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Environmental catalysis by tailored materials derived from layered minerals

Ewa M. Serwicka[a,*], Krzysztof Bahranowski[b]

[a] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Cracow, Poland
[b] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Cracow, Poland

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Abstract

The use of layered minerals for design and synthesis of catalytic materials applicable in environmental catalysis is illustrated by examples from authors' own works. Interest is focused on systems derived from hydrotalcite-like anionic clays and layered silicates. In the former case the centre of attention is the compositional flexibility of the hydrotalcite structure, in the latter expandability of the layered structure leading to microporous (PILC) and mesoporous (FSM) materials. The discussed fields of application include the examples of end-of-pipe processes and green chemistry reactions.

Keywords: Environmental catalysis; Layered mineral; Hydrotalcite; Montmorillonite; Pillared clay; Silicate; Kanemite; FSM-16

1. Introduction

The present concepts of catalyst design focus on application of the atom-by-atom or molecule-by-molecule strategy in preparation of new catalytic materials. However, beside atoms and molecules, which may be regarded as "bricks" in the architecture of new catalytic materials, nature provides also larger units, having the character of prefabricated building blocks, ready to be fitted into a desired construction. Layered minerals, with their structure consisting of stacked sheets, represent an abundant source of such elements. Appropriate manipulation of the lamellae allows for engineering of a variety of novel materials. The features of layered minerals most frequently exploited in various preparative approaches are: structure expandability, ion exchange properties and/or flexibility of the layer composition.

This paper reviews the use of layered minerals for design and synthesis of catalytic materials applicable in environmental catalysis, basing on authors' own experience. Interest is focused on systems derived from hydrotalcite-like (Htl) anionic clays and layered silicates. The discussed fields of application include the examples of end-of-pipe processes and green chemistry reactions.

2. Anionic clays

Although the abundance of anionic clays, also known as hydrotalcites or layered double hydroxides, in natural environment is rather limited, the materials can be relatively easily obtained in a synthetic way [1,2]. Their structure can be derived from the layered mineral brucite $Mg(OH)_2$, consisting of stacked sheets of Mg^{2+} ions surrounded octahedrally with hydroxyls (Fig. 1). Partial substitution of Mg^{2+} with cations of higher charge renders the layers positive and the excess charge is compensated by the presence of anions in the interlayer. The mineral containing Mg and Al in the brucite sheet and carbonate in the interlayer is known as hydrotalcite, but there is a number of other di- and tri-valent cations, including transition metal ions, which may form the brucite sheet, as well as a variety of possible charge balancing anions. In general, the materials may be described with the formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]A_{x/n}{}^{n-} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent (e.g. Mg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}) and trivalent (e.g. Al^{3+}, Cr^{3+}, Ga^{3+}, Co^{3+}, Mn^{3+}, Fe^{3+}, V^{3+}) cations, respectively,

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* Corresponding author. Tel.: +48-12-639-5118; fax: +48-12-425-1923.
E-mail address: ncserwic@cyf-kr.edu.pl (E.M. Serwicka).

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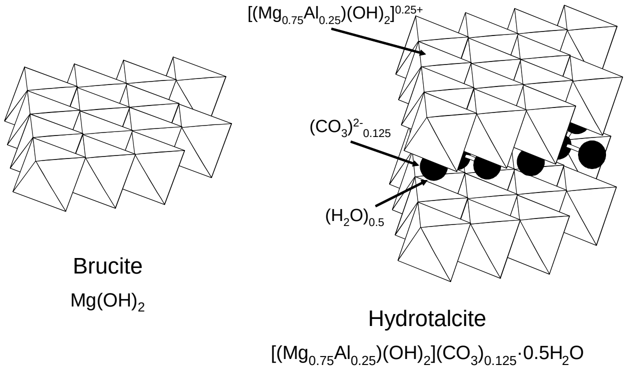

Fig. 1. Relation between the brucite and the hydrotalcite structures.

