Polish J. Chem., **75**, 307–328 (2001) **REVIEW ARTICLE**

Clays as Catalysts for the Removal of Nitrogen Oxides

by E.M. Serwicka

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
30-239 Kraków, ul. Niezapominajek 8, Poland
e-mail: ncserwic@cyf-kr.edu.pl

(Received October 27th, 2000)

A comprehensive coverage of literature on the design and application of clay-derived catalysts for the removal of nitrogen oxides (deNOx), encompassing both the cationic and the anionic clay materials is given. Emphasis is put on the versatility of clays, which renders them excellent materials for an intelligent catalyst design. DeNOx processes discussed include SCR by ammonia and hydrocarbons, reduction of NO with CO and decomposition of N_2O.

Key words: clays, hydrotalcites, pillared clays, NOx removal, environmental catalysis

1. Introduction

Air pollution with nitrogen oxides is nowadays one of the major environmental concerns. Emission of NO_x contributes to the formation of smog and acid rain and to the depletion of the ozone layer. Essentially, three groups of catalytic techniques, known as deNOx processes, can be applied for the removal of nitrogen oxides: non-selective reduction, selective reduction and decomposition. All of them eliminate nitrogen oxides by converting them to nitrogen, with water, carbon dioxide and/or oxygen appearing as nontoxic byproducts. One speaks about the non-selective process if the reduction of NO_x is possible only in the absence of oxygen, because otherwise the latter would react preferentially with the reductant employed. The selective process may be carried out in the presence of excess oxygen, due to the ability of the reducing agent to react preferentially with NO_x rather than with O_2. Decomposition of NO_x to nitrogen and oxygen represents a particular challenge, as it does not involve other chemical reagents and is, therefore, the “cleanest” of all deNOx methods.

At present, the most common method used for NO_x abatement on a large scale is the selective catalytic reduction (SCR) with ammonia [1,2]. Recently, however, the use of hydrocarbons as the reducing agents gains on importance, as they are less hazardous in handling than ammonia. The latter method is also important for lean-burn (oxygen-rich) petrol and diesel engines, where the conventional three-way catalysts, operating in the non-selective manner and efficient only in the absence of excess oxygen, cease to be effective in NO reduction [3,4].

Although a great number of catalytic systems for NO_x removal, including supported noble metals, pure and mixed metal oxides, or modified zeolites, have been reported as efficient, still many efforts are directed at investigation of new types of deNO_x catalysts.

In the last years a number of reports have appeared, in which the design of a deNOx catalyst involved the use of layered minerals. The most commonly used minerals are often referred to as cationic or anionic clays, where the terms “cationic” and “anionic” describe the nature of species located in the interlayer domains of these solids. The aim of this paper is to review the recent literature reports on the design and application of clay-derived catalysts for NOx abatement.

2. Cationic clays

The cationic clays are commonly encountered in nature. They belong to the family of phyllosilicates, whose main building units consist of negatively charged layers, composed of octahedral sheets, in which metal centres are most frequently Al or Mg, sandwiched between Si-O tetrahedral sheets. The negative charge of the layers stems from the partial substitution of the structure-forming cations by cations of lower valency. For instance, in the case of montmorillonite (Fig. 1) Mg^{2+} replaces Al^{3+} in the

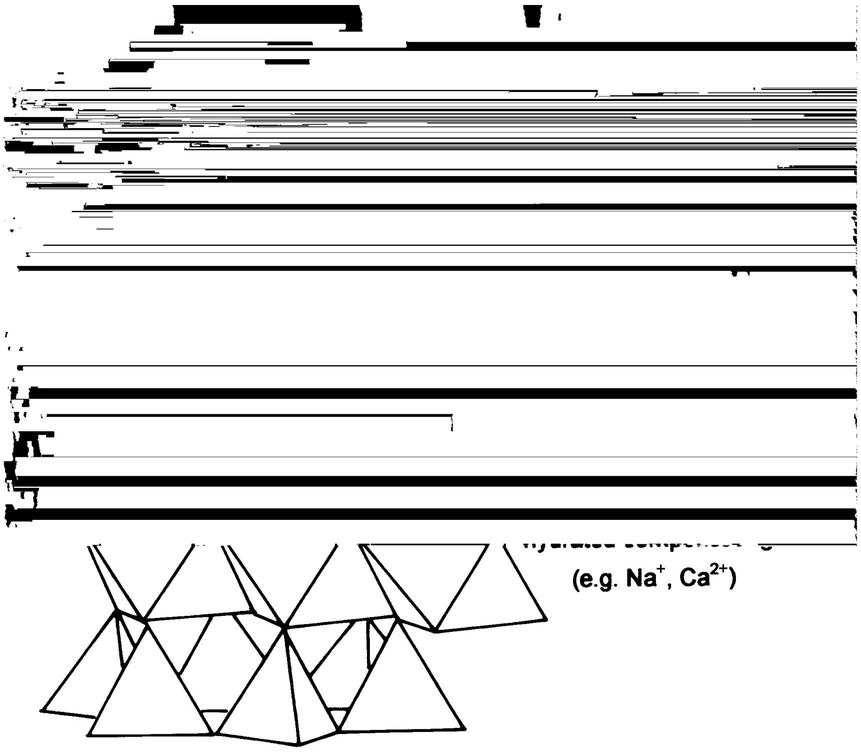

Figure 1. Structure of montmorillonite.

octahedral layer, in hectorite the Mg^{2+} ions of the octahedral sheet are substituted with monovalent lithium cations and in beidellite the substitution occurs within the tetrahedral sheets, with Si^{4+} being replaced by Al^{3+}. The excess negative charge is neutralized 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 to the design and development of clay-based zeolite-like materials, known as pillared interlayered clays (PILCs). The first reports on PILCs date back to the late seventies/early eighties, when three patents by Vaughan, Lussier and Magee, describing the idea of pillaring, methods of preparation and stabilization of pillared materials have been issued [5–7]. 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, propping open the silicate layers. Upon high temperature treatment the oligomers undergo dehydration and dehydroxylation, forming nanoparticles of respective oxides, which link permanently the silicate sheets (Fig. 2). As a result the large surface area

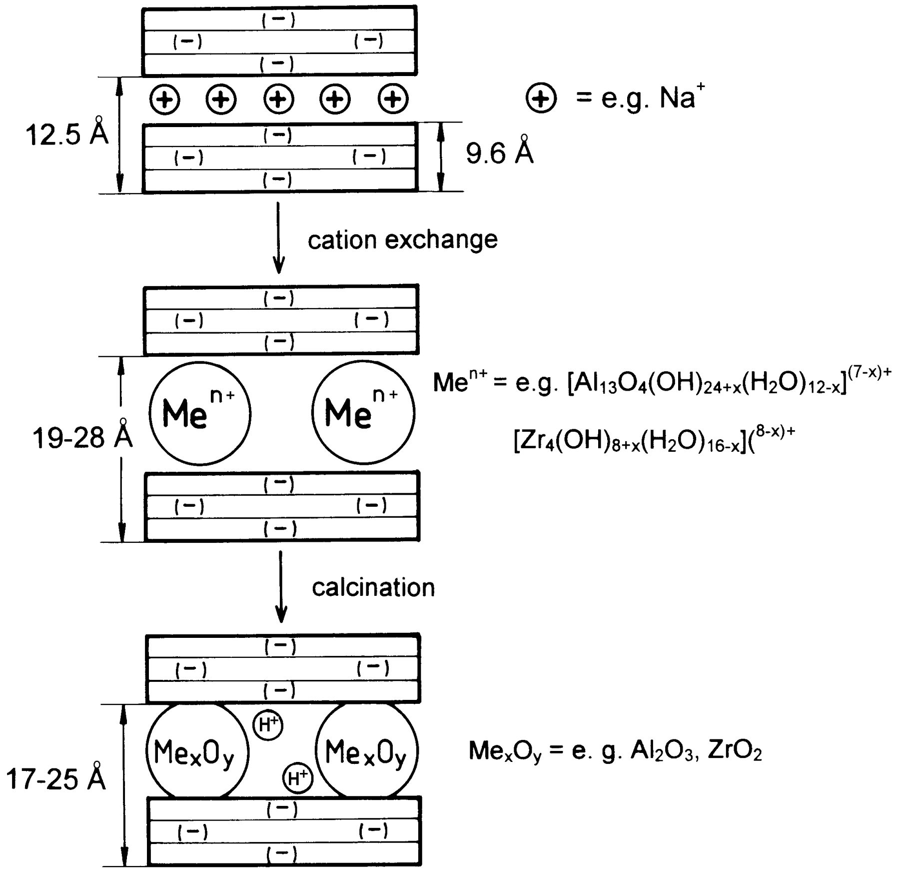

Figure 2. Schematic representation of the pillaring procedure.

(up to 500 m^2/g), highly porous and thermally stable solids are formed, whose acid-base and redox properties can be controlled by an appropriate modification of the preparation procedure and doping. For these reasons PILC materials, from the very moment of their discovery, have attracted an ever-increasing interest as adsorbents and catalysts and several comprehensive reviews dealing with the methods of their synthesis and surface and catalytic properties are available [8–12].

