specific parameters, thus, it cannot be clearly stated which of the parameters plays a key role in each step.

Beside to other parameters affecting the synthesis, stability and utilization of zeolites, the presence of a heteroatom in the original aluminosilicate structure is undoubtedly another of them. The average bond length of Si-O is about 0.159-0.161 nm and Al-O about 0.174 nm<sup>28</sup>.

The more Al is in the structure, the larger unit cell dimensions can be expected. The amount and the different size of the extra-framework cations counterbalancing the negative charge caused by Al in the framework also affects the resulting geometry.

In addition to the before mentioned isomorphically substituted heteroatoms, reference should be made to the time when the aim was mainly improving the catalytic properties of zeolites, then boron was the hot candidate (the average bond length of B-O is about 0.146 nm). However, only high-silicate counterparts to aluminosilicates were able to prepare, even several types of new frameworks, but they were less thermally stable and together with the weak acidic properties the resulting boron substituted zeolites did not confirm potentials<sup>21</sup>.

The introduction of gallium into the structure seemed promising (the average bond length of Ga-O is 0.182 nm, thus quiet long). Ga-analogues of a large range of zeolites have been prepared. Structures with Si/Ga molar ratios less than 5,



are unstable for creation the H-form, higher ratios can be changed to the H-form. Bronsted acidity was somewhat lower than that of aluminosilicates and is thermally dependent. Until limited temperature, where Ga remains within the framework, is Bronsted acidity similar, above that temperature, some of the Ga change the position to extra-framework and act as strong Lewis acids. However, the moisture present proved to be a major problem in the application of these materials compared to aluminium counterparts, although some of the obtained catalytic results were favourable<sup>29</sup>.

More interesting was the incorporation of titanium into a purely silica structure (the average bond length of Ti-O is 0.175 nm)<sup>30</sup>, namely Ti in **MFI** was given its name titanosilicalite (**TS-1**), which has many applications especially in oxidation reactions with activated hydrogen peroxide under mild conditions<sup>31</sup>. Another potential of these materials may be their application in photocatalysis, while the photocatalytic activity of TiO<sub>2</sub> in various forms is known<sup>32</sup>.

Tin substitution (the average bond length of Sn-O is 0.191 nm)<sup>33</sup> has proven to be very beneficial and promising, mainly due to increased Lewis acidity. Tin(IV) has been shown to be catalytically active in a wide range of reactions, mainly due to its specific activation of the carbonyl group, which makes tin unique among Lewis centres (compared to Ti and Zr)<sup>34</sup>.

In limited amounts, the incorporation of iron into the zeolite framework (the average bond length of Fe-O is 0.184 nm) is possible. However, the solubility of iron in an alkaline environment is restricted, since iron readily forms iron oxides-hydroxides that are stable and insoluble, making it difficult to



incorporate into the framework. Fe-zeolites are characterized by lower acidity than comparable aluminosilicates, moreover, zeolites with iron are less stable and, after calcination, iron tends to move to extra-framework positions.

Divalent zinc (the average bond length of Zn-O is 0.194 nm) in zeolites supports the formation of low-density frameworks with 3-membered rings (see later) and allows especially the synthesis of phosphate molecular sieves-based structures.

However, the incorporation of germanium was exceptional (the average bond length of Ge-O is 0.174 nm). In order to better understand this unique property, it should be appreciated that the heteroatom incorporation affects not only the catalytic properties of the resulting structure but also the stability/instability of the structure itself. Substitution has resulted in one more connection, which is the stabilization of secondary building units (SBUs, more detailed explanation is below) caused by the heteroatom incorporation. In other words, stable structure of zeolites crystallizes in the presence of some heteroatoms, although in pure aluminosilicates it would be unstable. While conventional Si and Al zeolites prefer 5- and 6-membered rings, for some heteroatoms, 3- and 4-membered rings are preferred. And it is precisely the case of the mentioned germanium. Germanium causes zeolites to crystallize with preferential localization into these double-4-rings (D4R) as SBUs.

It has been shown that even a small addition of  $\text{GeO}_2$  can significantly reduce the crystallization time (as opposite to the pure aluminosilicate form), due to the lower angles of Ge-O-Ge and thus less stress, therefore the structure is more stable (while the angle Si-O-Si is  $148^\circ$ , in the case of Ge-O-Ge it is



130°). In addition, it has been shown that up to 3 Ge per D4R unit can be incorporated. This, together with combinations of different structure direction agents (SDAs), led to the creation of several new germanosilicate structures characterized by low framework density and multidimensional channel system, often with 14-member or more "pore opening". Other studies focused on the effect of germanium in zeolite synthesis with several SDAs used. In summary, the presence of germanium in the synthesis mixture, with an optimal Si/Ge molar ratio around 2, controls the synthesis of new zeolites rather than SDA alone<sup>35</sup>.

Finally, the easy tendency of zeolites to hydrolyse where germanium occurs led to the unique discovery that layered precursors could be prepared from germanosilicates and their subsequent modifications opened up opportunities for the synthesis of new structures<sup>35</sup>.

The interest in synthesis of zeolite-based catalysts is mainly due to the following reasons:

- Zeolites are highly ordered, crystalline materials with a precisely defined channel structure
- Several structural types of zeolites, varying in size and type of channels and the presence or absence of cavities in the structure
- It is possible to influence the concentration of catalytically active centres located in the channel system by changing the chemical composition of a given structural type of zeolite



- Since the size of the zeolite channels is comparable to the kinetic diameters of simple organic molecules, it is possible by suitable choice of the structural type of zeolite to exclude some reactants from the actual catalytic reaction or to prevent the formation of bulky intermediates (shape selectivity)
- Active centres, their localization and surroundings at the atomic level can be modified by replacing some elements in the zeolite framework or by introducing functional groups into the zeolite framework
- Chemical and structural properties of molecular sieves can be specifically modified after their synthesis by subsequent modifications
- Molecular sieves are environmentally friendly<sup>23</sup>

The following chapter will introduce the actual structure of zeolites, channels, cavities and lower-level arrangements.





## 2.4. Structure of zeolites

Structural chemistry of silicon is one of the most interesting areas in inorganic chemistry. The number of very different structural motifs based on the same basic tetrahedron with central silicon is impressive. These tetrahedrons can form a miscellaneous grouping from the simplest isolated tetrahedrons, through various cyclic, isle or chain structures, to two-dimensional and three-dimensional structures, including zeolites.

The basic structural unit of zeolites is the tetrahedron  $\text{TO}_4$  ( $\text{T} = \text{Si}, \text{Al}$ ), in which the central T atom is coordinated by four oxygen atoms. The possibility of incorporating another ion into the three-dimensional structure of the zeolite depends mainly on the ion diameter and the ion ability to form a tetrahedral coordination. The ion diameter of the cation is related to the size of the oxygen diameter according to the Pauling criterion<sup>36</sup>. The following  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$  and  $\text{Ge}^{4+}$  ions best meet this criterion. On the other hand, silicates of various structural types with  $\text{Fe}^{3+}$ ,  $\text{Ga}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$  or  $\text{Zn}^{2+}$  ions were prepared. The results show that although the size of the ion plays an important role, the ability of tetrahedral coordination is often more important.

The individual tetrahedra in the zeolite are connected via oxygen bridges that surround the central atom and are located at top of the tetrahedra. Two adjacent T atoms are always linked by only one bridging oxygen atom. Which



means that two T atoms do not share the edge or even a tetrahedron plane.