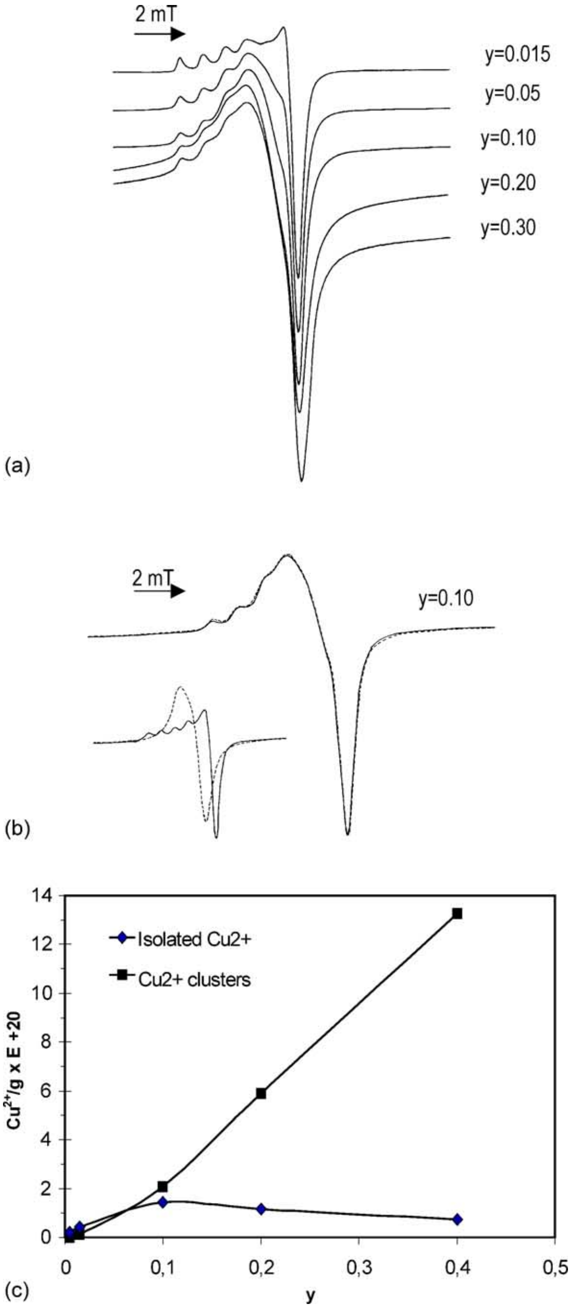

Fig. 2. (a) ESR spectra of $[(Zn_{1-y}Cu_y)_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}$ samples recorded at 77 K, (b) experimental (solid line) and calculated (dashed line) ESR signal of $y = 0.1$ sample showing components of the calculated spectrum (insert, isolated centres—solid line, clustered species—dashed line, (c) dependence of the content of isolated and/or clustered Cu^{2+} species on y (after [6]).

A^{n-} is the interlayer anion compensating the layer charge (e.g. $CO_3{}^{2-}$, NO^{3-}, Cl^-, $SO_4{}^{2-}$, $V_{10}O_{28}{}^{6-}$, $Mo_7O_{24}{}^{6-}$, $PV_2Mo_{10}O_{40}{}^{5-}$, $C_6H_4(COO)_2{}^{2-}$), 'x' describes the degree of substitution within the brucite layer (usually $0.2 < x < 0.34$). The ability of the hydrotalcite structure to accommodate so many variables opens enormous possibilities for designing tailor-made materials [3–5]. An important feature of the hydrotalcite-like materials is their limited thermal stability and ease of formation of mixed oxide phases. Due to the homogeneous interdispersion of constituting elements in the hydrotalcite matrix, the mixed oxides formed upon thermal decomposition of anionic clays possess unique properties, unattainable by other preparative procedures. For this reason hydrotalcite-like materials gain increasing importance as extremely attractive precursors of multicomponent catalysts for many reactions of industrial interest [4].