Mechanistic studies on the catalytic reduction of nitrogen oxides indicate that an active catalyst should exhibit surface acid and/or redox sites [3,13]. PILCs posses acid properties of both Lewis and Brønsted type, with a larger contribution from the former. The degree and the nature of acidity may be controlled by an appropriate preparation procedure, *i.e.* by choice of the initial clay, type of the intercalated oligocation, acid treatment prior to intercalation, conditions of thermal treatment *etc*. Redox centres may be generated either at the stage of pillar formation, or in the post-pillaring treatment by inserting transition metal ions changing easily their oxidation state. However, one has to bear in mind that even PILCs, into which no transition metal ions have been introduced purposefully, possess redox sites due to the presence of some transition metal impurities, in particular Fe^{3+} ions, whose occurrence either as lattice substitutions or in the form of extralattice contaminations is common in natural clays. In view of the above, PILCs represent excellent materials for designing deNOx catalysts.

2.1 Selective catalytic reduction of NO by NH_3: The first report on the application of pillared clay catalysts for selective catalytic reduction of NO with NH_3 appeared in 1992 [14]. In this work Yang *et al.* investigated a series of PILC samples with pillars made of Al, Zr, Ti, Fe or Cr oxide clusters. They used as a reference a $V_2O_5/TiO_2/WO_3$ sample, whose composition resembled that of a commercial deNOx catalyst. The results of the catalytic tests showed that the activities of the pillared samples, expressed in rate constants of NO consumption, decreased in the order Cr-PILC > Fe-PILC > Ti-PILC > Zr-PILC > Al-PILC, with Cr-PILC being more active than the reference $V_2O_5/TiO_2/WO_3$ sample, although its activity was severely decreased by the presence of SO_2 in the gas feed. The activity of Fe-PILC was comparable with that of the reference sample and the catalyst was resistant to SO_2, which made it particularly interesting. In the following papers Young and co-workers investigated various Fe-containing pillared clays, including delaminated Fe-PILC materials, *i.e.* clays with disordered stacking of the layers [15], mixed Fe_2O_3/Cr_2O_3 deposited by impregnation on Ti-PILC support [16], and Fe^{3+}-exchanged Ti-PILC catalysts [17–21]. All these materials proved very active, with the most interesting results obtained for the catalysts prepared by ion exchange. The latter were more active than the commercial vanadia/titania reference catalyst and their performance could be further improved by acid treatment [18] and doping with ceria [21]. In particular, it has been demonstrated that the activities of the catalysts were directly related to their acidity rather than to the iron content [18], as shown in Fig. 3. The NO conversion over four different catalysts increased with an increase in Brønsted acidity, but decreased with the increase in the iron content. The authors concluded that the mechanism of SCR over Fe^{3+}-ex-

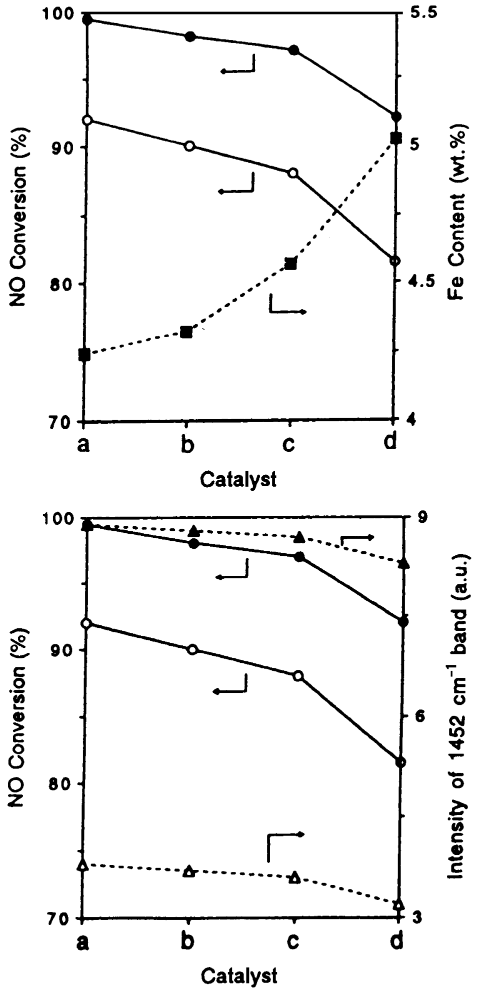

Figure 3. Relationship of NO conversion with iron content and Brønsted acidity (indicated by band intensity at 1452 cm^{-1}) of the Ti-pillared montmorillonite catalysts doped with Fe by ion exchange: a) Fe-Ti-PILC prepared from acid-treated clay, b) Fe-Ti-PILC prepared without additional pretreatment, c) Fe-Ti-PILC doped with Fe after treatment of the pillared clay with NH_3, d) Fe-Ti-PILC doped with Fe after treatment of the pillared clay with NaOH. (●) NO conversion at 400°C with H_2O and SO_2, (o) NO conversion at 400°C without H_2O and SO_2, (■) Fe content, (Δ) Brønsted acidity, (▲) Brønsted acidity after sulfation, after [18].

changed pillared clays differed from that on vanadia catalysts, generally believed to occur *via* an Eley-Rideal type of interaction, involving reaction of a strongly adsorbed ammonia species with a gaseous or weakly adsorbed NO molecule to form N_2 [1,13,22,23]. In contrast, the kinetic studies of the reaction mechanism over Fe^{3+}-exchanged Ti-PILC catalysts suggested that the process occurred according to a Langmuir-Hinshelwood mechanism [24]. In the proposed scheme NO molecules, adsorbed at the catalyst surface, underwent oxidation to adsorbed NO_2 and reacted with

NH_3 adsorbed at neighbouring acid sites to give an active complex, which finally reacted with NO to produce N_2 and H_2O. In view of this mechanism, the beneficial role of the cerium dopant consisted in the enhancement of the oxidation of NO to NO_2. The possibility of such a mechanism has been suggested earlier by Perathoner and Vaccari [25], who carried out an extensive study on an Al-PILC (AZA) and a mixed Fe/Al-PILC (FAZA) samples, used as references by the Concerted European Action-Pillared Layered Structure, launched in 1991 and sponsored by the European Community (CEA-PLS). High NO conversions were observed for both Al-PILC and Fe/Al-PILC catalysts, with the latter being particularly active. The performance of the catalysts could be further improved by the doping with copper ions (Fig. 4). Looking for explanation of their results the authors recalled that the dominant reaction pathway over catalysts such as Cu/Al_2O_3 and Cu/ZSM-5 [26] involved the reaction of oxidized NO (NO_2 or nitrite) with ammonia adsorbed at Brønsted acid sites. On the other hand, ammonia adsorbed at Lewis acid centres, in the absence of a fast reaction with NO, could be oxidized to N_2 or NO, thus, reducing the overall efficiency of SCR. Although the investigated PILC materials had a relatively comparable surface acidity characteristics, with both Lewis and Brønsted sites present, the Fe/Al-PILC sample contained a larger number of Brønsted centres and weaker Lewis acid sites. The authors argued that, if the same reaction mechanism operated for PILC catalysts, the better performance of the Fe-containing PILC catalyst could be assigned to the nature of its surface acidity, which suppressed the rate of the side reaction of ammonia oxidation. In line with this supposition, the beneficial role of Cu additive was assigned to the enhanced rate of oxidation of NO to NO_2.

In view of the fact that the commercial catalyst for SCR of NO with ammonia is based on vanadium oxide supported on titania, the design of a corresponding system involving PILC structures represented a particular challenge for material chemists.

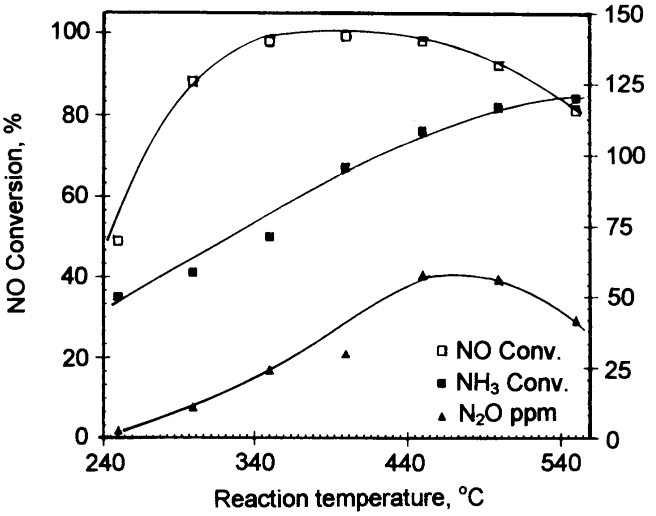

Figure 4. Catalytic performance of Cu-doped Al-Fe-pillared clay in SCR of NO with ammonia. Reaction conditions: NO = 1000 ppm, NH_3 = 1200 ppm, O_2 = 3.5%, GHSV = 30000 h^{-1}, after [25].