The presence of aluminium in the structure of the tetrahedron introduces a charge into the structure. In accordance with Lowenstein's rule, the two aluminium tetrahedrons in the zeolite structure cannot be interconnected by an oxygen bridge. Originally it was assumed that aluminium ions occupy positions as far as possible from each other (the so-called Dempsey rule<sup>37</sup>), but the presence of these so-called aluminium pairs has been shown to affect mainly the redox properties of transition metal cations located in the channel structure of zeolites and are therefore present<sup>23</sup>.

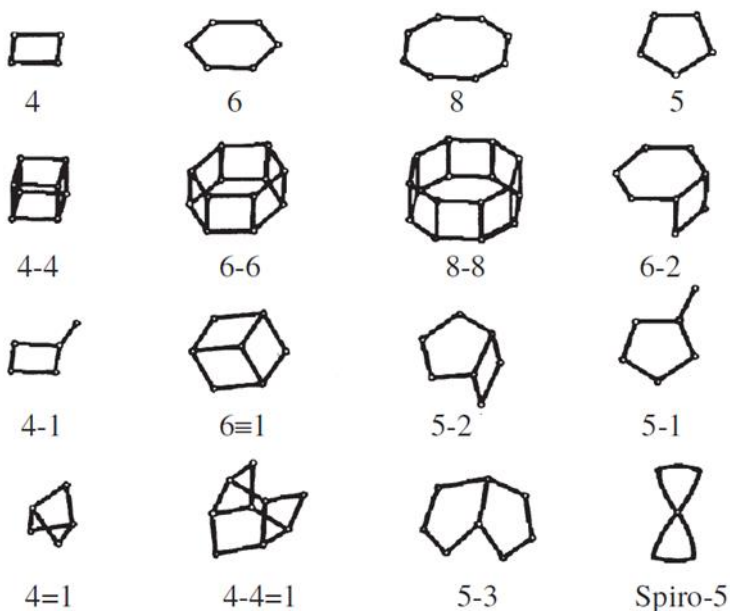
Tetrahedrons  $TO_4$  in zeolites form simple formations that are regularly repeated throughout the structure of a given structural type zeolite or combine into larger units. **Figure 22** demonstrates these so-called secondary building units (SBUs).

As it can be seen from the picture, the simplest secondary building units are planar formations (square, pentagon, hexagon), others are already three-dimensional, forming e.g. a cube or a hexagonal prism. The number of T atoms in these secondary building units (SBUs) is either even, then these units consist mainly of structural types of zeolites with a low Si/Al molar ratio or odd, these units being typical of high-silicate zeolites, since they do not allow regular alternation of silicon and aluminium.

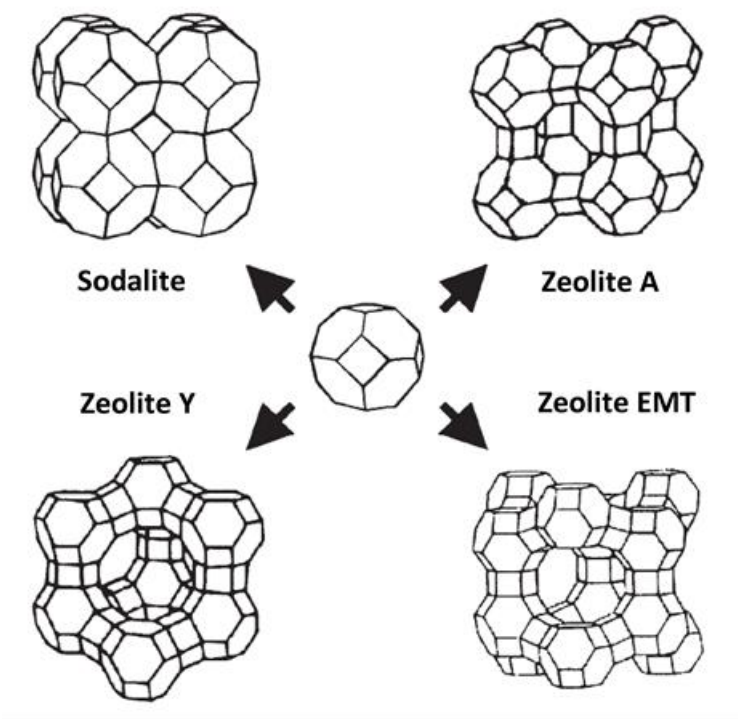
The interconnection of secondary building units leads to the creation of three-dimensional formations. One of the most well-known (cuboctahedron, combination of cube and



octahedron = sodalite unit) is the cornerstone of many zeolites, see **Figure Z3**. Direct interconnection of sodalite units through four-membered rings leads to the structure of sodalite. When these four-membered rings are interconnected by an oxygen bridge, zeolite A is formed. Connection of the sodalite units by the six-member rings over the oxygen bridges leads to a zeolite Y or **EMT** structure that differs in the relative position of the sodalite units in space.



**Figure Z2:** Images of secondary building units (SBUs)<sup>23</sup>



**Figure Z3:** Zeolites structures formed by the combination of sodalite units<sup>23</sup>

In **Figure Z3** there are also different entrances to the channel structure of these zeolites, defined by 8 T atoms (or oxygen)



for zeolite A, and 12 T atoms for zeolites Y and **EMT**. It is the size of the entrance of channel opening into the structure of zeolites that plays a crucial role in their use in adsorption or catalysis, since it clearly defines which molecules can penetrate into the channel structure and which do not. This demonstrates the definition of one of the important properties, namely shape selectivity and the term molecular sieve. The above example shows shape selectivity over reactants. Other types of shape selectivity are shown in **Figure Z4**.

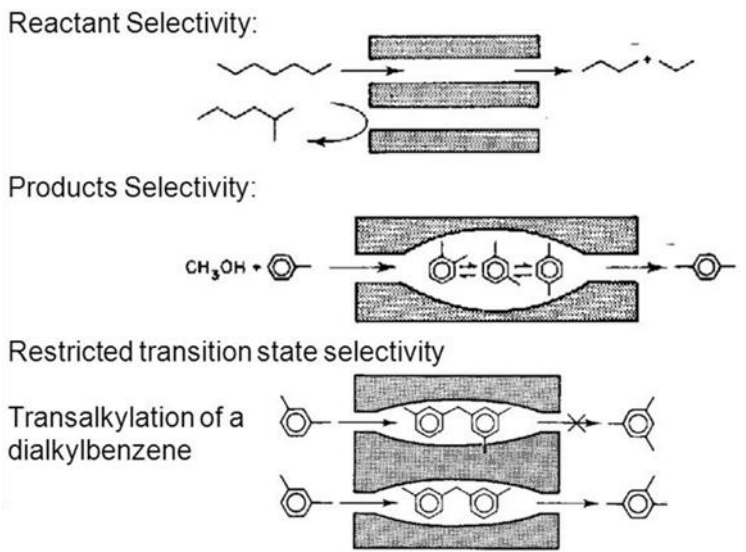
Specifically, it is the effect of the zeolite structure on entry and exit of molecules due to their dimensions and spatial orientation, as well as the constraints within the channels and cavities due to their shape and size. Thus, which molecules can enter or exit the channel structure of the zeolite and which intermediates are preferred with respect to the spatial possibilities within the channel system.