A quality of particular importance is the compositional flexibility of hydrotalcites, allowing for precise control of the material properties with respect to the content of a given element. This is well illustrated by our work on Cu, Zn, Al hydrotalcite catalyst for low energy cost (333–365 K), liquid phase oxidation of aromatic hydrocarbons using hydrogen peroxide as an eco-friendly oxidant [6]. Incidentally, this is also a rare example of the catalytic application of the hydrotalcite material in its intact, undecomposed form. The catalyst design based on the catalytically inert Zn, Al hydrotalcite matrix, in which Zn was gradually substituted with active Cu^{2+} centres, according to the formula $[(Zn_{1-y}Cu_y)_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}$, with the value of y ranging from 0 to 0.4. The XRD patterns of all samples were typical of a hydrotalcite phase. The ESR spectra of the materials with $y > 0$ were characteristic of paramagnetic Cu^{2+} ions and their lineshapes changed with increasing copper content (Fig. 2a). Analysis of the spectra showed that they could be deconvoluted into two components: one with a well resolved hyperfine structure, typical of isolated copper ions, and the other, with unresolved hyperfine pattern and larger linewidth, associated with clustered copper species (Fig. 2b). The concentration of both types of species varied with y—while the amount of clustered copper ions steadily increased, the isolated centres reached a maximum number around $y = 0.10$ (Fig. 2c). The activity of the materials in the low temperature oxidation of aromatic hydrocarbons depended strongly on the catalyst composition. The yield of the selective oxidation products initially strongly increased with the growing amounts of copper dopant, then passed through a maximum at an intermediate value of y, and rapidly decreased for higher copper contents. This is illustrated in Fig. 3 showing the data obtained at 333 K for

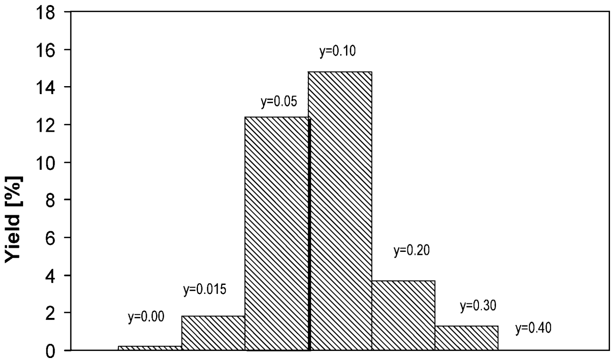

Fig. 3. Yield of products (methylphenol and benzaldehyde) in selective oxidation of toluene over $[(Zn_{1-y}Cu_y)_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}$ samples (after [6]).

toluene, with maximum yield to both ring and methyl group oxidation products attained at $y = 0.1$. Coincidence of the maximum catalytic activity towards selective oxidation with the maximum number of isolated copper species led to the conclusion that isolated Cu^{2+} ions acted as active centres in the process. Further analysis of the results showed that clustered copper species were not only inactive in oxidation but, additionally, accelerated the non-productive decomposition of hydrogen peroxide resulting in the rapid loss of the reaction yield. The above example illustrates the attractive feature of catalysis by undecomposed hydrotalcite materials, for which the catalytic performance may be directly related to the well defined, model structure, allowing for identification of the catalytically active sites and facilitating elucidation of the reaction mechanism.

The ability of the hydrotalcite matrix to host a number of different elements distributed homogeneously at the atomic level is also responsible for the fact that the mixed oxide phases produced upon thermal decomposition of these materials possess unique properties, which cannot be matched by those of oxidic materials obtained from other types of precursors [2,4]. This has been demonstrated, for instance, in our study of hydrotalcite-derived Cu–Cr–O mixed oxide catalysts for complete oxidation of volatile organic compounds, where an excellent copper oxide/copper chromite catalyst obtained by thermal decomposition of $[Cu_{0.67}Cr_{0.33}(OH)_2](NO_3)_{0.33}$ hydrotalcite showed activity much higher than the mixed oxide material of the same composition obtained from conventionally prepared precursors [7]. Therefore, when we next faced the problem of designing a catalyst capable of efficient removal of volatile organic compounds containing nitrogen, whose widespread use in synthetic fibres manufacturing turned out to have genotoxic effects on the exposed workers [8], our first choice was to build upon our experience with Cu, Cr hydrotalcites [9]. Dimethylformamide (DMF), a popular solvent, has been chosen for the catalytic tests. The aim of the reaction was to oxidise the organic part to CO_2 and to convert the nitrogen component to N_2, both at a possibly low temperature. Such a task represents quite a challenge, because catalysts with high oxidising power, active in total combustion of organic compounds, tend to oxidize the nitrogen component to nitrogen oxides, which is an obviously unwanted effect. Indeed, the starting copper–chromium catalyst reached 100% DMF conversion at temperature as low as 457 K, but combustion was accompanied by a simultaneous massive evolution of various nitrogen oxides. In order to reduce the oxidising ability, the catalyst design included introduction into the structure of the hydrotalcite precursor of neutral, diluting divalent and/or trivalent layer-forming elements, such as Zn and Al. Further modification was aimed at adding centres potentially active in the catalytic reduction of evolving nitrogen oxides, hence the choice of vanadium, the major component of industrial $deNO_x$ catalysts [10,11]. Vanadium was incorporated into the hydrotalcite structure as interlayer $V_2O_7{}^{4-}$ or $V_{10}O_{28}{}^{6-}$ anions. Optimisation of the catalyst composition was carried out under the assumption that the level of DMF conversion and the level of selectivity to N_2 had to be higher than 80%. Results of the optimisation depended strongly on the temperature of thermal decomposition of the hydrotalcite precursor. The data for materials calcined at 673 K are presented as an example in Fig. 4a, showing the temperature windows in which the performance of the investigated catalysts met the above criteria. Best results have been obtained for materials prepared from multicomponent hydrotalcite precursors,