One could expect, that the use of titania pillars as a carrier for V centres would not only help to overcome some disadvantages of the conventional titania support, such as a relatively low surface area, poor mechanical strength and limited sintering resistance, but also induce new properties due to the nanometer dimensions of the support particles.

In 1993 Bahranowski *et al.* [27] described for the first time the synthesis of vanadium-doped titania-pillared montmorillonite clay. Vanadium was introduced into the pillared clay as VO^{2+} vanadyl cations either at the stage of pillar intercalation, referred to as co-pillaring, or in the post-pillaring treatment by means of cation exchange. ESR investigation of the catalysts demonstrated that in all samples V dopant was anchored to the titania pillars [27,28]. The catalysts have been tested in SCR with ammonia, their performance being compared with the activity of a reference sample, containing one monolayer of V_2O_5 deposited by impregnation on TiO_2 support [29] (Fig. 5). It turned out that already the undoped titania-pillared sample showed appreciable activity (Fig. 5a), assigned by the authors to the presence of the iron oxide im-

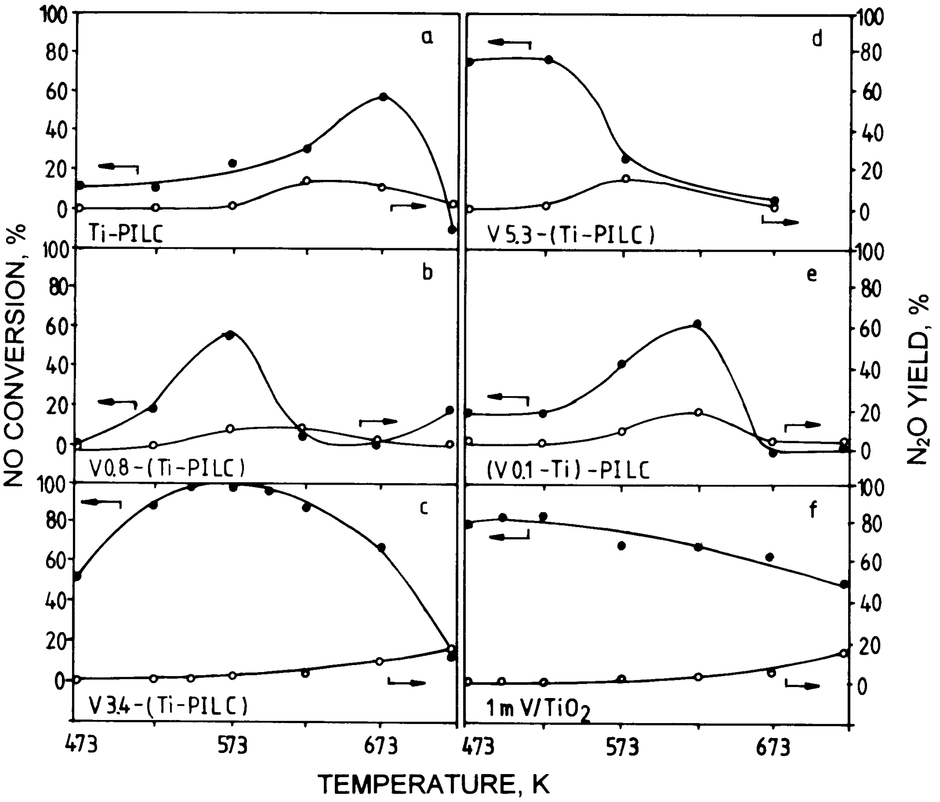

Figure 5. NO conversion and N_2O yield in SCR of NO with ammonia over V-doped Ti-pillared montmorillonite catalysts: a) Ti-PILC matrix, b) – d) Ti-PILC doped by ion exchange with increasing amounts of vanadium, e) V-Ti co-pillared sample, f) monolayer vanadia-titania (48 m^2/g) reference catalyst. Reaction conditions: NO = NH_3 = 1000 ppm, O_2 = 2%, GHSV = 10000 h^{-1}, after [29].

purity. The observation was in line with the described in the former section experiment of Yang *et al.* [9], who reported that the pure Ti-PILC catalyst showed some activity in SCR of NO with ammonia, although lower than that observed for Cr-PILC and Fe-PILC samples. The moderate activity of Ti-PILC was also confirmed by del Castillo *et al.* [30], who pointed out a high resistance of Ti-pillared clay catalysts to the presence of SO_2. Addition of a small amount of vanadium initially shifted the maximum activity to a lower temperature (Fig. 5b). Further increase in the V content led to the substantial increase of the activity and to the widening of the temperature window corresponding to high NO conversion (Fig. 5c). At still higher loading, the maximum activity was shifted towards lower temperature (Fig. 5d), apparently due to the appearance of the polymeric V species [31]. The maximum of NO conversion, observed on the co-pillared sample, occurred at a higher temperature than in the case of samples doped with V by exchange procedures (Fig. 5e). Noteworthy, the N_2/N_2O selectivity differed for catalysts doped by different methods. In the V-doped samples prepared by the exchange technique, the maximum NO conversion appeared before the N_2O concentration reached its peak (Fig. 5b-d). On the other hand, in the case of the co-pillared catalyst, the maximum N_2O yield coincided with the maximum NO conversion (Fig. 5e), pointing to the less selective properties of V centres present in this sample. Indeed, the ESR study confirmed that different methods of doping result in formation of vanadyl species possessing different electronic structure [27,28]. The best pillared clay catalyst (Fig. 5c), obtained by exchange with vanadyl ions at an extent of exchange below the level where significant amounts of polymeric V species appeared, performed better than the reference V_2O_5/TiO_2 sample. The results showed clearly that the deposition of vanadium on titania pillars led to novel systems of properties different from those of the reference material prepared in a conventional way.

Recently, it has been demonstrated that also Ti-PILC catalysts, containing vanadium introduced by impregnation, are very active in the SCR of NO with ammonia, their performance being competitive to the conventional vanadia/titania system and to the commercial $V_2O_5/TiO_2/WO_3$ catalyst [32,33]. Moreover, the materials showed good tolerance to sulfur dioxide and water vapour, whose presence in the reaction feed additionally improved the catalytic activity. IR investigation of the interaction of the V-Ti-PILC catalysts with the reactants of the SCR process have shown that the molecular scheme for NO reduction by ammonia involves gaseous or weakly adsorbed NO and ammonia adsorbed at the surface acid sites, *i.e.* is similar to that proposed for conventional vanadia/titania catalysts [33]. Bahranowski *et al.* [34] studied also the effect of doping with vanadium on the SCR activity of zirconia-pillared montmorillonite (Fig. 6). The applied doping procedures included cation exchange with vanadyl ions of the uncalcined or calcined Zr-pillared clay and the addition of the vanadyl cations to the pillaring agent in the process of co-pillaring. Already the undoped Zr-pillared montmorillonite displayed a significant activity, higher than that of Ti-PILC tested in similar conditions (Fig. 5a) [29]. Insertion of vanadium into the calcined or uncalcined Zr-pillared matrix caused an increase of the activity in temperatures below 350°C and a rapid fall above this temperature. The explanation of the latter effect was found in the experiment with the reaction feed containing only ammonia and oxygen, which demonstrated that above 350°C the V-containing catalyst, in contrast to undoped Zr-PILC, was active in oxidation of ammonia to NO (Fig. 6, dotted lines). Interestingly, the activity of the co-pillared sample was lower than that of pure Zr-PILC matrix. It has been argued that in the case of co-pillaring the pillars retained sulfate anions from the vanadyl sulfate solution used in the preparative procedure and that this contamination was responsible for the decrease of SCR activity. This is in accordance with the earlier observation by del Castillo *et al.* [30], who reported a lowering of the SCR activity of Ti-PILC subjected to sulfating treatment.

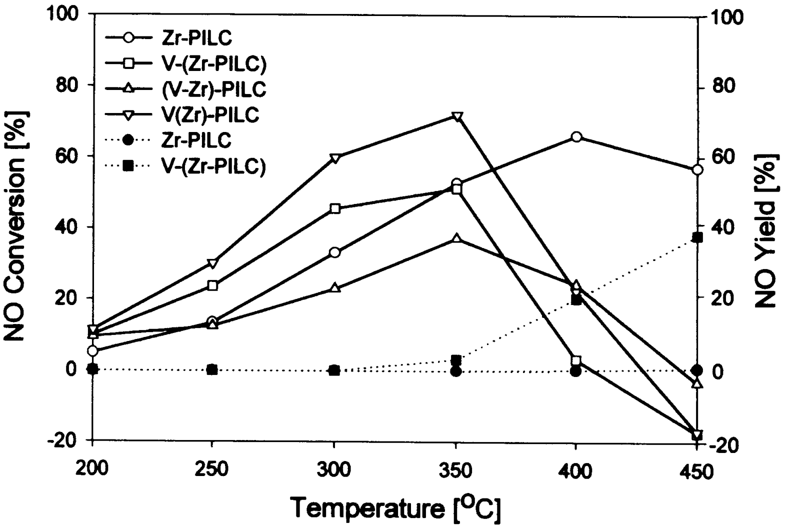

Figure 6. Temperature dependence of NO conversion in SCR of NO with ammonia over V-doped Zr-pillared montmorillonite catalysts (solid lines) and of NO yield over Zr-PILC and V-(Zr-PILC) catalysts (dotted lines). Reaction conditions: NO = NH_3 = 1000 ppm, O_2 = 2%, GHSV = 10000 h^{-1}, after [34].