A typical number of T atoms in the channel opening is  $T = 7, 8, 9, 10, 12, 14$ . Zeolites with 8-rings (T atoms) possess pore dimensions up to 0.4 nm, referred to as small-pore zeolites. Small pore zeolites are typically used as ion exchangers and desiccants. Zeolites with 10-T-rings with pore dimensions up to 0.55 nm are named as medium pore zeolites. Zeolites with 12-T-rings, pore dimensions up to 0.75 nm, are called large pore zeolites and zeolites with more than 12-T-ring are extra-large pore zeolites. Medium and large pore zeolites are typical industrial catalysts<sup>38</sup>.

In addition to the size of the zeolite channels, the number and shape of the channel opening, together with their intersection or independency, also play an important role in



adsorption and catalysis. The actual channel structure may be one-dimensional, with individual channels not intersecting, two-dimensional or three-dimensional. In the case of some zeolites, large cavities are formed at the intersection of their channel structure, the size of which significantly exceeds the size of the channel opening. The multidimensional channel structures may possess channels of the same size or of different sizes. An interesting case is for example zeolite **MCM-22**, where the channel structure consists of two non-intersecting channel systems<sup>23</sup>.



**Figure Z4:** Shape selectivity of zeolite structures due to variable channel and pore sizes; reactant selectivity, product selectivity and transition state selectivity<sup>39</sup>



## **2.5. New approaches in structure organization - Hierarchical zeolites**

The motivation for creating more complex structures is given mainly by the fact that microporous materials, despite all their advantages, have mainly limitations in their dimensions. I.e. larger molecules cannot reach active centres (molecular sieve effect), when they are larger than the corresponding microporous scale (up to 2 nm). And then, limited rate of diffusion may lead to preference of undesirable products in reactions (diffusion driven selectivity), blocking of active centres, and overall reduction of the desired activity of materials.

Hierarchical zeolites are, much more generally said, all microporous materials that contain another porous system. According to the IUPAC classification, micropores are defined by sizes up to 2 nm, mesopores 2-50 nm and macropores have a size larger than 50 nm. Therefore, hierarchical materials according to pore size distribution are those containing at least two types of pore sizes in their structure<sup>40,41</sup>.

Hierarchical zeolites thus increase the external surface area, meaning the surroundings around the micropores (better accessibility), and not just the geometric surface; and increase the rate of diffusion of molecules and the availability of active centres. The issue can be presented as reaching desired places, and the movement itself in the narrow ancient streets (active centres in micropores), where the crowd can slow



down and get stuck. When one main wide street (mesopores and/or macropores) leads to them, the movement itself is more unrestricted, faster and also the desired place is achieved faster<sup>42</sup>.

Thus, it is necessary to create another porous system in or with microporous zeolites (and zeolite-like materials) to obtain a hierarchical system. All preparation strategies are based on a few general procedures such as crystallization, aggregation, extraction and their combinations.

The creation of another porosity can be done:

- a) in the zeolite materials themselves (all zeolitic system)
- b) by combination of zeolites with other materials (zeolitic composite materials), see later at the end of the chapter.

All zeolitic systems can be distinguished according to geometric and structural characteristics with regard to given procedures into:

- Hierarchical zeolite single crystals (further porosity within the crystal itself)
- Hierarchical monolithic zeolite materials (broken blocks of the original zeolite with other larger pores)
- Hierarchical intergrown zeolite sheets (individual sheets or layers randomly grown-together, criss-cross, creating larger pores between them)
- Hierarchical organised porous aggregates (smaller nanocrystals or nanosheets)<sup>40,41</sup>.





All zeolitic materials can be prepared by *bottom-up* approaches, then another porosity is formed during crystallization. (Note: *Bottom-up* approach means classical preparation, formation of zeolite from initial precursors  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ).

Another possibility is *top-down* procedures (selective extraction of specific sites from pre-prepared structures, e.g. desilication), which are post-synthesis steps (by e.g. leaching in an acidic and/or alkaline environment). These procedures can be applied both in the purely zeolite system and in the existing hierarchical system. (Note: The *top-down* approach simply means that the zeolite structure is first prepared and then modified to create a structure with different parameters).

In more detail, *bottom-up* approaches for introducing additional porosity into the system always occur in the crystallization process, during the formation of the zeolite itself, by the addition of another component (second different template, one template with multiple functions, crystal growth modifying additives, two closely related crystalline system with grow-together approach, aggregation process pre-formed zeolite nanocrystals).

Specifically, methods are hard-template, soft-template, and non-templating ones. For the hard-templating method (also solid-templating) it is characteristic that the template is in a solid form throughout the formation of the hierarchical zeolite and is present in a relatively stable form. These templates consist of, for example, carbon templates (carbon particles, tubes, fibres, aerogels), biological templates (such as starch, wood, bacteria), polymer templates (e.g.



polystyrene, polyurethane), and inorganic templates (e.g. silica or calcium carbonate nanoparticles)<sup>40,41</sup>.

However, the surface properties of the (hard-)template have to correspond to those in the reaction mixture, be stable at a given temperature, and finally, the structure of the hierarchical zeolite has to remain stable even after removal of the template, by extraction or calcination. However, the removal of hard-templates often leads to some degree of structure collapse and thus a decrease in the crystallinity of the hierarchical materials. On the other hand, these templates effectively affect the size and shape of the pores in the resulting material.

Soft-templates, in contrast to hard-templates, act as micelles that control either the formation of mesopores or both, micro- and mesopores together. Surfactants connect building units to form crystalline mesopores. The surfactant has two roles; the hydrophilic part plays the role of a structure direction agent for zeolite-formation (ammonium surfactants) or anchoring the surfactant to the zeolite (organosilane surfactants), while the hydrophobic parts play a role for the later formation of mesopores. During (mainly) hydrothermal synthesis, the surfactant forms micellar layers which further influence the growth of the zeolite structure, while the growth is limited in a certain direction (the principle of hydrophilic and hydrophobic parts, respectively), thus resulting in layered materials. Depending on the surfactant concentration and reaction conditions, layered structural modifications can be obtained, namely layered-like structures (with porosity outside the layer) or sponge-like structures (with porosity inside the layers grown-together).



In addition, layered-like morphology contains the porosity in three levels:

- the primary porosity given by the microporous zeolite structure in layers
- secondary, given mesopores between layers
- tertiary porosity given by macropores between individual aggregates or assemblies nanosheets

It is important to note that these types of surfactants are tailor-made to the individual needs of specific cases. Another case is the use of commercial surfactants such as cetyltrimethylammonium bromide (CTAB) in the so-called secondary soft-templating. The commercial surfactant is not added directly to the synthesis mixture, when a physical mixture of the amorphous mesoporous silica and the zeolite phase is normally formed, but after some period of the aging in the second step. Then it causes assembly of subunits to form another mesoporous ordering<sup>40,41</sup>.

A special case of the *bottom-up* approach is the so-called non-templating method. One method utilizes the self-assembly effect of some types of zeolites, where nanocrystals or crystalline formations tend to aggregate by growing together, forming another type of porosity (often by hydrothermal or dry-gel techniques). The degree of grow together then affects the number of mesopores, which are however relatively unstable and are able to lose by mechanical or thermal stress.

A second example is the use of isostructural crystalline phases such as e.g. zeolite **MFI/MEL**. Different crystal growth of these two phases (under certain conditions) then causes the formation of mesopores between them.