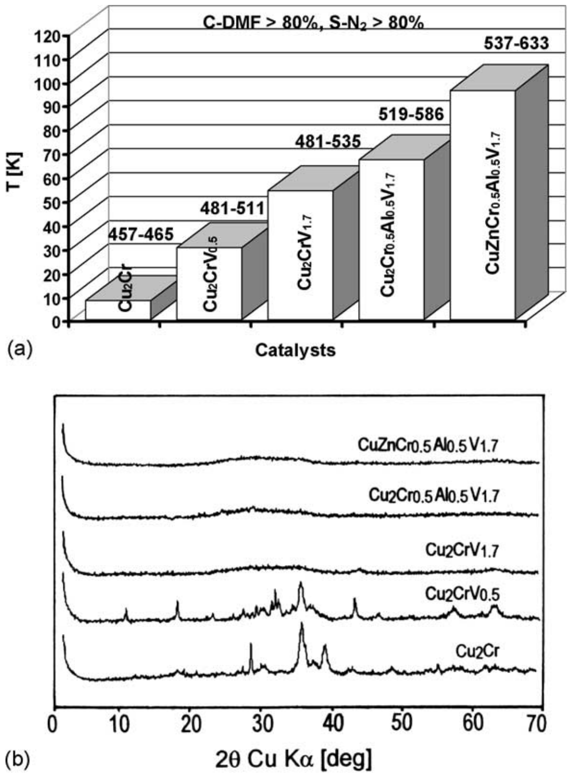

Fig. 4. (a) Optimisation of the hydrotalcite-derived mixed oxide catalysts for destruction of DMF—temperature windows and temperature ranges fulfilling the condition of >80% DMF conversion and >80% selectivity to N_2, (b) XRD patterns of the catalysts (after [8]).

whose XRD characteristics showed amorphous structures typical of intermediate mixed oxide phases resulting from hydrotalcite decomposition (Fig. 4b). The importance of amorphousness of the mixed oxide phase was confirmed by the generally poorer performance of the same hydrotalcite catalysts calcined at higher temperature (773 K), at which all samples showed the presence of crystalline phases.