Recently Chmielarz *et al.* [35] described yet another type of modified clay catalysts for SCR of NO with ammonia. The intention of the authors was to combine the properties of promoted active carbons, known to be active in the low temperature SCR processes [36] with the mechanically and structurally robust pillared clay structures. Indeed, the composite materials, prepared from Zr-pillared montmorillonite by formation of a carbonaceous deposit and doped with manganese ions, proved active and selective in the SCR reaction. In particular, it was noted that the catalysts prepared from acid-pretreated montmorillonite were more active than the materials based on untreated clay and that all modification steps, *i.e* pillaring, carbon deposition and manganese promotion, increased the activity.

2.2 Selective catalytic reduction of NO by hydrocarbons: The first reports on the possibility of selective catalytic reduction of NO by hydrocarbons in the presence of oxygen, by Iwamoto [37] and Held *et al.* [38], appeared in 1990. The catalysts employed for this process were ion-exchanged zeolites, of which the Cu^{2+}-exchanged ZSM-5 turned out particularly active. Five years later Yang and Li [16] reported that Cu^{2+}-exchanged Ti-PILC in the selective catalytic reduction of NO with ethylene yielded activities higher than that of Cu-ZSM-5. Moreover, the performance of the clay catalyst was only slightly adversely affected by the presence of SO_2 and H_2O. Later investigations by this group, in which ion-exchanged Ti-, Zr- and Al-pillared montmorillonites and Al-pillared laponite (synthetic hectorite) were screened for their catalytic activities in SCR of NO by ethylene, demonstrated that pillared clays possessed superior properties with respect to Cu-ZSM-5 [39–41]. Among many samples studied, the Cu^{2+}-exchanged Ti-PILC catalysts and the Cu^{2+}-exchanged Al-pillared laponite proved most active in this reaction (Fig. 7). The temperature programmed reduction study of the catalysts indicated that the reducibility of copper centres present in Cu-Ti-PILC was higher than in the Cu-ZSM-5 catalyst. Thus, the higher SCR activity of the former was associated with the relative ease with which the redox cycle between Cu^{2+} and Cu^{+} could occur.

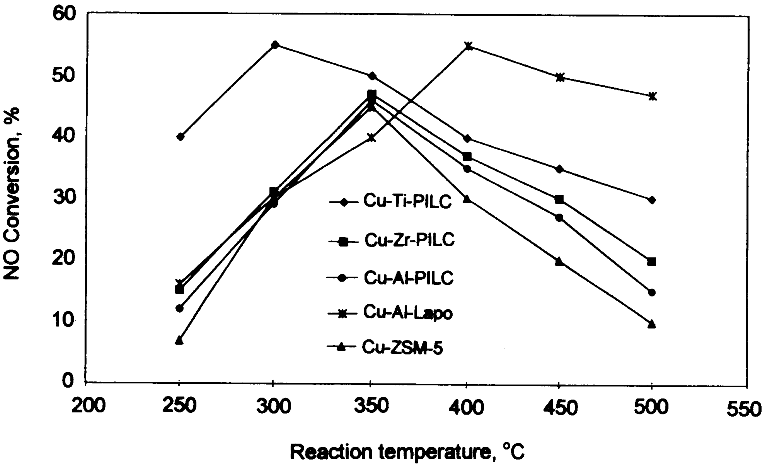

Figure 7. Catalytic performance of Cu-doped pillared clays and a reference Cu-ZSM-5 sample in SCR of NO with ethylene. Reaction conditions: NO = C_2H_4 = 1000 ppm, O_2 = 2%, GHSV = 60000 h^{-1}, after [40].

The use of saturated hydrocarbons as potential reductants in SCR of NO over pillared clay catalysts gave negative results. Perathoner and Vaccari [25] investigated the reaction carried out over Cu^{2+}-doped Al-PILC (AZA) and mixed Fe/Al-PILC (FAZA) catalysts, using propane as the reducing agent. The authors found that both Al-PILC and Fe/Al-PILC, either with or without Cu were inactive in the SRC of NO with propane in the presence of oxygen (Fig. 8). On the other hand, the addition of comparable amounts of Cu to the alumina support promoted the conversion of NO and propane at the lower reaction temperatures. The authors argued that, in contrast to alumina, the pillared clay catalysts lacked sufficiently strong acid centres, able to generate the active hydrocarbon species. In consequence, the addition of copper did not cause any promotion of the activity of pillared clay catalysts in NO reduction with propane. Also Yang *et al.* [40] reported that the Cu^{2+}-exchanged Ti-PILC catalyst, which performed very well in SCR with ammonia and ethylene, turned out inactive when methane was used as the reducing agent.

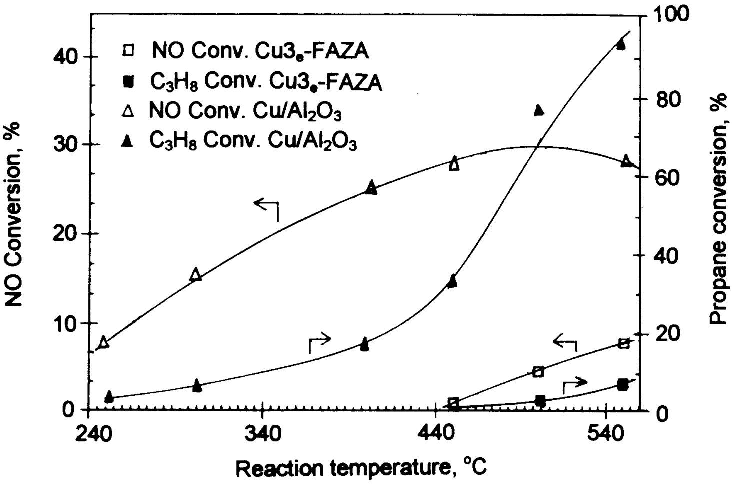

Figure 8. Comparison of the catalytic performance in SCR of NO with propane of Cu-doped Al-Fe-pillared clay and Cu/Al_2O_3. Reaction conditions: NO = 800 ppm, C_3H_8 = 3200 ppm, O_2 = 2%, GHSV = 10000 h^{-1}, after [25].

2.3 Catalytic reduction of NO with CO: The catalytic reduction of nitric oxide with carbon monoxide is the major reaction pathway for removal of nitrogen oxides from automobile exhaust. The automotive catalysts consist mainly of noble metals supported on porous carriers. A very important factor in using noble metal catalysts is the good dispersion of the active phase, allowing preparation of efficient catalysts with possibly low amount of the precious metal component. Papayannakos *et al.* [42,43] argued that the microporous texture of pillared clays makes them an interesting alternative to conventional supports and designed catalysts for reduction of NO with CO, using as supports for the active rhodium species the Al- and Al/Fe-pillared montmorillonites (AZA and FAZA, respectively) and the Al-pillared saponite. The materials contained 0.06 wt.% Rh introduced by impregnation. Their catalytic performance was compared with a Rh/alumina sample with the same amount of rhodium and a typical automotive exhaust converter COMCAT, containing 0.33 wt.% Pt, 0.06 wt.% Rh, 5.23 wt.% Ce on alumina/cordierite support. The best activity was observed when the alumina-pillared montmorillonite was used as a support. The catalyst, denoted Rh-AZA, was not only distinctly better than other clay-supported samples, but its performance was superior both to the commercial automotive converter and to the reference Rh-alumina material (Fig. 9). The specific nature of rhodium species present in this catalyst was confirmed by the temperature programmed desorption of hydrogen, which demonstrated that Rh impregnated on the AZA support possessed a particularly high ability to bind adsorbed hydrogen species.

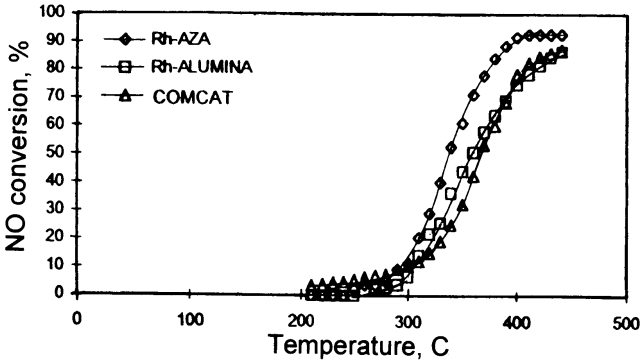

Figure 9. NO conversion in the reaction of reduction of NO with CO over Rh-doped Al-pillared clay (Rh-AZA), reference Rh-ALUMINA and commercial automotive converter COMCAT. Reaction conditions: NO = 1%, CO = 2% ppm, after [43].

