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Layered clays as SCR deNOx catalysts

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Abstract

The application of cationic layered clays as DeNOx catalysts with both ammonia or hydrocarbons as reducing agents was discussed. Several preparation procedures: acidic treatment, pillaring, introduction of active material or carbon deposits were described and the influence of these procedures on catalytic activity in SCR deNOx reaction were discussed. The conclusions about possible mechanisms are drawn on the basis of the data obtained. A special attention was paid to the role of acidic and redox sites. The effect of poisoning molecules (SO_2 and H_2O) on catalytic activity and selectivity was considered.
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Keywords: Clays; NO removal; Ammonia; Hydrocarbons

1. Introduction

The removal of nitrogen oxides from outgases is one of the most challenging problems of 21st century. Until now the only method of NOx removal from stationary sources used on industrial scale has been selective catalytic reduction with ammonia. The most frequently used catalyst is $V_2O_5/WO_3/TiO_2$ prepared in the form of a monolith [1]. The solution is, however, far from ideal and new catalytic materials are required to improve the following properties: high activity at either low (<250 °C) or high (>400 °C) temperature range, broader temperature window, higher resistance to water and SO_2, and last, but not least, the possibility of using reducing agents other than ammonia, preferably hydrocarbons such as methane, propane, propene etc. Many of the aspects mentioned above have been studied for layered clays—a large class of materials, abundant in natural environment and fairly cheap, which can also be prepared in the monolith form. Layered compounds as catalysts have attracted interest for many years now. Because of their high acidity, acidic-treated clays were the first cracking catalysts. Although this application is obsolete now because of low hydrothermal stability of these catalysts, they are still taken into account in other reactions, both in organic industry and environmental protection.

In this paper, possible applications of cationic layered clays in the removal of nitrogen oxides from outgases are discussed.

2. What are layered clays?

There are many types of compounds with layered structures. The layers are either neutral and bonded together by dispersion forces or hydrogen bonds, or charged (negatively or positively) and called cationic and anionic clays, respectively. The excessive charge in these materials is neutralized by exchangeable ions present in the interlayer space [2]. In case of possible NOx removal applications, smectites (cationic clays), especially montmorillonites, have been most often considered. However recently, hydrotalcites (anionic clays) have also focused considerable attention [3]. Montmorillonites are dioctahedral minerals of an idealized formula $M_x(Al_{2-x}Mg_x)(Si_4O_{10})(OH)_2\cdot zH_2O$, built of two tetrahedral Si–O sheets with an octahedral Al-based sheet in-between. The excess negative charge originates from partial substitution of Al^{3+} by Mg^{2+} and is neutralized by the appropriate number of cations in the interlayer space.

3. Methods of preparation and their effect on catalytic properties in DeNOx

3.1. Reduction with ammonia

Fig. 1 shows an idealized scheme of montmorillonite together with a typical scheme of preparation. The interesting feature of this type of materials is the possibility to tailor their properties, both textural and chemical (acidity, redox