An interesting case is the creation of micro/mesoporosity (hierarchical structure) of zeolite type **MFI** by the method of two temperatures. At lower temperatures, pre-crystalline clusters are formed, which subsequently aggregate at higher temperatures and cause defects. Defects generate oriented crystal growth, thereby creating another type of porosity, the pure zeolite core being surrounded by a shell of meso- or macropores<sup>40,41</sup>.

In addition to *bottom-up* approaches, *top-down* methods have been mentioned. These are always post-synthesis modifications of preformed zeolites or zeolite crystals. Procedures are:

- extraction methods, removal of atoms from the zeolite framework
- delamination/rearrangement of layered zeolites or their precursors
- dissolution of the zeolite and subsequent recrystallization

Removal of framework atoms (such as Al, Si, B, and Ge) results in additional porosity. Bond-breaking of framework atoms can be caused by:

- chemical treatment (e.g. in an acidic, alkaline or hydrogen peroxide environment)
- hydrothermally (e.g. steaming)
- physical processes (e.g. radiation)
- and a combination of methods to obtain the desired properties<sup>40,41</sup>.



In addition, the extraction at the end of the synthesis is necessary step in all cases. Hierarchical materials are formed with meso- or macropores in zeolite crystals with a wide range of pore size distribution.

Dealumination, i.e. removal of aluminium from the zeolite framework, is carried out in an acidic environment at a higher temperature or by steam (500-600 °C) to form mesopores in the crystals. An overall change in structure and the increase molar ratio Si/Al, i.e. a change in the acidic properties of the resulting material, is not always desirable. Therefore, the method is limited to aluminium-rich zeolites and still the connectivity of the resulting mesopores is quite low.

Desilication, the removal of silicon from the framework, takes place without any significant influence on the acidic properties of the zeolite. This occurs with a dilute alkaline solution (organic and inorganic) at elevated temperature. The resulting pores are often interconnected, and, in addition, their size/volume can be influenced by reaction conditions, time, temperature, type and amount of base, etc. For example, in the previously mentioned zeolite structure **MFI**, the method is optimal at molar ratio Si/Al around 20-50. However, as the degree and amount of desilication increases, the amount of aluminium in the framework rises as well, thereby aluminium is partially removed to the extra-framework positions, where it can negatively affect material properties. However, the combination of acid and basic treatment causes successful removal of these undesirable species as well as damaged fragments by washing. In addition, note to case of Al-free zeolites, the surface of these zeolites has to be protected from the alkaline environment to



prevent the original zeolite from partially or completely dissolution.

Delamination and assembly are methods related to layered structures or those capable of forming layered precursors. Additional porosity can be introduced between the separate layers, similar to the known cases with clays and clay-based materials, primarily by intercalation and/or pillaring. Compared to clays, layered zeolites with hierarchical structure and additional porosity can be newly obtained by silylation technique or ADOR method (assembly-disassembly-organization-reassembly, more in the following chapter)<sup>43</sup>.

These techniques create micropores within the sheets and additional porosity results from the space between them (mesopores) and between aggregated sheets (often macropores). To create additional porosity, the following techniques are needed to separate the layers from each other, intercalation/swelling (expansion of interlayer space). Subsequently, the expanded layers can be reassembled and stabilized by pillaring or completely separated and finally delaminated. The intercalation of the surfactant between layers can lead to the complete separation of the layers (delamination). Otherwise, the arrangement so-called „house of cards" is created, with a wide range of mesopores distribution due to the irregular ordering of individual sheets (not to delamination). In the case of the pillaring method, the stacked zeolite sheets are swollen with an inorganic material (liquid silica source), which partially dissolves to form  $\text{SiO}_2$  and then bonds layers as a  $\text{SiO}_2$  network. Calcination produces a stable structure with silica pillars and additional porosity between them<sup>40,41</sup>.



Dissolution and recrystallization are classified as combined methods because they are a destructive top-down approach (alkaline treatment) with a bottom-up approach in the recrystallization step. Under mild conditions, the zeolite is partially dissolved in alkaline environment and the resulting particles are stabilized by a surfactant addition. In the next step, recrystallization, the surfactant plays the role of structure-directing agent and at the same time results the formation of mesopores (after surfactant removal)<sup>40,41,44</sup>.

Zeolite composites mainly include compaction processes (aggregation) and coating procedures (formation of layers on the support). Composites contain at least two components, an active zeolite one and a binding component or support (to ensure system stability). In the case of compaction methods, a binder, which is put (wedged) between the parts of the zeolite, prevents re-connectivity of the zeolite parts during the process. In addition, binder causes the formation of mesopores, which facilitates transport between the active sites of the zeolite. Compaction is accomplished by techniques such as pelletizing, granulating, extrusion, spray-drying and others. The binder can be clay such as kaolin, silica, alumina and others that improve the mechanical properties of the material.

The coating-based approach utilizes a pre-prepared support whose surface is functionalized (coated) with a zeolite component, resulting in a very open porous structure (often macroporous). Supports include wide range of materials such as ceramics, metals and oxides, where the coating is carried out by methods such as dip-coating, slurry-coating or so-called reactive coating to fix the zeolite component to the surface of the support<sup>41</sup>.



## 2.6. New approaches in structure organization – 2-dimensional zeolites

The boundary between hierarchical zeolites and 2-dimensional zeolites is often very delicate, one group overlaps with the other, but it is possible to follow typical features for each of them. This chapter, like the previous one, is focused on some of them for 2D-materials.

A milestone in zeolite chemistry was the synthesis of 2D zeolites<sup>45</sup> and mesoporous molecular sieves in the 1990s<sup>46,47</sup>. The effort to create a material that would solve the diffusion problem and at the same time be able to control the formation of the mesoporous system, offered the possibility of synthesizing the mesoporous molecular sieves **MCM-41** and **SBA-15**<sup>48</sup>. However, it has been shown that amorphous mesoporous molecular sieves characterized by a regular long-distance structure (2-dimensional), are not able to compete with zeolites in the field of acid properties<sup>49</sup>.

Although the first layered zeolite was prepared more than fifty years ago, the synthesis of zeolite **MCM-22** with MWW topology in the 1990s received great interest<sup>45</sup>.

It was shown that MWW can be prepared in two ways. Firstly, by direct synthesis, which was generally the procedure for the preparation of 3D zeolites at that time, here **MCM-49**<sup>50</sup>, or via a layered precursor, referred to as **MCM-22(P)**. This precursor showed character of one-unit-cell layers separated by structure-directing-agent molecules<sup>51</sup>.





To stabilize the layered precursor, post-synthesis modifications such as pillaring or intercalation have been known, in particular, from the treatment of clay layered materials<sup>52-55</sup>.

Similar modifications thus yielded a very interesting zeolite material, **MCM-36**, which combined the advantages of zeolite properties (especially acidic properties) with the presence of mesopores due to pillaring<sup>56</sup>.

In catalysis, it also showed surprising and promising properties offering a wide range of applications for 2D zeolites and their modified counterparts<sup>57</sup>.

Another boom came with the possibility of delaminating the precursor **MCM-22(P)** to form the **ITQ-2** structure. Moreover, it was shown that its catalytic properties outperformed those of the pillared counterpart. Promising catalytic properties have opened the way for large molecules, unfeasible in catalysis in the presence of microporous zeolites<sup>58,59</sup>.