3. Layered silicates

Layered silicates used in catalyst design are chiefly represented by the family of smectites. The most frequently investigated material is montmorillonite, whose structure is presented in Fig. 5a. The main building unit of this mineral is a negatively charged layer composed of two tetrahedral Si–O sheets sandwiching an octahedral Al-based sheet. The excess negative charge of the layers stems from partial substitution of Al^{3+} by Mg^{2+} and is neutralised by the presence of compensating cations in the interlayer space. The ability of the compensating cations to be easily exchanged with other cationic species led in the past to the design and development of clay-based zeolite-like materials, known as pillared interlayered clays (PILCs) [12]. Basically, the concept of pillaring consisted in converting layered clay minerals into highly porous structures by exchanging the charge compensating cations with large inorganic polymeric oxy-hydroxy cationic species, which propped open the silicate layers (Fig. 5b). Upon high temperature treatment, the oligomers transformed into nanoparticles of respective oxides, linking permanently the silicate sheets. PILCs, with their large surface area, high pore volume, and pore size tunable from micropore to low mesopore range have immediately attracted interest as potential adsorbents and catalysts. Synthetic procedures and catalytic/molecular sieve applications of pillared clays have been recently reviewed by Kloprogge [13] and Ding et al. [14]. Our studies of these materials included examples of their application in environmental catalysis, both for the green chemistry reactions and for the end-of-pipe processes [15–17]. In the latter case we started with designing deNO$_x$ catalysts. In view of the fact that the commercial catalyst for selective catalytic reduction of NO with ammonia is based on vanadium oxide active phase supported on a modified titania carrier, the design of a corresponding system, involving PILC structures represented a particular challenge. To follow this path of investigation we have developed a method of doping titania-pillared montmorillonite with vanadium by means of cation exchange in such a way that V centres were anchored exclusively to Ti-pillars [18,19] and then tested the materials in SCR of NO with NH_3 [20]. The performance of a V-Ti-PILC catalyst, together with that of a reference V/TiO_2 sample prepared by impregnation, is illustrated in Fig. 6. The results show clearly, that in a wide temperature range the PILC catalyst is more efficient in NO removal than the reference sample, and confirm that the deposition of vanadium on titania pillars leads to novel systems, of properties different from those of supported material prepared in a conventional way. Catalytic performance of the clay samples depended on the level of doping with vanadium (0.8–5.3 wt.%), and best results were obtained for catalyst with intermediate V content. Application of ESR analysis allowed for rationalisation of this result, as it demonstrated that doping of Ti-PILC support with vanadium by means of cation exchange led to the appearance of two types of V species: monomeric, dominating at low V contents, and polymeric, prevailing at high levels of doping. Optimum catalytic properties have been obtained with material with possibly high V content but below the level where significant amounts of polymeric V species appeared.

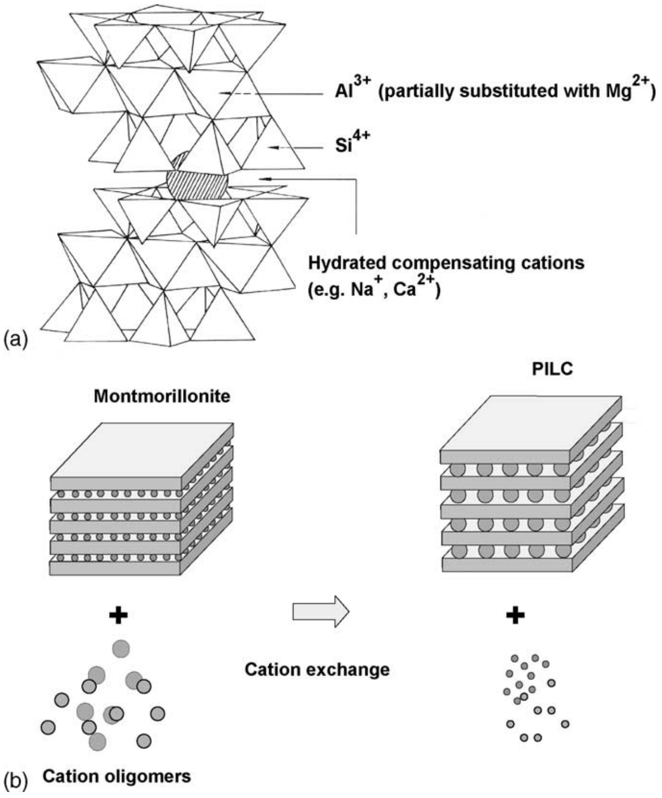

Fig. 5. (a) Structure of montmorillonite, (b) scheme of pillaring process.