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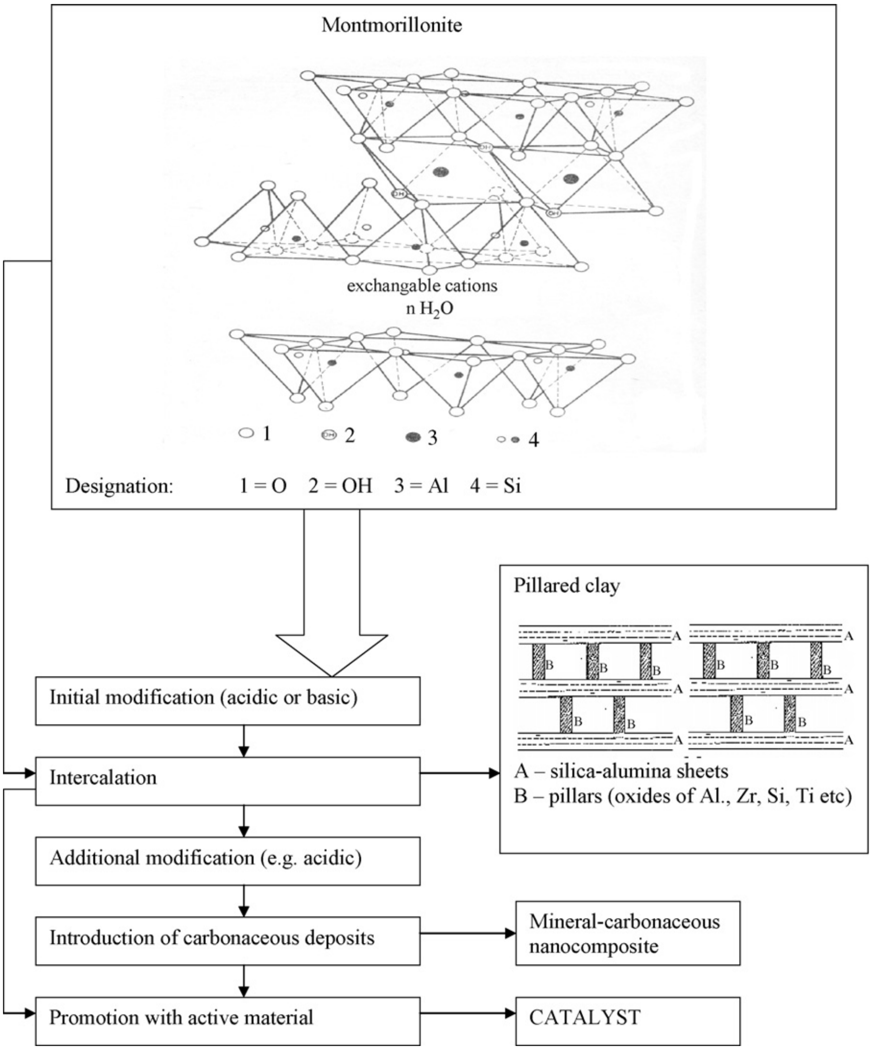

Fig. 1. The structure of montmorillonite and the possible ways of its modification (the most often used preparation route follows the arrows on the left-hand of the picture).

properties, etc.). The preparation procedure may consist of several steps, such as: acidic (or rarely, basic) pretreatment, intercalation, introduction of carbonaceous deposits and/or promotion with active materials. All of these preparation steps were found to influence catalytic performance in NO reduction.

Intercalation, most often called pillaring, provides a possibility of tailoring porous structure, through the exchange of compensating cations with polymer inorganic hydroxycations of dimensions larger than the original ions. Their subsequent calcination results in rigid structures, which are either ordered three-dimensionally or disordered in the *z*-direction (the so called delaminated structures). The former contain mainly micropores and the latter additionally macropores. The size of micropores is 0.4 to ca. 2 nm and depends on the type of pillars [2]. Pillaring results also in the considerable increase of specific surface area from ca. 200 to 400 m^2/g. This rise depends also on the type of pillars. In some cases delaminated clays were found to be more efficient in DeNOx than orderly structured ones (cp. Fe_2O_3-pillared or delaminated Fe_2O_3-pillared [4], Ti-pillared delaminated montmorillonite [e.g. 5] or Cu^{2+} promoted Al_2O_3-pillared laponite [6]).

Active material may be introduced as the last step of the preparation but the influence of the simultaneous introduction of active phase and pillars on catalytic behavior was also studied [7,8]. Chmielarz et al. [7] found that the simultaneous insertion of pillars and copper gave less active catalyst than a sequential process (first pillaring and then promotion). Similarly, DeNOx activity was different for zirconia pillared clays promoted with vanadium cations after pillaring and those containing vanadia introduced during co-pillaring [8].