Another milestone in the synthesis and application of these promising materials was the work applying specially designed bi-functional structure directing-agents. When one molecule of structure-directing agent was used for both the growth and formation of microporous layers and mesopores, all in one-pot synthesis without the application of post-synthesis procedures, as described above in cases of hierarchical structures. Thus, a layered zeolite of the **MFI** type was prepared, and a new field of research was open in the chemistry of zeolites<sup>60</sup>.



What is the nature of 2-dimensional zeolites? They have a framework of covalently bonded central atoms, however, unlike the 3D framework of conventional zeolites, in one direction is not propagated, crystal growth is occurred only in two directions. Usually the layer width is given by one unit-cell dimension, which is up to 3 nm. There are 20 known zeolites and zeolite-like structures that exist in some type of layered form, namely: **AFO, AST, CAS, CDO, FER, IPC-6, IPC-7, IPC-9, HEU, MEL, MFI, MTF, MWW, NSI, OKO, PCR, RTH, RRO, RWR** and **SOD**<sup>43</sup>.

Layered (2D) zeolites can be prepared by direct synthesis or post-synthesis procedures. Direct synthesis offers up to eight different forms of arrangements (see **Figure Z5**).

Layers of thickness up to 3 nm (one unit-cell) are finished on the surface by terminal silanol groups ( $\equiv \text{Si-OH}$ ). The layers are separated by the molecules of structure directing agents (ordered multi/lamellar precursor) that can be removed by calcination at temperatures above 500 °C. The released silanol groups then condense by the so-called toptactic condensation, which means that the topology of the layers does not change, there are no shifts or rearrangements, the opposite silanol groups react with loss of water, and the silicons are bonded with bridged oxygen to form 3D zeolite.

Comparing the zeolites, **MCM-22** prepared from this type of synthesis from the precursor **MCM-22(P)** and zeolite **MCM-49** from direct hydrothermal synthesis, there is a noticeable difference in the aluminium content. Consequently, similar structures can sometimes be reached, but this is not always (see below). There are known cases where a toptactic condensation results in a structure not yet known by direct

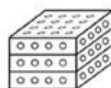


hydrothermal synthesis; or by comparing the structures direct and the one requiring a layered precursor, many changes typical of the given type of synthesis have occurred (more in ref. 62).

By calcination, it is not always possible to obtain a regular 3D zeolite from the ordered multilamellar precursor. The reason is the lateral disorder of layers.

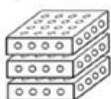
Detemplated and disordered materials can be obtained by acid extraction of the structure-directing agent. Subsequent calcination of such disordered and detemplated materials, however, leads to obtain even more disordered resultant ones. It was shown that the layers are often submerged in each other, the individual layers are not bonded via O-bridges but are strengthened by H-bonds (not covalent). Also, their interlayered space as well as the texture properties are smaller than the 3D counterparts. Therefore, the name of Sub-zeolites was introduced<sup>43</sup>. The reason could be a mismatch at the positions of the opposite silanol groups. Sometimes intercalation can be helpful, i.e. the introduction of bulky organic molecules into the interlayer, with following calcination.

Disordered multilamellar precursor and delaminated monolayers are formations known so far only for the MWW family. It is assumed that these forms are created also in other structural types, but their identification and clear separation one from the other is substantial.



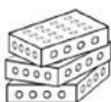
**3D zeolite**

e.g. MCM-49



**Ordered multilamellar precursor**

e.g. MCM-22(P)  
(MWW)



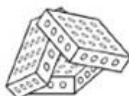
**Sub-zeolite (disordered/detemplated)**

e.g. IPC-1



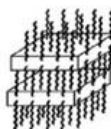
**Disordered multilamellar precursor**

e.g. EMM-10(P)  
(MWW)



**Delaminated monolayers**

e.g. MCM-56  
(MWW)



**Multilamellar precursor with surfactant**

e.g. MFI



**Unilamellar precursor with surfactant**

e.g. MFI



**Self-pillared**

e.g. MFI-MEL

**Figure Z5:** Overview of different forms of 2D zeolites prepared by direct synthesis with given structure examples (according to Ref 61).



Thus, of the type of disordered multi-lamellar precursor (shown in **Figure Z5**), the only known structure is **EMM-10(P)**. It differs from 3D zeolite in certain disordering of layers and moreover, they are not bound by each other by O-bridges, but by H-bonds (creating stacked/folded twisted layers). Interestingly, after calcination, these materials exhibit comparable properties to zeolite **MCM-22**<sup>63</sup>.

Similarly, the only representative of delaminated monolayers is zeolite **MCM-56** from the MWW family<sup>64</sup>.

Delamination proceeds through a number of post-synthesis steps (see below). This arrangement is called as "house of cards", where the individual layers can be imagined as random (i.e. irregularly) arranged lamellas over themselves, sometimes partially submerged. However, compared to the corresponding 3D zeolite **MCM-49**, they have a comparable specific surface area ( $400\text{--}500\text{ m}^2\cdot\text{g}^{-1}$ ), but in addition, delaminated monolayers possess significantly higher proportion of external surface area attributed to mesopores in the interlayer. Which makes this material potentially interesting, suitable for additional procedures as well as further study<sup>65</sup>.

Next in the list is the multi/unilamellar precursor with a surfactant. As mentioned above, specially designed surfactants/structure directing agents (SDAs) have opened a new direction in the synthesis of zeolites and this is precisely that case. The SDA molecule has the dual function, a) the promoting crystal growth in the hydrophilic part, while b) long non-polar (hydrophobic) ends prevent growth in a particular direction; giving **MFI**-nanosheets as multilamellar and unilamellar precursors with surfactants integrated



between the lamellas<sup>66</sup>. A multilamellar arrangement can be imagined as individual lamellas with a one-cell unit thickness of about 2 nm, separated by an interlayer with surfactants, of about 4 nm from each other. In order to avoid mistaking with the swelling method (see below), it should be emphasized that a) in this case the SDA molecule cannot be removed simply by acidic washing/leaching, as the hydrophilic parts of the surfactants are actively integrated in the layers and b) that calcination does not yield complete 3D zeolite. It seems that the layers are so far apart that the full condensation is not possible as in the case of the similar zeolite **MCM-22**, and the structure collapses with partial growing together (partial condensation), again showing the positive effect of the presence of mesopores in **MFI** nanosheets (in comparison with classic **MFI** structure).

The case of unilamellar precursor with surfactant has been published only for three types of structures: **MFI** and two types from the MWW family. The monolayers are randomly ordered, and the calcination does not cause the condensation of the layers. The arrangement is similar to the house of cards, but the idea of overlapping layers with partial ingrowth of layers is better suited. Again, there is a significant increase in BET area and an increasing of pore volume attributed to the presence of mesopores<sup>66</sup>.

Self-pillared zeolites are an example of how thin the boundary is in the definition of hierarchical and 2D zeolites. This case has already been described in the previous chapter; it is a possibility to prepare material with mesopores in the structure by a relatively simple synthesis route. Thus, in this example, the additional mesopores are created in structure of **MFI** nanosheets with a small addition of its twin **MEL**, as a

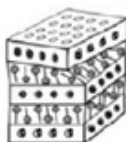


result of different growth of both types of crystals under given conditions. In addition, it is important to mention that this procedure requires only simple SDA and calcination. The disadvantage of the process is that it is only applicable to twins/pairs of anisotropic grow materials which, moreover, promote crystal growth in certain formations for reproducible results<sup>67</sup>.