Recently, we have obtained very interesting results in developing a clay-based catalyst for removal of chlorinated volatile organic compounds (CVOCs) [21–23], which constitute a major portion of the hazardous solvent wastes released into the environment by industry. Catalytic combustion aims at the total conversion of chlorine, contained in the organic molecule, into HCl, and oxidation of the organic part into H_2O and CO_2, all at a possibly low temperature. It has been argued, that this process requires both acid and redox centres [24]. The catalyst design focused on combining acidic properties of a pillared clay with redox properties of an appropriately chosen dopant. Best results have been obtained with chemically resistant and thermally robust titania- or zirconia-pillared montmorillonites, doped

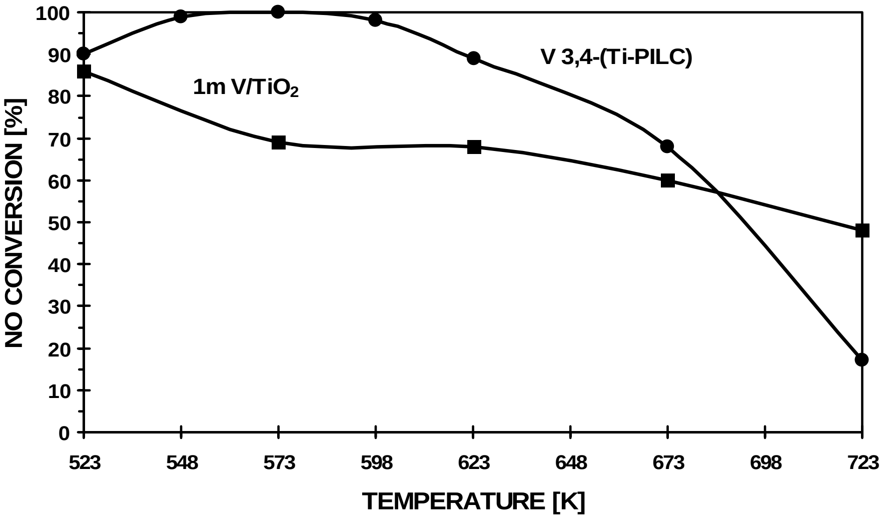

Fig. 6. Catalytic performance of vanadium catalyst supported on Ti-pillared clay and of conventionally prepared V/TiO_2 sample in reaction of selective catalytic reduction of NO with NH_3 (after [20]).

with Pd. The catalysts turned out much more active than the commercial Pd/Pt/γ-alumina CVOC catalyst, as illustrated on the example shown in Fig. 7, where 90% conversion is reached at temperature ca. 150 K lower than in the case of the reference sample.

Another aspect of the catalyst engineering based on layered silicates involves synthesis of silica-based ordered mesoporous molecular sieves, whose history started in 1992 with the Mobil discovery of MCM-41 mesoporous silica materials with unprecedented characteristics [25]. It was followed shortly by the announcement from the Toyota and Waseda University laboratories of synthesis of analogous materials, derived from the mineral kanemite, and referred to as FSM-16 [26]. Kanemite belongs to the family of layered silicates and chemically is a sodium silicate of the formula $NaHSi_2O_5 \cdot 3H_2O$, built of interchanging negatively charged zig-zag tetrahedral silicon-oxide-hydroxide layers and positively charged layers of easily exchangeable hydrated sodium cations (Fig. 8). The discovery consisted in finding that under appropriate conditions intercalation of cationic surfactants between the kanemite layers led to the formation of ordered mesoporous solids. Fig. 9 illustrates the originally proposed hypothetical mechanism of the synthesis, which assumed exchange of sodium cations with