Some of the pillared-clay catalysts showed activity higher than the commercial vanadia–titania systems. The examples of such behavior were described by Serwicka and Bahranowski [9], Long and Yang [10–13] and Cheng et al. [14]. Serwicka and Bahranowski [9] showed that titania pillared clay modified with vanadia showed a better performance in a broad temperature window (between ca. 523 and 673 K) than the conventionally prepared V/TiO_2 catalyst. Long and Yang [10,11] studied a commercial vanadia–tungsta–titania catalyst (V_2O_5/WO_3/TiO_2) and titania pillared clay similarly promoted. In these cases, the catalysts contained 4.4% V_2O_5 and 8.2 WO_3. Two observations are worth mentioning: (i) NO conversion was similar (ca. 92–93%) for both catalysts at 350 and 375 °C, but higher for pillared clay at 400 and 450 °C, and (ii) selectivity to N_2 was in the temperature range of 350–450 °C between 100 and 98% for V-pillared clay and 97–81% for the commercial system [10,11]. Fe or Ce–Fe-promoted Ti-pillared montmorillonite was somewhat inferior at 300 and/or 350 °C in comparison to a commercial V–W–Ti–O system but it showed better activity and selectivity to nitrogen at higher temperatures, especially between 400 and 450 °C [12]. Cheng et al. [14] compared titania pillared clays promoted with 7.5 wt.% iron and 2.5 wt.% chromium oxides with the commercial V_2O_5 catalyst from an unnamed US producer. For the clay catalyst at 375 °C, first order rate constants were 305 and 192 cm^3/g for a mixture without or with the addition of SO_2 and H_2O, respectively. For the commercial catalyst the respective k values were 158 and 129 cm^3/g, i.e. even in the presence of H_2O and SO_2 the clay-based catalyst was ca. 40% more active than the commercial one. Selectivity was also very good—the amount of formed N_2O was below 1%.

The introduction of pillars and transition metal cations modifies acidity of the system, in consequence affecting the catalytic activity. Additionally, acidic treatment may be used. The preparation procedure consisting of acidic treatment, pillaring with zirconium hydroxycations and promoting with manganese cations provided more active DeNOx catalysts than similarly prepared systems with the omission of the first step [15,16]. Fig. 2 compares conversion in DeNOx reaction for these two types of catalysts at different temperatures [15].

The promotion with carbon deposits was also found interesting, leading to more active catalysts for both pillared and non-pillared systems [17–23]. Chmielarz et al. [17] prepared mineral-carbonaceous nanocomposites by sorption of polymer from aqueous solution on zirconia pillared clays either initially pretreated (acidic pretreament) or untreated. The sorbed polymer was then turned into carbonaceous deposit by carbonization in nitrogen. Such modification improved activity, as can be seen in Fig. 3 [17]. Non-pillared montmorillonite covered with carbonaceous deposit was also studied as a support. The catalysts were prepared by carbonization of deactivated non-pillared clays (waste from edible oil industry) and promoted with manganese and/or iron oxides. It was shown that so-prepared systems had high activity in the low-temperature region between 140 and 250 °C [20–23].

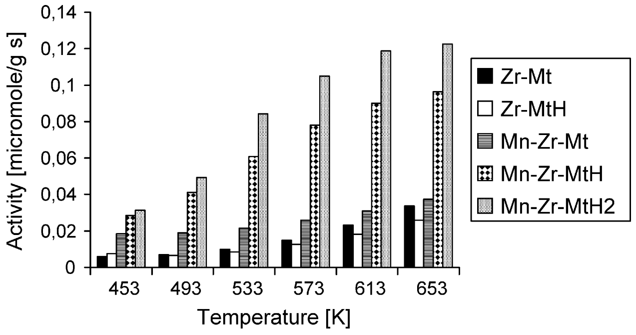

Fig. 2. NO conversion in DeNOx (NH_3) reaction for catalysts based on zirconia pillared clays (untreated or pretreated with acid) promoted with manganese; designation: Mt—montmorillonite; MtH—montmorillonite treated with acid; Zr—Mt montmorillonite pillared with zirconium hydroxycations; Mn—introduced active material (manganese oxides/hydroxides); 2—second preparation (both preparations differ in some details of active material introduction) (based on data from [15]).