3. Anionic clays

The anionic clays, also known as hydrotalcites or layered double hydroxides, are much less common in nature than the cationic clays, but can be relatively easily obtained in a synthetic way [44–46]. 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. 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 trivalent cations, including transition metal ions, which may form the brucite sheet as well as a variety of possible charge balancing anions (Fig. 10). In general, the materials may be described with the formula $[M(II)_{1-x}M(III)_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M(II) and M(III) are divalent and trivalent cations respectively, A^{n-} is the interlayer anion compensating the layer charge, x describes the degree of substitution within the brucite layer. The ability of the hydrotalcite-like structure to accommodate so many variables opens enormous possibilities for designing tailor-made materials.

An important feature of the hydrotalcite-like materials is their rather limited thermal stability. Due to the homogeneous interdispersion of constituting elements, 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 importance as extremely attractive precursors of multicomponent catalysts for many catalytic reactions of industrial interest [12,44,47]. In particular, new and promising applications have been reported in the field of deNOx research.

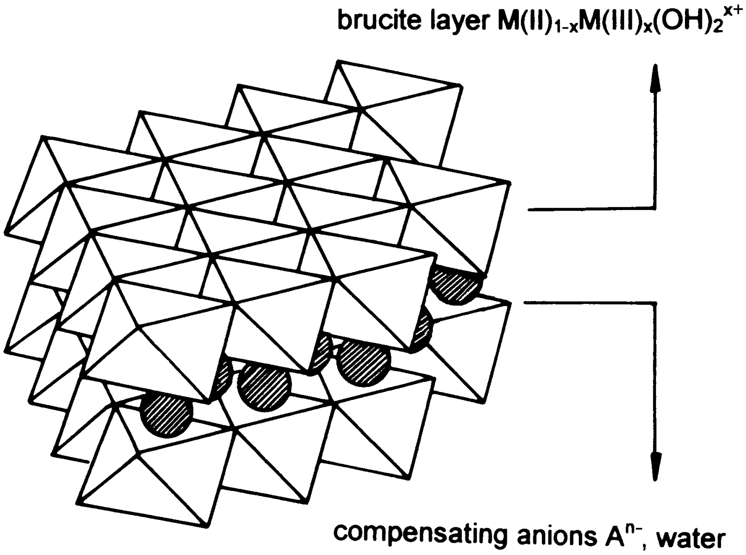

Figure 10. Structure of a hydrotalcite-like compound.

3.1 Selective catalytic reduction of NO by NH_3: In 1996 Gazzano *et al.* [48] reported the results of SCR tests, in which hydrotalcite-derived catalysts exhibited improved catalytic performance when compared to the analogous supported catalysts with Cu-containing sample being particularly promising. In view of this, Montanari *et al.* [49] undertook a thorough investigation of Cu-containing mixed oxide phases, obtained by calcination of hydrotalcite precursors of the general formula $[Cu_xMg_{0.71-x}Al_{0.29}(OH)_2](CO_3)_{0.145}$. For the sake of comparison, a catalyst obtained by impregnation of the calcined Mg/Al hydrotalcite with copper was also prepared. It has been demonstrated, that in the presence of oxygen in the reaction feed the Cu/Mg/Al mixed oxide catalyst derived from the hydrotalcite precursor of the highest Cu content ($x = 0.072$) exhibited a behaviour comparable to that of a commercial $V_2O_5/WO_3/TiO_2$ catalyst (Fig. 11). The result could be regarded as one of the best reported in the literature for either CuO supported on high-surface area oxides or Cu-zeolites. The authors pointed out that in order to get a highly active and selective catalyst, a fine tuning of the precursor composition and adjustment of the pretreatment conditions was necessary. Interestingly, the catalyst prepared by impregnating the hydrotalcite-derived Mg/Al mixed oxide phase with a comparable amount of copper gave poorer performance, indicating the importance of the atomic dispersion of copper sites provided by the Cu-containing hydrotalcite precursor. Łojewski *et al.* [50] reported that also in the case of Mg/Cr/Al and Mg/Fe/Al mixed oxide catalysts tested in the SCR process, the materials prepared from a hydrotalcite precursor, containing all cations within its structure performed better than the samples prepared by impregnation of Cr or Fe on the hydrotalcite-derived Mg/Al mixed oxide support.

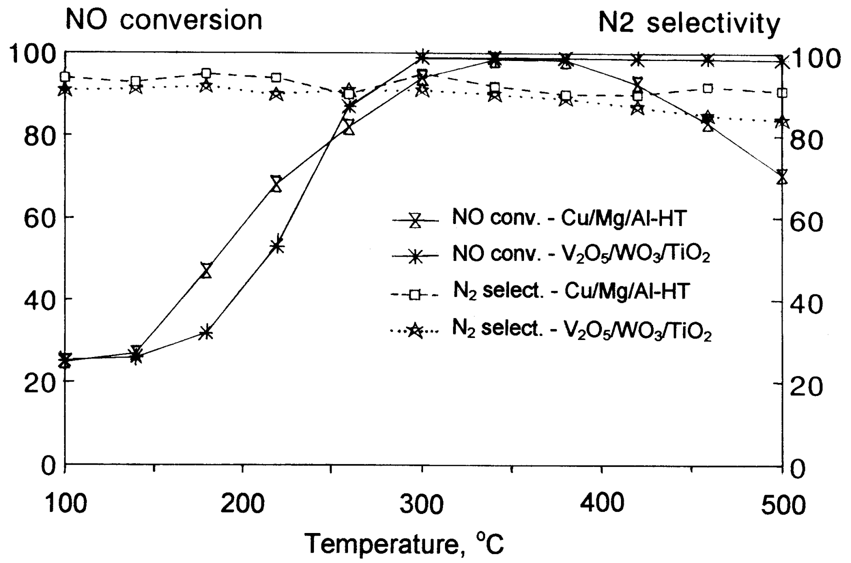

Figure 11. Comparison of the catalytic performance in SCR of NO with ammonia over hydrotalcite-derived mixed oxide Mg-Cu-Al system and a commercial $V_2O_5/WO_3/TiO_2$ catalyst. Reaction conditions: NO = 6000 ppm, NH_3 = 7500 ppm, O_2 = 3%, GHSV = 10000 h^{-1}, after [49].

Interesting observation concerning the mechanistic aspects of SCR with ammonia over Cu/Mg/Al mixed oxide catalysts prepared via hydrotalcite-type precursors were made by Trombetta *et al.* [51], who employed FT-IR spectroscopy for investigation of the ammonia adsorption and oxidation on these solids. The latter reaction is the most important side-reaction occurring in the system at high temperatures. It has been found that the SCR reaction occurs between gas phase NO and NH_3 strongly adsorbed on Cu-containing phases and/or highly dispersed CuO clusters. In contrast to the SCR over V-based catalysts, the mechanism of the reaction over Cu-containing hydrotalcite-derived materials did not involve Brønsted acid sites, absent on the surface of these samples, thus, evidencing that Brønsted acidity is not always a key requirement for SCR with ammonia.

3.2 Selective catalytic reduction of NO by hydrocarbons: Simultaneously with the works on the application of hydrotalcite-derived catalysts in SCR of NO with ammonia, several papers appeared describing the activity of such materials in the catalytic reduction of NO with hydrocarbons [52–57]. Bahranowski *et al.* [52] investigated the activity of Cu-Cr-O mixed oxide catalysts, obtained by calcination of the hydrotalcite precursors of Cu/Cr ratios 3, 2 and 1 in SCR of NO with propane. The calcined hydrotalcites were composed of $CuCr_2O_4$ and CuO. The contribution of the latter increased with the Cu content and so did its crystallinity. All materials proved active in the SCR process, although their performance in the presence of oxygen depended strongly on the Cu/Cr ratio (Fig. 12). At the oxygen concentration sufficiently below that required for the stoichiometric reaction of hydrocarbon combustion, equal 1%, each of the investigated catalysts was capable of converting the whole nitric ox-

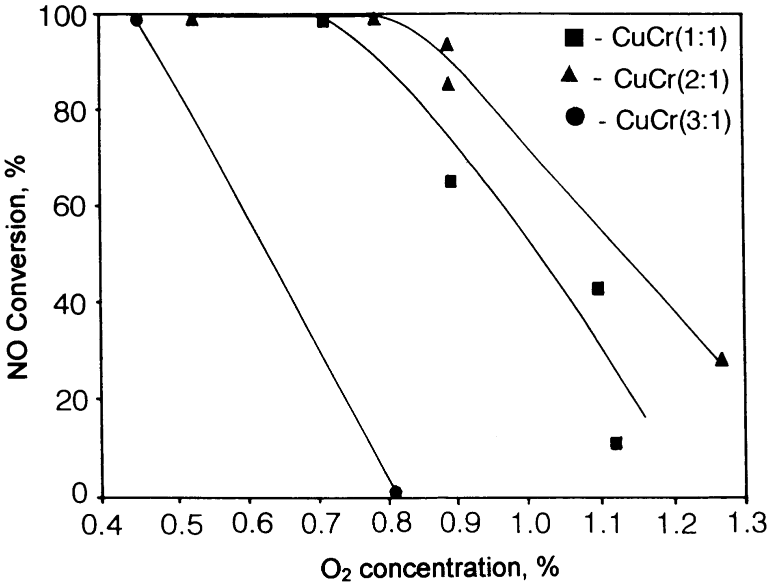

Figure 12. Dependence of the NO conversion on the oxygen content in the feed in SCR of NO with propane over hydrotalcite-derived Cu-Cr mixed oxide catalysts of different Cu/Cr ratios. Reaction conditions: NO = 1000 ppm, C_3H_8 = 2000 ppm, GHSV = 10000 h^{-1}, after [52].