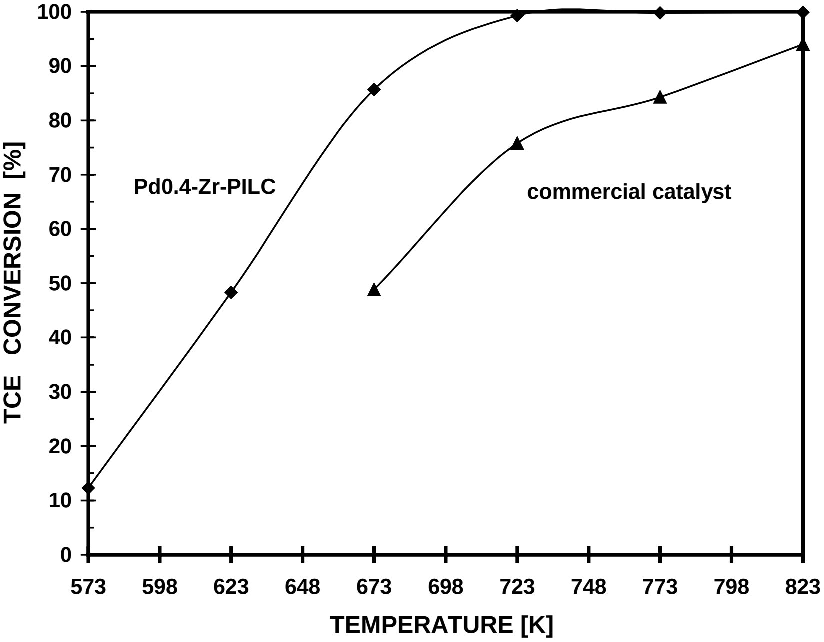

Fig. 7. Catalytic activity of Zr-PILC supported Pd catalyst in destruction of trichloroethylene (TCE) in comparison with the performance of a commercial CVOC catalyst.

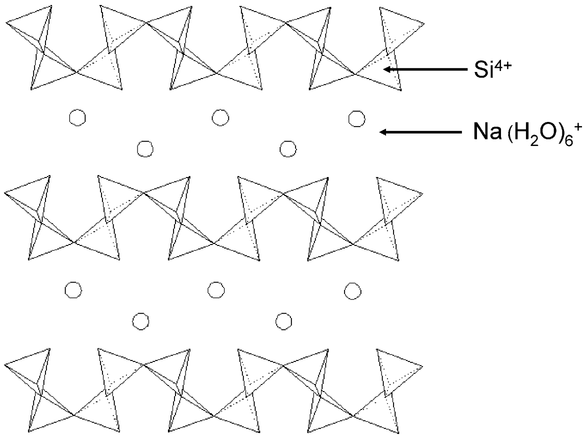

Fig. 8. Structure of kanemite.

micellar aggregates of the surfactant, folding of the negatively charged layers around the positively charged micelles (hence term FSM—folded sheet mesoporous material) with formation of a hexagonal honeycomb structure, and, finally, removal of organic template by calcination at high temperature. At present this mechanism has been modified, as the evidence appeared that the kanemite layers disintegrate partially in the course of FSM formation [27,28].

The most important feature of these solids is an ordered hexagonal array of uniform pores, of diameters tunable in the range 2–10 nm, very high surface area (over 700 m^2/g) and high thermal stability (up to 800–900 °C). In contrast to the MCM-type materials, investigated world-wide in many laboratories, the research into the properties of FSM solids has been predominantly carried out in Japanese laboratories. In our studies of porous supports prepared from layered minerals we naturally turned to FSM-type solids. The existence of regular mesopores opens new possibilities in preparation of supported catalysts, especially in respect of green chemistry reactions catalysed by bulky organometallic macromolecules. So-called heterogenization of well-known homogeneous catalysts such as Schiff bases, phtalocyanines, metalloporphyrins and enzymes is currently a major trend in the studies of their application in catalysis [29]. The use of the support enables an easy separation of the catalyst from the reaction medium, frequently has a stabilising effect on the catalytic centres and ensures their isolation, which, in many cases, is a prerequisite of the catalytic activity. The conventional microporous solids, including zeolites, fail as possible host structures, due to the incompatibility between the small pore size and large dimensions of catalytically active macromolecules. This obstacle can be easily overcome in the case of mesostructures.