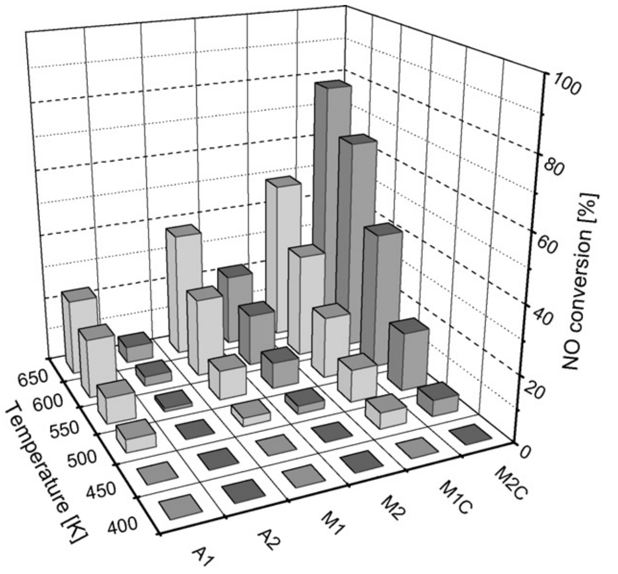

Fig. 3. NO conversion in DeNOx (NH_3) over differently pillared clays: A1 and A2 montmorillonite untreated or pretreated with acid; M1 and M2 zirconia pillared A1 and A2; M1C and M2C carbon-montmorillonite nanocomposites based on M1 and M2 (based on data from [17]).

3.2. Reducing agents other than ammonia

Recently much attention has been paid to replacing of ammonia as a reducing agent by hydrocarbons. The main reason lies in high toxicity of NH_3. This enforces strict control of ammonia slip which in industry is limited to 5 ppm in outgases [1]. It is obtained under industrial conditions by (i) working at the stoichiometric ratio of $NH_3/NO < 1$, thus decreasing the efficiency of the method, and/or (ii) by costly electronic control of ammonia dosage. Table 1 summarizes examples of more recent studies where reducing agents other than ammonia were tested: methane [24,25], ethene [6,25,26], propane [25,27], propene [25,28–30], as well as alcohols, acetone [25], hydrogen, carbon monoxide [31–33] and hydrogen + carbon monoxide mixtures [31]. From Table 1 several interesting facts may be noted:

(i) The type of layered clay plays an important role in DeNOx process [6,24,30]. In some cases clay-based catalysts were found to be more efficient than those based on other supports, such as ZrO_2 [24] or ZSM-5 [26]. It was postulated that redox sites necessary for the reaction were different in both cases [6,26].
(ii) The method of promotion with active material decided the end result, e.g. in the case of the introduction of CuO_x, ion exchange method was found much more efficient than wet impregnation [29].

Table 1
Catalytic performance of pillared and non-pillared clays in selective catalytic reduction of NO with hydrocarbons or other reductants (with the exception of NH_3)