ide present in the reaction feed to nitrogen. The limiting oxygen contents, above which the NO conversion rapidly decreased, depended on the catalyst composition, with the Cu/Cr = 2 catalyst withstanding the highest O_2 concentrations. The XRD analysis indicated that in the better performing samples the excess CuO phase was of poorer crystallinity. In continuation of this work Bahranowski *et al.* [53] investigated the SCR of NO with propane over hydrotalcite-derived catalysts, in which the redox function was provided by incorporation of vanadium. The V-containing hydrotalcite precursors were prepared by intercalation of Mg-Al and Zn-Al hydrotalcite matrices with decavanadate anions. It has been found that the catalytic activity of the calcined materials depended in a critical way on the nature of divalent cation. The catalyst containing Mg was almost inactive in NO conversion, while the one with Zn showed appreciable activity. The authors suggested that, in view of the otherwise similar physicochemical characteristics of both materials, the observed difference in the SCR activity was due to the higher acidity of the zinc-containing mixed-oxide phase. Mulukutta and Detellier [54] investigated the ability of Ni-Al-mixed oxides, prepared by thermal decomposition in vaccum of a $[Ni_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125}$ hydrotalcite, to catalyse the reduction of NO with methane in a static system and referred the results to the behaviour of pure NiO. The gas chromatographic analysis of the gas mixture, after the reaction, showed that in the case of the hydrotalcite-derived catalyst 95% of NO could be converted, of which *ca.* 40% to N_2O. Interestingly, in the presence of oxygen the same sample converted NO completely and no N_2O could be detected. This fact was not commented upon and as the paper did not provide any physicochemical characterization of the mixed oxide samples, it is difficult to speculate on the cause of this effect. However, bearing in mind that the calcination of the precursor was carried out in vacuum, it seems likely that the observed change in the spectrum of the reaction products in the presence of oxygen was caused by the oxidation of nickel centres to give higher valent species of different catalytic properties. In analogous reactions the conversion of nitric oxide over pure NiO was at the level of 20%, with significant evolution of N_2O.

Another aspect of the NO_x removal by reduction with hydrocarbons concerns the emissions from the petrochemical plants with fluid catalytic cracking (FCC) units. Here, the catalyst must be able to operate in very severe conditions [55], *i.e. ca.* 750°C, and in the presence of other gases such as CO, CO_2, SO_2, O_2 and H_2O. Shannon *et al.* [56] investigated the deNOx activity of the mixed oxides, prepared by the thermal decomposition of magnesium-rich Cu-Mg-Al hydrotalcites and shown previously to be active in the removal of SO_x in the FCC process. It has been demonstrated that the materials were catalytically active towards both the NO reduction in the presence of propane and its decomposition in the absence of the reducing agent. The *in situ* structural studies showed that during NO reduction in the presence of propane, most of the copper was found to be in the Cu(0) state. For NO decomposition, the catalytically active species have been identified as Cu(I). Corma *et al.* [57] continued this line of research and demonstrated that the Cu/Mg/Al mixed oxide catalyst, obtained from the hydrotalcite precursor and working under the conditions encountered in the regenerator of the FCC unit, was capable of removing both the NO (by a reduction and/or decomposition reaction) and the SO_2 (by an oxidative and/or reductive process). The XPS and XAES analysis confirmed that sites active in NO removal were Cu(0) and Cu(I) species. Interestingly, when the NO removal in the presence of SO_2

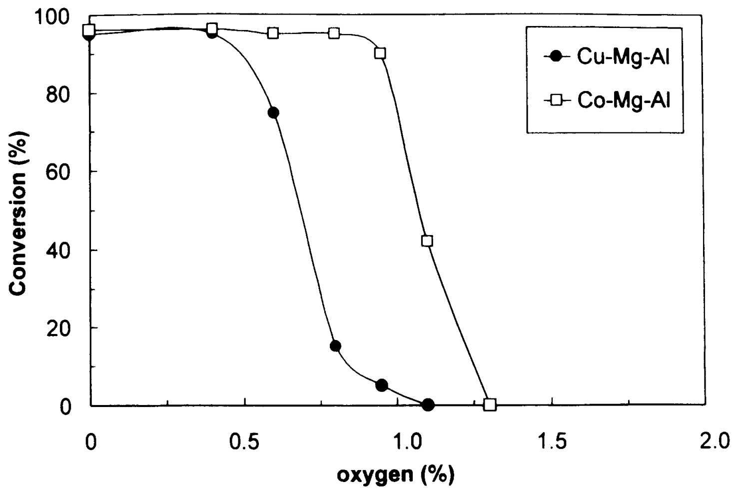

Figure 13. Dependence of the NO conversion on the oxygen content in the feed in SCR of NO with propane over hydrotalcite-derived Cu-Mg-Al and Co-Mg-Al mixed oxide catalysts. Reaction conditions: NO = 400 ppm, C_3H_8 = 400 ppm, GHSV = 210000 h^{-1}, after [52].

took place at low oxygen concentrations, the active centres consisted of copper-sulfur species, which were more active than the original copper sites. Recently, Palomares *et al.* [58] demonstrated that a Co/Mg/Al mixed oxide material derived from the hydrotalcite precursor also fulfils the requirement of a deNOx catalyst applicable in a FCC unit. This catalyst was also shown to withstand higher concentration of oxygen in the reaction feed (Fig. 13).

3.3 Catalytic reduction of NO with CO: Only one group reported the results on the catalytic reduction of NO with CO. Liu *et al.* [59] found that the Co-Cu-Al mixed oxide system obtained by calcination of the hydrotalcite precursors was very active in this process. The activity was particularly spectacular for cobalt-rich materials, the best performance being given by the catalyst in which the Co/Cu/Al ratio was equal to 7/1/1. The NO conversion on this catalyst reached 100% at a very low temperature of only 120°C.

3.4 Decomposition of N_2O: The catalytic decomposition of nitrous oxide has become an important branch of deNOx research. For many years N_2O was considered to be relatively harmless. It is only in the last decade that its negative impact on the environment became a matter of an increasing concern. Two main reasons render N_2O an undesired contamination of the atmosphere. First, due to its strong ability to absorb infrared radiation, it adds to the overall greenhouse effect [60,61]. Second, N_2O subjected to photolysis and oxidation processes in the startosphere initiates a chain reaction resulting in depletion of the ozone layer [60,62]. The main sources of anthropogenic N_2O emission are cultivated soils, biomass burning, combustion processes and chemical industry, especially plants manufacturing adipic and nitric acids [63]. From practical point of view, only the emissions associated with combustion and chemical production can be subjected to human control and reduced in a reasonably short time span. Catalytic decomposition of N_2O is the preferred means for removal of this contaminant, because it does not require the use of other chemicals. Various catalysts have been reported as active in N_2O decomposition, including supported metals, zeolites, pure and mixed oxides, and details are available in the relevant reviews [64,65]. In 1994 Kannan and Swamy [66] reported that the decomposition of nitrous oxide proceeded with spectacular efficiency on calcined hydrotalcites, with Ni-Al mixed oxide giving the best performance, followed by Co-Al and Cu-Al systems. Although the catalytic experiments were carried out in a static reactor and as such bore limited relevance for the realistic process conditions, nevertheless they clearly demonstrated the superior properties of Ni and Co-containing hydrotalcite catalysts with respect to the metal exchanged zeolites, known as the best catalysts to date. A couple of years later Armor *et al.* [67] described the experiments, in which the hydrotalcite-derived catalysts were subjected to catalytic tests under simulated process conditions. The results showed, that under flow conditions, the relative activities of the materials differed from those obtained in the static reactions. Here, the samples obtained by thermal decomposition of the cobalt-aluminium precursor gave the best performance. In particular, they offered enhanced activity over previous zeolite catalysts for removing N_2O (Fig. 14) and were significantly more active at lower tempera-

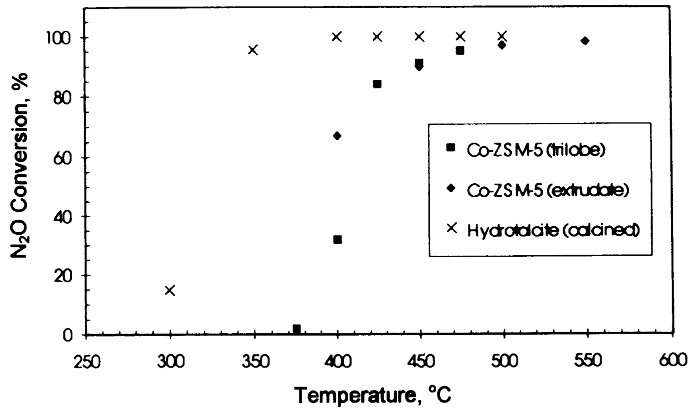

Figure 14. Comparison of the activity in N_2O decomposition of hydrotalcite-derived Co-Al mixed oxide system and Co-ZSM-5 catalysts. Reaction conditions: N_2O = 10%, H_2O = 2%, O_2 = 2%, GHSV = 16000–18000 h^{-1}, after [67].