In view of this, we concentrated our research on the role of mesoporous silica supports in determination of catalytic properties of organometallic macromolecules. We have chosen a cationic manganese porphyrin (MnTMPyP) as the tested catalyst, due to its well recognised ability to carry out, in the homogeneous systems and in the presence of single oxygen donors, epoxidation of carbon–carbon double bonds [30]. This transformation is of great practical utility, as the ensuing epoxides are important intermediates in organic synthesis. We focused our attention on the room temperature oxidation of cyclohexene, using iodosobenzene as the single oxygen donor [31–33]. To anchor MnTMPyP on a FSM carrier we have used a mesoporous support, which has been partially aluminated ($Si/Al = 20$) to create centres requiring charge compensation and to ensure firm trapping of metalloporphyrin cations [33]. The data illustrating the catalytic performance of this material are presented in Table 1 and compared with the results of catalytic tests carried out with unsupported MnTMPyP (homogeneous system) and MnTMPyP supported on MCM-41 aluminated to a similar degree. As expected, unsupported MnTMPyP gave epoxide as the main oxidation product, with 85% selectivity. The remaining 15% consisted of allylic alcohol and/or ketone. Deposition of MnTMPyP on FSM-16 support resulted in a spectacular enhancement of the catalytic performance along the epoxidation pathway. The catalytic activity measured as a turnover frequency of cyclohexene conversion increased by almost 100% with respect to the homogeneous reaction, and an important improvement of the already high epoxide selectivity has been observed. Interestingly, mesoporous silica support of the MCM-41 type affected the catalytic properties of MnTMPyP in a different way. The activity remained at the level of the homogeneous reaction, but the selectivity pattern was seriously affected due to the appearance of a much larger amount of allylic oxidation products. We have observed previously important dependence of the selectivity pattern in cyclohexene oxidation on the nature of the mesoporous silica supports and attributed this effect to the different distribution of MnTMPyP species in the mesoporous structure (which, in turn, follows the Al distribution within the walls of mesoporous carrier) [32]. We argued that

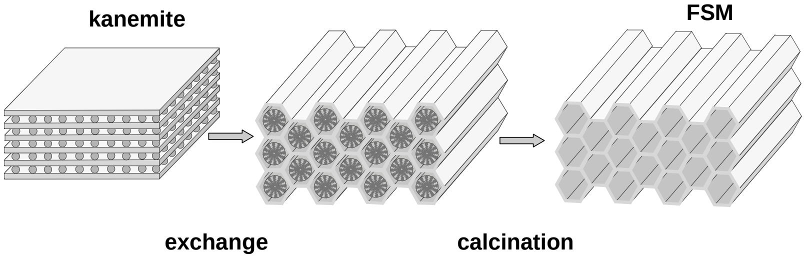

Fig. 9. Illustration of the “folded sheet” mechanism originally proposed by Inagaki et al. [26].

Table 1
Oxidation of cyclohexene with PhIO over pure and supported MnTMPyP[a]

Catalyst	Activity (%)[b]	Selectivity to epoxide (%)	Selectivity to allylic products[c] (%)
Unsupported MnTMPyP	27	85	15
MnTMPyP/FSM-16 (Si/Al = 20)	52	91	9
MnTMPyP/MCM-41 (Si/Al = 23)	27	55	45

[a] Room temperature, argon atmosphere, 16 h, cyclohexene:PhIO:MnTMPyP = 800:20:1, solvent: 3 ml of dichloromethane and methanol (1:2), MnTMPyP concentration 0.7 mmol/L.

[b] Moles cyclohexene consumed/maximum possible cyclohexene cosumption based on the PhIO added.

[c] Cyclohexenol and cyclohexenone.

metaloporphyrin centres buried inside of the channels experience steric hindrances preventing formation of the intermediate required for the epoxidation pathway and are capable of catalysing only allylic oxidation, while species anchored at the external pore wall surface are free of such a restriction and preferentially catalyse epoxidation. From this reasoning it follows that the unique properties of aluminated FSM supports are associated with the preferential location of Al centres at the external pore wall surface. It explains also the much higher activity of FSM-16 support as compared to the MCM-41 one, since in the former case the MnTMPyP sites located preferentially at the external pore walls do not experience diffusion limitations playing undoubtedly an important role in the case of catalytic sites anchored at the internal pore walls of the latter.

4. Concluding remarks

The fundamental scientific challenge of today is protecting human environment while simultaneously ensuring economical growth and profit. Environmental catalysis, targeted at minimising toxic emissions and development of energy-saving, waste-free processes has a leading role in the realisation of this goal, and design of novel catalytic materials is one of the possible approaches. The examples presented in this work illustrate only some of the attractive features of layered minerals that appeal to material chemists involved in the catalyst development. Large spectrum of possible structural, textural and compositional modifications applicable to layered minerals, ease of forming composite materials, wide range of preparation variables allowing for controlled manipulation of catalytic functions makes them extremely interesting materials for catalytic applications, worth broad recognition and exploration.

Acknowledgements

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