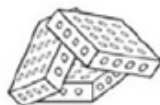
In order to maintain the formation of layers/lamellas and to support the presence of additional pores (often mesopores), several post-synthesis procedures is applied to stabilize the structure (see **Figure Z6**). These procedures include, swelling, pillaring, delamination, stabilization of ordered precursor (Interlayer Expanded Zeolite, IEZ), and stabilization by colloidal suspension.

The successful intercalation of long organic molecules between layers and lamellas (known from the chemistry of layered clays) was one of the evidences that layered forms of zeolites can be prepared. The best-known intercalating/swelling agent is hexadecyltrimethylammonium cation, which separates the layers and allows further processes. If calcination occurs directly, the result is 3D zeolite or Sub-zeolite. If the following processes, such as pillaring or delamination, are applied, separation of layers can be achieved.

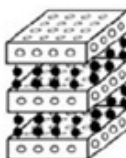
After the first step (swelling), where the layers are separated and expanded, the second step for pillaring introduction is applied. The most common inorganic pillaring agent is amorphous  $\text{SiO}_2$ , which causes stabilization of the separated zeolite layers. The disadvantage is just the amorphous character of the mesoporous pillars.



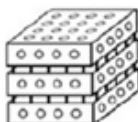
**Swollen precursor**



**Delaminated swollen precursor**



**Pillared zeolite  
(inorganic, organic)**



**Stabilized ordered precursor  
(interlayer expanded zeolite)**



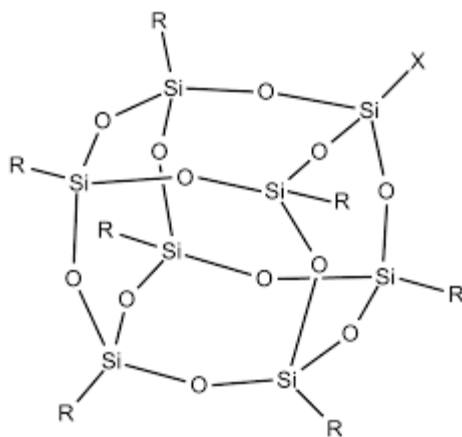
**Colloidal suspension**

**Figure Z6:** Overview of different forms of 2D zeolites prepared by post-synthesis procedures (according to Ref. 61).





Organic pillars always introduce a certain degree of thermal instability into the structure. However, it was shown that mesopores can be introduced into the zeolite structure by functional pillaring (e. g. by silsesquioxanes, see **Figure 27**), but the introducing of functional groups (e. g. by amination) to produce, for example, linkers with basic properties and thereby the formation of a bifunctional acid-base catalyst (acidic properties given by the zeolite character of the layers and alkaline properties in pillars in the interlayer space) can be achieved also by post-synthesis modifications of the pillars<sup>68</sup>.



**Figure 27:** Structure of organic linkers in pillaring process, silsesquioxanes linkers (where R = H, alkyl, aryl or alkoxy), for more details see ref. 69.



The first delaminated zeolite was **ITQ-2** from the MWW family. Other materials were prepared according to the above-mentioned procedure with a step including swelling, such as pre**FER**. Later there was an effort to replace the harsh basic conditions of swelling (see later). Delaminated zeolites have a random orientation and tendency to arrange either edge-to-face or face-to-face, which leads to the formation of mesopores between layers. The degree of delamination is not easy to determine, the key parameter is the value of the specific surface area (significant increase next to the corresponding 3D zeolite) as the main indicator of delamination<sup>58,70,71</sup>.

Method of stabilized precursor can be understood as a special case of pillaring, where a swelling step is not used, a bridging agent is introduced directly. Alkoxysilanes have proven as an optimal choice for bridging the layers (e.g. diethoxydimethylsilane is an ideal silylating agent). The added agent reacts with the terminal silanol groups to form bridges between the individual zeolite layers, and the remaining methyl groups are then oxidized to hydroxyl groups during the calcination. Generally, linkers between layers can be recorded as: (layer-Si)-O-Si(OH)<sub>2</sub>-O-(Si-layer). The resulting material differs from the corresponding zeolite only by increasing the pore opening between the layers, e. g. **MCM-22** has a 10-ring opening and stabilized MWW-IEZ has a 12-ring opening, hence the name Interlayer Expanded Zeolites (IEZs)<sup>72</sup>.

The colloidal suspension method, simply said, is stabilizing layered precursors in a liquid medium. Thus, there is no collapse of the layers, no merging or no interconnection. In the work 73, exfoliated **MFI** layers stabilized in polystyrene,



where nanosheets did not aggregate in suspension. Later this group made a suspension of detemplated nanosheets even in water. This could be used for formation of zeolite films<sup>74</sup>.

As mentioned earlier, the introduction of organic molecules as Structure-Directing Agents (SDAs) marked an important breakthrough in zeolite synthesis; and what about the introduction of specially designed bifunctional SDA. As for lamellar zeolites, their *bottom-up* syntheses can be easily differentiated from those using simple SDAs and those using special-designed surfactant-SDAs.

The disadvantage of simple SDAs (quaternary ammonium salts, cyclic amines, etc.) is that they are not very selective, i.e., they can synthesize multiple types of zeolite structures. Typical examples are the MWW family structures. Hexamethyleneimine as SDA can affect the synthesis of **MCM-49** as 3D zeolite, **MCM-22(P)** as ordered multilamellar precursor and **MCM-56** as delaminated one. Which of the structural types are finally formed depend on reaction conditions such as composition, temperature, etc.

On the other hand, there are cases where one type of SDA supports the formation of only one layered type, e. g. the aforementioned disordered multilamellar precursor **EMM-10(P)**, where SDA is penthamethonium bromide. Otherwise, similar types of precursors may result in other structures depending on the different nature of SDAs and synthesis conditions (e. g. **CDO** and **FER** zeolites). Finally, it should be noted that the final product can be influenced by post-synthesis steps<sup>75</sup>.



It was the unpredictability of conventional surfactants that led scientists to search for the most targeted SDA structures. The previously mentioned bifunctional SDA was a breakthrough. These are molecules containing in one molecule both a hydrophilic part supporting the formation of the zeolite phase itself (often quaternary ammonium groups) and a hydrophobic part which acts as a zeolite growth inhibitor.

It was shown that the nature of the hydrophobic chain can influence the resulted structure formation. Long alkyl chains (Ryoo group method) form micelles which prevent the growth of zeolite. If the alkyl groups are replaced by aromatic (Che group results), they interact with each other through aromatic ring electrons (in biphenyls or naphthyl) and the formed layer of interacting aromatic molecules prevents the growth of zeolite in this direction<sup>60,66,76</sup>.

Based on these two directions, a number of SDAs was studied. At least 5 main types surfactant-SDA can be distinguished according to the type of layered structure directing.

- Single-alkyl-tail surfactant-SDA
- Single-aromatic-tail surfactant-SDA
- Gemini type surfactant-SDA
- Bolaform type surfactant-SDA
- Triply Branched surfactant-SDA

Single-alkyl-tail surfactant-SDA with structure:  $C_{22}H_{42}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}$  (denoted as  $C_{22-6-6}$ ) directs the single-unit cell formation of **MFI** nanosheets, either as ordered multilamellar MFI or disordered unilamellar



MFI according to reaction conditions. The thickness of the nanosheet layer can be modified by the amount of quaternary ammonium groups, but the minimum is two, and in the case of the alkyl chains to prevent crystallization, the optimal number of carbon in chain is 10-22.