ture range. Large beds of these catalysts under simulated processing conditions were shown to perform effectively for over 175 h with a nitrous oxide stream containing water vapour, thus, proving their resistance to hydrothermal deactivation. In a search for the optimum performance of the Co-based systems, the authors have discovered that the addition of magnesium to the hydrotalcite precursor, to give a ternary Co-Mg-Al system, increased the activity. Also, a partial replacement of Al by La resulted in a material of appreciable activity. However, the most spectacular improvement of the catalyst performance was obtained upon addition of small amounts of rhodium. The calcined Co-Al-Rh hydrotalcite provided 100% conversion of N_2O to nitrogen and oxygen at a process temperature of 300°C, which was *ca.* 150°C lower than the 450°C required for Co-ZSM-5 to yield comparable conversion. The catalytic tests in a flow reactor have been independently reported by Centi *et al.* [68]. In a paper screening the catalytic properties of noble and transition metal containing oxides and zeolites in decomposition of N_2O, the authors investigated also the hydrotalcite-derived Ni-Al and Cu-Al mixed oxides, *i.e.* systems similar to those reported earlier by Kannan and Swamy [66] as showing significant activities in a static reactor. However, when tested in a flow system, the catalysts gave a rather poor performance with appreciable conversions only above 500°C. The authors observed that the activity of the catalysts could be significantly improved when the materials were pretreated by reduction with hydrogen followed by reoxidation with nitrous oxide. The results of Kannan and Swamy [66] and Armor *et al.* [67] proved a potent stimulant for the research teams involved in the field of N_2O decomposition and a number of papers based on the ideas presented in the concerned articles appeared recently. Thus, Dandl and Emig [69] investigated in detail the behaviour of a hydrotalcite-derived Co-Al-La mixed oxide catalyst. The authors confirmed the high activity of the calcined solid and carried out a numerical modelling of the reaction kinetics. From a number of possible reaction mechanisms, the best fitting scheme of nitrous oxide decomposition involved: a) adsorption of oxygen by cleavage of N_2O, b) reaction of gaseous N_2O with adsorbed oxygen, and c) spontaneous desorption of molecular oxygen. Kannan [70] broadened the spectrum of the possible hydrotalcite compositions, including iron and chromium as the M(III) cations in the brucite sheet, but neither substituent resulted in an improved performance with respect to the solids where M(II) cations were paired with aluminium. Kannan and Swamy [71] investigated the influence of the method of precursor synthesis and of the Co/Al ratio on the catalytic performance of calcined cobalt-aluminium hydrotalcite. The authors observed that the samples prepared by co-precipitation at a constant pH were more active than the corresponding materials obtained by increasing the pH to the desired value in the course of precipitant addition to the solution of metal nitrates. The second factor determining the overall activity was the surface concentration of cobalt, whose increase enhanced the efficiency of the process. The work of Pérez-Ramírez *et al.* [72] reinvestigated the effect of Mg, Rh and La addition to Co- and Ni-based hydrotalcite precursors on the activity of the calcined material. In agreement with previous findings of Armor *et al.* [67], the authors confirmed the positive role of all promoters. In particular, a beneficial influence of Mg on the catalyst stability and resistance towards mixtures of SO_2 and O_2 has been stated, an observation vital for the potential application of these materials in the removal of N_2O from off-gas generated by fluid bed combustors. In another paper, the authors reported that the addition of Pd to the Co-La-Al hydrotalcite precursor resulted in a mixed oxide catalyst of activity approaching that of the best to date reported Co-Al-Rh mixed oxide material (Fig. 15) [73]. The catalyst exhibited also a better stability in the time-on-stream experiments, while the Rh-containing material underwent a partial deactivation.

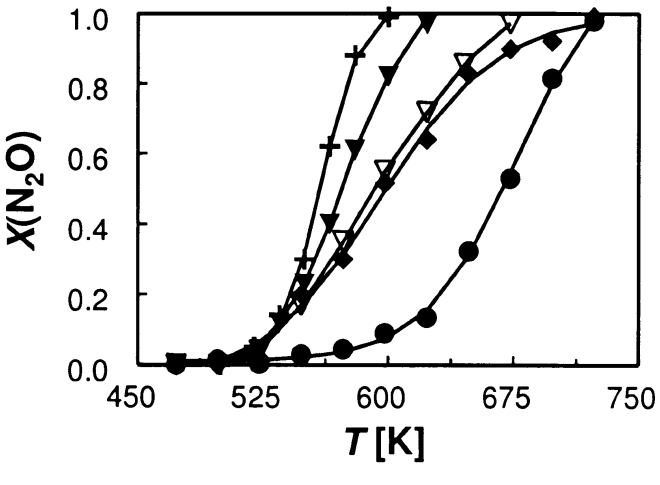

Figure 15. Comparison of the activity in N_2O decomposition of various hydrotalcite-derived mixed oxide systems: (●) Co-Al (Co/Al = 3/1), (◆) Co-La-Al (Co/La/Al = 3/1/1), (V) Co-Pd-La-Al (Co/Pd/La/Al = 3/0.01/1.1), (▼) Co-Pd-La-Al (Co/Pd/La/Al = 3/1/1/1) and (+) Co-Rh-Al (Co/Rh/Al = 3/0.02/1). Reaction conditions: N_2O = 0.1%, GHSV = 120000 h^{-1}, after [73].

At the end of this section it is worthwhile to quote a series of papers by Zeng *et al.* [74–77], who investigated the catalytic performance in the decomposition of concentrated N_2O flow over catalysts prepared from Al-free Mg-Co hydrotalcite and/or hydroxide-hydrotalcite precursors. Although the initial solution of Mg and Co salts used for the co-precipitation of the precursor contained only divalent cations, the partial oxidation of Co^{2+} to Co^{3+} during the precipitation provided the trivalent substituent required for the formation of a hydrotalcite component. The authors observed that the thermal treatment of such precursors resulted in the high surface area spinel phases already below 300°C. The composition and the pretreatment of the precursor could be tuned to give a Mg-Co spinel catalyst of optimum properties, which could be placed among the best reported in the literature for the low temperature decomposition of N_2O.

4. Concluding remarks

The examples of catalytic applications of cationic and anionic clays given in this review illustrate the great potential of these materials as catalysts or catalyst precursors. Although both types of clay differ very much from the point of view of their chemical nature, with phyllosilicates on one hand and layered hydroxides on the other, they possess also obvious similarities. Their major common feature is the layered structure. Also, the compounds may be looked upon as related by sort of an inverse symmetry. While cationic clays possess negatively charged layers, balanced by cations in the interlayer, the layers in the anionic clays carry positive charge, compensated by the presence of interlayer anions. However, from the point of view of material chemists, intent on discovering new catalytic materials, the most important common feature of both types of clays is the enormous spectrum of possible modifications to which the solids can be subjected, without loosing their essential characteristics. Appropriate preparation procedure and pretreatment allow synthesis of materials, whose structural, textural, acid-base and redox properties can be modified in a controlled manner. In such a way tailor-made products can be obtained, according to the requirements of a specific reaction, examples of which have been given above. The worldwide recognition of this fact by the scientific community resulted in an ever-increasing number of publications on the catalytic aplications of clays, a significant interest being focused on environmental issues. The research into deNOx processes, reviewed in this article, provides spectacular examples of an intelligent catalyst design with use of clay materials. However, the potential of clay minerals is still far from being exploited and the announcement of new exciting discoveries will come as no surprise.

Acknowledgment[*]

The financial support by the Polish State Committee for Scientific Research, within research projects 3 T09A 079 14 and 6 P04D 040 14 is gratefully acknowledged.

REFERENCES

1. Bosch H. and Janssen F., *Catal. Today*, **2**, 369 (1988).
2. Heck R.M., *Catal. Today*, **53**, 519 (1999).
3. Amiridis M.D., Zhang T.J. and Farrauto R.J., *Appl. Catal. B*, **10**, 203 (1996).
4. Traa Y., Burger B. and Weitkamp J., *Micropor. Mesopor. Mater.*, **30**, 3 (1999).
5. Vaughan D.E.W., Lussier R.J. and Magee J.S., U.S. Patent 4, 176,090 (1979).
6. Vaughan D.E.W., Lussier R.J. and Magee J.S., U.S. Patent 4, 248,739 (1981).
7. Vaughan D.E.W., Lussier R.J. and Magee J., U.S. Patent 4, 271,043 (1981).
8. Pinnavaia T.J., *Science*, **220**, 365 (1983).
9. Burch R., *Catal. Today*, **2**, 185 (1988).
10. Figueras F., *Catal. Rev. Sci. Eng.*, **30**, 457 (1988).
11. Kloprogge J.T., *J. Porous Mater.*, **5**, 5 (1998).
12. Vaccari A., *Appl. Clay Sci.*, **14**, 161 (1999).
13. Busca G., Lietti L., Ramis G. and Berti F., *Appl. Catal. B*, **18**, 1 (1998).
14. Yang R.T., Chen J.P., Kikkinides E.S., Cheng L.S. and Cichanowicz J.E., *Ind. Eng. Chem. Res.*, **31**, 1440 (1992).
15. Chen J.P., Hausladen M.C. and Yang R.T., *J. Catal.*, **151**, 135 (1995).
16. Yang R.T. and Li W., *J. Catal.*, **155**, 414 (1995).
17. Cheng L.S., Yang R.T. and Chen N., *J. Catal.*, **164**, 70 (1996).
18. Long R.Q. and Yang R.T., *Catal. Letters*, **59**, 39 (1999).
19. Long R.Q. and Yang R.T., *J. Catal.*, **186**, 254 (1999).
20. Long R.Q. and Yang R.T., *J. Catal.*, **199**, 22 (2000).
21. Long R.Q. and Yang R.T.,. *Appl. Catal. B*, **27**, 87 (2000).
22. Topsøe N.-Y., Dumesic J.A. and Topsøe H., *J. Catal.*, **151**, 241 (1995).
23. Miyamoto A., Kobayashi K., Inomata M. and Murakami Y., *J. Phys. Chem.*, **86**, 2945 (1982).
24. Long R.Q. and Yang R.T., *J. Catal.*, **190**, 22 (2000).
25. Perathoner S. and Vaccari A., *Clay Miner.*, **32**, 123 (1997).
26. Centi G. and Perathoner S., *Appl. Catal. A*, **132**, 179 (1995).
27. Bahranowski K. and Serwicka E.M., *Coll. Surf.*, **72**, 153 (1993).
28. Bahranowski K., Łabanowska M. and Serwicka E.M., *Appl. Magn. Reson.,* **10**, 477 (1996).
29. Bahranowski K., Janas J., Machej T., Serwicka E.M. and Vartikian L.A., *Clay Miner.*, **32**, 665 (1997).
30. del Castillo H.L., Gil A. and Grange P., *Catal. Lett.*, **36**, 237 (1996).
31. Went G.T., Leu L.-J., Rosin R.R. and Bell A.T., *J. Catal.*, **134**, 492 (1992).
32. Chae H.J., Nam I.-S., Kim Y.G., Yang H.S., Choi H.C. and Song S.L., *Stud. Surf, Sci. Catal.*, **125**, 595 (1999).
33. Long R.Q. and Yang R.T., *Appl. Catal. B*, **24**, 13 (2000).
34. Bahranowski K., Bielańska E., Janas J., Machej T. and Serwicka E.M., *Polish. J. Environm. Stud. Suppl. I*, **9**, 7 (2000).

---

[*] The author's fee was financed by the Association for Author Rights Collective Administration of Scientific and Technical Works KOPIPOL with a seat in Kielce from the remuneration collected on the basis of Art. 20 of the Law on Author Right and Related Rights.

35. Chmielarz L., Dziembaj R., Grzybek T., Klinik J., Łojewski T., Olszewska D. and Papp H., *Catal. Lett.*, **68**, 95 (2000).
36. Grzybek T., Pasel J. and Papp H., *PCCP*, **1**, 341 (1999).
37. Iwamoto M., in *Proceedings of the Symposium on Catalytic Technology for Removal of Nitrogen Oxides*, Catal. Soc. Japan, 1990, pp. 17–22.
38. Held W., König A., Richter T. and Puppe L., *SAE Paper 900*, 469 (1990).
39. Li W., Sirilumpen M. and Yang R.T., *Appl. Catal B*. **11**, 347 (1997).
40. Yang R.T., Tharapiwattananon N. and Long R.Q., *Appl. Catal. B*, **19**, 289 (1998).
41. Sirilumpen M., Yang R.T. and Tharapiwattananon N., *J. Mol. Catal. A*, **137**, 273 (1999).
42. Philippopoulos C., Gangas N. and Papayannakos N., *J. Mater. Sci. Lett.*, **15**, 1940 (1996).
43. Morfis S., Philippopoulos C. and Papayannakos N., *Appl. Clay. Sci.*, **13**, 203 (1998).
44. Cavani F., Trifirò F. and Vaccari A., *Catal. Today*, **11**, 173 (1991), and the references therein.
45. de Roy A., Forano C., El Malki K. and Besse J.P., in: M.L. Occelli, H.E. Robson, (Eds.), *Expanded Clays and Other Microporous Solids*, vol. 2, Reinhold, NY, 1992, p. 108, and the references therein.
46. Rives V. and Ulibarri M.A., *Coord. Chem. Rev.*, **181**, 61 (1991), and the references therein.
47. Vaccari A., *Catal. Today*, **41**, 53 (1998).
48. Gazzano E., Montanari B. and Vaccari A., in: E. Herrero, O. Annunziata, C. Perez (Eds.), *Actas XV Simp. Iberoamericano de Catalisis*, Vol. 3, Univ. Nacional Cordoba, Cordoba, Argentina, 1996, p.1967.
49. Montanari B., Vaccari A., Gazzano M., Käßner P., Papp H., Pasel J., Dziembaj R., Makowski W. and Łojewski T., *Appl. Catal. B*, **13**, 205 (1997).
50. Łojewski T., Dziembaj R., Chyży R., Vaccari A. and Montanari B., *Polish J. Environm. Studies*, **6**, 71 (1997).
51. Trombetta M., Ramis G., Busca G., Montanari B. and Vaccari A., *Langmuir*, **13**, 4628 (1997).
52. Bahranowski K., Bielańska E., Janas J., Machej T., Matachowski L. and Serwicka E.M., *Polish J. Environm. Studies*, **6**, 59 (1997).
53. Bahranowski K., Dula R., Gaweł A., Janas J., Machej T. and Serwicka E.M., *Polish J. Environm. Studies*, **6**, 65 (1997).
54. Mulukutla R.S. and Detellier C., *J. Mater. Sci. Lett.*, **16**, 752 (1997).
55. Mann R., *Catal. Today*, **18**, 509 (1993).
56. Shannon I.J., Rey F., Sankar G., Thomas J.M., Maschmeyer T., Waller A.M., Palomares A.E., Dent A.J. and Greaves G.N., *J. Chem. Soc., Farad. Trans.*, **92**, 4331 (1996).
57. Corma A., Palomares A.E., Rey F. and Márquez F., *J. Catal.*, **170**, 140 (1997).
58. Palomares A.E., López-Nieto J.M., Lázaro F.J., López A. and Corma A., *Appl. Catal. B*, **20**, 257 (1999).
59. Liu Y., Wang X, Yang X. and Wu Y., *React, Kinet. Catal. Lett.*, **68**, 399 (1999).
60. Crutzen P.L., *J. Geophys. Res.*, **76**, 7311 (1971).
61. Kramlich J.C. and Linak W.P., *Prog. Energy Combust. Sci.*, **20**, 149 (1994).
62. Crutzen P.L. and Howard C.J., *Pure Appl. Geophys.*, **116**, 497 (1978).
63. Armor J., *Appl. Catal. B*, **1**, 139 (1992).
64. Larsson R., *Catal. Today*, **4**, 235 (1989).
65. Kapteijn F., Rodríguez-Mirasol J. and Moulijn J.A., *Appl. Catal. B*, **9**, 25 (1996).
66. Kannan S. and Swamy C.S., *Appl. Catal. B*, **3**, 109 (1994).
67. Armor J.N., Braymer T.A., Farris T.S., Li Y., Petrocelli F.P., Weist E.L., Kannan S. and Swamy C.S., *Appl. Catal. B*, **7**, 397 (1996).
68. Centi G., Galli A., Montanari B., Perathoner S. and Vaccari A., *Catal. Today*, **35**, 113 (1997).
69. Dandl H. and Emig G., *Appl. Catal.*, **168**, 261 (1998).
70. Kannan S., *Appl. Clay Sci.*, **13**, 347 (1998).
71. Kannan S. and Swamy C.S., *Catal. Today*, **53**, 725 (1999).
72. Pérez-Ramírez J., Overeijnder J., Kapteijn F. and Moulijn J.A., *Appl. Catal. B*, **23**, 59 (1999).
73. Pérez-Ramírez J., Kapteijn F. and Moulijn J.A., *Catal. Lett.*, **60**, 133 (1999).
74. Qian M. and Zeng H.C., *J. Mater. Chem.*, **7**, 493 (1997).
75. Zeng H.C., Qian M. and Pang X.Y., *Stud. Surf. Sci. Catal.*, **116**, 485 (1998).
76. Chellam U., Xu Z.P. and Zeng H.C., *Chem. Mater.*, **12**, 650 (2000).
77. Xu Z.P. and Zeng H.C., *Chem. Mater.*, **12**, 2597 (2000).