Interestingly, when a bulk MFI seed is added to this type of SDA (method of seeding), the nanosponge-like MFI morphology results instead of uni/multilamellar one<sup>77</sup>.

Single-aromatic-tail surfactant-SDA possess the structure:  $\text{C}_6\text{H}_5\text{--C}_6\text{H}_4\text{--O--C}_{10}\text{H}_{20}\text{--N}^+(\text{CH}_3)_2\text{--C}_6\text{H}_{13}$  (denoted as  $\text{C}_{\text{Ph-Ph-10-6}}$ ) and it directs the formation of single-crystalline zeolite nanosheet (SCZN-1) with multilamellar ordering of MFI, but it appears to be more ordered (3D zeolite can be created during calcination). Interestingly, unlike the previous SDA type, only one quaternary ammonium salt is sufficient in a molecule<sup>76,78</sup>.

Designing surfactant-SDA molecules of these two types, interchanging or introducing additional units into the molecule (e.g., a bulky adamantane-type carbon chain adjacent to a quaternary ammonium group caused interesting structural modifications, see 79), could be another direction in the field of zeolite syntheses.

Gemini type surfactant-SDA (Gemini-type triammonium surfactant) consists of three parts, the hydrophilic part (containing three quaternary ammonium groups) is terminated on both sides by hydrophobic ends. The structure is:  $\text{C}_{18}\text{H}_{37}\text{--N}^+(\text{CH}_3)_2\text{--C}_6\text{H}_{12}\text{--N}^+(\text{CH}_3)_2\text{--C}_6\text{H}_{12}\text{--N}^+(\text{CH}_3)_2\text{--C}_{18}\text{H}_{37}$  and denoted as:  $\text{C}_{18}\text{-N}_3\text{-C}_{18}$ <sup>80</sup>.



These syntheses result in zeolite layers even thinner than a one-unit cell. Nanosheets are 1.5 nm thick, so they are referred to as single-pore zeolite. Interestingly, substitution of alkyl linkers between quaternary ammonium groups for phenyls causes that nanosponge-type zeolites can be obtained with larger pore-opening. The reason is the role of these SDAs parts, here more like bulky void fillers.

Bolaform surfactant-SDA consists of a hydrophobic part in the middle (biphenyls between alkyl chains) terminated on both sides by hydrophilic parts (each end contains two quaternary ammonium groups separated by alkyl linkers). Structure is:  $\text{C}_6\text{H}_{13}-\text{N}^+(\text{CH}_3)_2-\text{C}_6\text{H}_{12}-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_n-\text{N}^+(\text{CH}_3)_2-\text{C}_6\text{H}_{12}-\text{N}^+(\text{CH}_3)_2-\text{C}_6\text{H}_{13}$ , denoted as:  $\text{BC}_{\text{Ph-n-6-6}}$ . With this SDA, multilamellar **MFI** nanosheets were prepared. Moreover, single-crystalline zeolite nanosheets (**SCZN-2**) similar to the self-pillared one was synthesized. **MFI** nanosheets were associated with a  $90^\circ$  rotational boundary under precisely given conditions and with SDA ( $\text{BC}_{\text{Ph-n-6-6}}$ ,  $n = 6$  and  $8$ ), which was a geometrically comparable counterpart<sup>78</sup>.

The structure of the Triply-branched surfactant-SDA can be demonstrated as a branched trisubstituted benzene ring. Benzene is substituted at the 1,3,5 positions through O-bonds with long (C12) alkyl chains terminated by two quaternary ammonium groups with C6-linkers and C6-alkyl ends. The substitution chain at each position can be recorded, starting from basic central benzene, as:  $\text{Ph}-\text{O}-\text{C}_{12}\text{H}_{24}-\text{N}^+(\text{CH}_3)_2-\text{C}_6\text{H}_{12}-\text{N}^+(\text{CH}_3)_2-\text{C}_6\text{H}_{12}$ , the whole molecule is denoted as:  $\text{TC}_{\text{Ph-12-6-6}}$ . Again, the electron interaction of aromatic rings of SDA molecules plays a role in the formation of micelles, while the other three hydrophilic parts support the crystallization of **MFI**. This type of surfactant-SDA controls



the formation of 2-4 nm thick MFI nanosheets with 90° rational structure. The new mesoporous **ZSM-5** structure with inter-crossed nanosheets resembles a self-pillared arrangement<sup>76,78</sup>.

Top-down procedure was first described in 2011, Čejka and co-workers designated it for the synthesis of 2D zeolites. It is necessary to understand that this is an extraordinary step, which makes possible to prepare zeolites by until then unknown mechanism, under different conditions, and thus, we can expect completely new structures. The method is based on controlled decomposition (disassembly) of the original 3D zeolite into the corresponding zeolite layers<sup>81</sup>.

For the method it is essential that the original zeolite is a germanosilicate. About the properties of germanium in the zeolite structure was written before, however, in 2000s introducing germanium to the zeolite framework was an interesting topic and thanks to its incorporation several attractive structures were prepared. In addition, germanium occupies specific positions in the zeolite framework, preferentially in double-four rings. Moreover, under specific conditions, hydrolysis preferably takes place in positions with germanium, whereby layered precursors can be obtained (and the entire structure may not dissolve or recrystallize).

For the starting material to be suitable for this process (meaning 3D zeolite), the following conditions must be met:

- it must contain incorporated germanium in the structure
- germanium must be in specific positions (specifically in double-4-rings connecting units)



- the germanium content must be enough for complete separating of layers

The first works were performed on germanosilicate zeolite **UTL**. It was prepared by the classical hydrothermal procedure, i.e. bottom-up approach<sup>82</sup>.

For a clearer picture, germanium in double-4-rings can be thought as crystalline pillars between silicate layers. The germanium content is in molar ratio  $\text{Si/Ge} = 4.3 - 6.0$ , which means that 5-7 Ge-atoms occur in double-4-rings units (maximum is 8). Under mild acidic conditions, germanium is removed from the structure and pure silicate layers remain. This new material, named as IPC-1 (P) according to the Institute of Physical Chemistry, consists of silicate lamellas, of the ordered multilamellar arrangement type. Stabilization is performed by H-bridges of terminal silanol groups ( $\equiv\text{Si-OH}$ ) from the original sites corresponding to the double-4-rings. The layered structure was further subjected to the swelling treatment and pillaring<sup>81,83</sup>.

An apparent advantage is that the daughter structures are predictable. And this is the basic step for the proposed synthesis called ADOR, for the creation of new 3D zeolites. ADOR refers to the individual steps, assembly – disassembly – organization – reassembly. In short, the principle can be summarized as follows: the respective synthesized parent germanosilicate (assembly) is broken down into layered silicate in a controlled way (disassembly). Organization means modifying layers, stabilizing them, moving them, inserting pillars, etc. Finally, by topotactic condensation, the





corresponding 3D zeolite is obtained. It is important to note that the resulting zeolite has the same layer topology as the parent one, it differs by the connection/connectivity of layers<sup>84</sup>.

The main advantage and importance of 2D zeolites is the possibility of their modification. The simplest modification of the layered precursor is the removal of the surfactant. This can be done either by calcination (thermal combustion) or by chemical extraction. Calcination, i.e. heating at a higher temperature, removes all organic molecules and water, the released silanol groups interact with each other (in opposite layers) and the result is either 3D zeolite (3D framework) or sub-zeolite, where the layers are not in optimal positions, thus slightly collapse and result in layers merge into each other. Simply said, the interlayer distance in sub-zeolite is smaller than in 3D zeolite.

Extraction under acidic conditions, leads to removal of the surfactant, however it was also shown that, in some cases, the extraction step before the calcination leads to the formation of another structure (more in 75,85).

Also, the extraction process is useful when the surfactant is to be replaced by another intercalating agent, then the step of surfactant extraction is the first one<sup>86</sup>.

Intercalation to the interlayer of zeolite includes either a swelling (of the surfactant molecules) or pillaring process, or intercalation of organic molecules for a purpose of the layer manipulation.



Swelling or intercalation of long chains of quaternary ammonium salts was initially taken as the evidence of the layered structure. Swelling involves breaking the interlayer interactions (H-bonds) to incorporate the surfactant molecules between the layers together with the expansion of the interlayer space. It is a key step for other procedures such as pillaring (i.e. permanent intercalation), or delamination/exfoliation (i.e. separating the layers from each other).

When intercalating with hexadecyl-trimethyl ammonium cation, CTMA<sup>+</sup>, under basic conditions was performed (to H-bond breaking), the zeolite partially dissolves and an amorphous phase of the M41S type is formed, sometimes entirely MCM-41 (a mesoporous molecular sieve whose structural units correspond to those in zeolite, not in the crystalline but in the amorphous phase)<sup>87-89</sup>.

To avoid mistake whether or not layered counterparts are formed and also to estimate suitable conditions for intercalation, it is recommended to carefully analyse both as-synthesized and calcined swollen material (especially by XRD and sorption measurements, see below). When the layers are separated (after intercalation), the peak in the low-angle area shifts by about 5° Theta. After calcination, when all the organic matter is removed, this peak should disappear due to the connection of layers (either regularly or irregularly). In addition, the sorption capacity often decreases. While in the case of mesoporous amorphous phase M41S, the peak related to this phase remains in the low-angle area even after calcination and the sorption capacity is usually higher than that of 3D zeolites (due to the presence of mesopores).



The combination of hexadecyl-trimethyl ammonium cation (CTMA<sup>+</sup> cation) with organic hydroxide as tetramethyl ammonium hydroxide was shown to be a good swelling agent and milder basic conditions can be used to prevent partial dissolution of the zeolite.

The aim of zeolite pillaring is permanent stabilization of microporous zeolite layers (with all the advantages and features mentioned so far) while improving diffusion properties and mass transport. The pillaring itself must be preceded by a swelling step. On the other hand, e.g. multilamellar precursors of the **MFI** structure do not need a swelling step, since the layers are already sufficiently separated by long chains of SDA molecules (such as the bifunctional SDA C<sub>22-6-6</sub>).

The most common inorganic agent for pillaring is tetraethyl orthosilicate (TEOS), which hydrolyses when incorporated into the interlayer and after calcination, when the surfactant and water are removed, the subsequent condensation creates amorphous SiO<sub>2</sub> pillars<sup>90</sup>.

Interestingly, the pillars do not block the entire interlayer space and allow molecules access to the active centres in the zeolite layers. However, the disadvantage is the introduction of amorphous, i.e. inactive silica into the structure. This can be understood as a kind of dissolution of the crystalline layers into the amorphous phase. There was the effort to replace amorphous silica for example with Al<sub>2</sub>O<sub>3</sub> pillars, eventually in combination with Mg and Ba ions. This resulted in alumina-silica clusters in the interlayer space which caused an increase of Bronsted acidity. Combinations with Ba and Mg ions as the basic sites led to the MgO/BaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-**MCM-36** hybrid



materials, thus the formation of a bifunctional acid-base catalysts<sup>91</sup>.

In this regard, it is interesting to mention the combination of silica-titania pillaring, e.g. Ti-pillared-MFI structure, in combination of tetraethyl orthosilicate and tetrabutyl orthotitanate, where both silicate nanosheets and titanasilicate ones were pillared. Remarkable results can be observed in the catalysis of large molecules oxidation reactions against classical microporous Ti-zeolite, TS-1<sup>92,93,94</sup>.

A special case of pillaring is the formation of Interlamellar Expanded Zeolite (IEZ), the simplest connection of lamellas is carried out by incorporating one silicon between the silanol groups of layers. The result is interlamellar-stabilized zeolite, which differs only in larger pore-opening.

The introduction of a new  $\text{SiR}_2$  bridge into the structure can be performed either after previous swelling step or directly with the layered precursor. The process takes place in an acidic medium, with the addition of a silylating agent (alkoxysilane) at a higher temperature above 100 °C<sup>72</sup>. Calcination results in oxidation and formation of  $=\text{Si}(\text{OH})_2$ .

Interlamellar Expanded Zeolite (IEZ) are not considered as true zeolites, because they do not contain four-connected Si-bridges, instead of that the composition is: layer-Si-O-Si(OH)<sub>2</sub> -O-Si-layer. The only exception is the precursor **IPC-1(P)**, which contains terminal silanol groups that form a quadruplet on the surface of the layers. Thus, upon silylation, adjacent O-Si(CH<sub>3</sub>)<sub>2</sub>-O bridges interact to form single-four-ring units. Formed zeolite corresponds to the definition of true zeolite and is denoted as **IPC-2**<sup>95</sup>.



If the layers of the precursor allow different spatial arrangements, then their stacking is dependent on the nature of the intercalating agent. The process is referred as layered manipulation. An example is the layered precursor **IPC-1(P)**, which is obtained by hydrolysis of germanosilicate zeolite **UTL**. As already mentioned, layered precursors are formed at the double-4-rings (the original Ge location), so a quadruplet of the terminal silanol groups is present as well as the hypothesis for the formation of a true zeolite after calcination. According to Ref 94 there are theoretically four different structures that can be obtained from **IPC-1(P)**, but they differ in energy. This means that some energy is needed to move the layers out of the most energy efficient arrangement. Most preferred is a structure formed by direct calcination of the **IPC-1(P)** precursor or by calcination of the intercalated precursor by octylamine,  $\text{CH}_3-(\text{CH}_2)_7-\text{NH}_2$ , which stabilizes the layers for perfect overlap and subsequent condensation. The resulting structure is zeolite **IPC-4** (with 10-8R channels) with IZA code **PCR**.

Another type of intercalating agent has to be used to achieve the shift, choline was proposed,  $(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{OH}$ , since depending on the choline amount, different layer shifts can theoretically be achieved<sup>96</sup>.

Experimentally, the precursor **IPC-9(P)** was prepared in excess of choline. By calcination it forms the zeolite **IPC-9** with 10-7R channel system. Like **IPC-1(P)** with its interlamellar expanded zeolite (IEZ) as true zeolite **IPC-2** (12-10R channel system), also **IPC-9(P)** can be stabilized by alkoxysilane to produce true zeolite, **IPC-10** (with 12-9R channel).



Interestingly, the syntheses of zeolites **IPC-9** and **IPC-10** were previously considered as unfeasible, based on their framework energy and density<sup>97</sup>.



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