Support[a]	Active material	Reaction conditions	R[b]	Maximum NO conversion/% selectivity to N_2	Tested in the presence of			Ref.
					O_2	SO_2	H_2O	
Al-Mt, ZrO_2	0.6% Pd, Rh or Pt	$T = 300–500$ °C; 500 ppm NO, 5000 ppm R, 1.2% O_2; GHSV 4000 h^{-1}; $V = 3.6\ dm^3/min$	CH_4	ca. 60% at 400 °C Rh–Al-Mt; Sel. better for Mt based catalysts than ZrO_2 based ones	+	–	–	[24]
Al-Mt, Fe/Al-Mt, γ-Al_2O_3, ZrO_2, ZSM-5	Cu^{2+} (by ion exchange or incipient wetness)	$T = 200–600$ °C; 800 ppm NO, NO/R = 4, 2% O_2; GSVH 10000 h^{-1}	C_3H_8	Very low activity both for supports and catalysts	+2%	–	–	[27]
Ti-Mt	Cu, Ni or Fe	$T = 175–475$ °C; 1000 ppm NO, 1000 ppm R, 5% O_2, He; GSVH 15000 h^{-1}; $V = 125\ cm^3/min$	C_3H_6	55% at 260 °C for 7.4% Cu–Ti-Mt (Cu introduced by ion exchange)	+	–	±10%	[29]
Ti-Mt	6% Cu	$T = 200–350$ °C; ppm NO not given; 1000 ppm R, 5% O_2, He; $V = 125$ ml/min; GSVH 15000 h^{-1}	C_3H_6	55% conversion to N_2 at 235 °C	+	–	–	[45]
Al-Sp, Fe-Sp, Al/Fe-Sp	FeO_x	$T = 25–500$ °C; 9000 ppm NO, 1000 ppm R, Ar; GSVH 19000 h^{-1}	C_3H_6	ca. 80% activity decreases with O_2 content—reaches plateau at ca. 0.6% O_2	± (0.2–1.2%)	–	–	[28]
Al-Sp, MK, Al_2O_3	8 wt.% Fe	$T = 25–500$ °C; 9000 ppm NO, 1000 ppm R, Ar; GSVH 19000 h^{-1}	C_3H_6	ca. 90%	–	–	–	[30]
Ti-Mt, Zr-Mt Al-Mt, Al-Lp, ZSM-5	Cu^{2+} (by incipient wetness or ion exchange); for Ti–Mt also Fe, Ce, Co, Ag or Ga	$T = 250–500$ °C; 1000 ppm NO, 1000 ppm R, 2% O_2, $V = 250\ cm^3/min$; $m_{cat} = 0.5$ g	C_2H_4	ca. 60% at 300 °C for 5.9 wt.% Cu–Ti-Mt promoted with 0.5% Ce; Cu introduced by ion exchange	+	±500 ppm	±5%	[26]
Ti-Mt	Cu^{2+}	$T = 250–400$ °C; 1000 ppm NO, 250 ppm R, 2% O_2; $V = 150\ cm^3/min$; $m_{cat} = 0.5$ g	C_2H_4	ca. 90 and 80% at 300 °C (without or with SO_2 and H_2O, respectively) for Cu–Ti-Mt promoted with Ce	+	±1000 ppm	±5%	[63]
Al-Lp, Ti-Mt, ZSM-5	Cu^{2+}	$T = 250–500$ °C; 1000 ppm NO, 1000 ppm R, 0–4% O_2; $V = 250\ cm^3/min$; $m_{cat} = 0.5$ g	C_2H_4	ca. 80% at 500 °C for Cu^{2+}–Al-Lp	±0–4%	±500 ppm	±5%	[6]
Sp[c], Mt, ZSM-5	Ag, Fe, Mn, Co, Ni or Cu For Mt and Zeolite Ag	$T = 200–600$ °C; 900 ppm NO, 350–2700 ppm R, 9% O_2; $V = 66\ cm^3/min$; $m_{cat} = 0.2$ g	C_3H_6, C_3H_8, CH_4, C_2H_4, n-C_6H_{14}, C_6H_6, CH_3OH, C_2H_5OH, C_3H_7OH, acetone	ca. 40% at 350 °C for Cu-Sp; 51.2% for Ag-Sp in the presence of H_2O	+	–	±8%	[25]
Al-PILC	Rh	$T = 150–420$ °C; NO/CO = 0.5, 2760 ppm R; $V = 2\ dcm^3/min$; $m_{cat} = 1$ g	CO	Almost complete at ca. 420 °C	–	–	–	[32]
Al-Mt, Al-Sp	Rh	$T = 200$-450 °C; 1% NO, 2% R; $m_{cat} = 0.25$ g	CO	Almost complete at ca. 400 °C for Rh–Al-Mt	–	–	–	[33]
Ti-Mt, Zr-Mt, Al-Mt, Fe-Mt TiO_2/Al_2O_3	0.5% Pd	$T = 100–300$ °C; 500 ppm NO, 4000 ppm R, 10% O_2; GSVH 120000 dm^3/h; $V = 200\ cm^3/min$; $m_{cat} = 0.1$ g	4000 ppm H_2, 4000 ppm C0, or CO + H_2	76% at 140 °C for H_2 + CO (3:1); a mixture of H_2 + CO more efficient than each reductant alone; lost ca. 15% activity with H_2O	+	±	±5%	[31]

[a] Pillared clays: Mt, montmorillonite; Sp, saponite; Lp, laponite; MK, metakaolinite; PILC, unspecified clay; the preceding symbol –, type of pillaring cations.

[b] R = reducing agent.

[c] Not pillared.

(iii) Apart from NO reduction, a competing reaction of hydrocarbon oxidation was always observed. The latter prevailed at temperatures above ca. 260 °C over nitrogen oxide reduction which led to a maximum activity of DeNOx at ca. 260 °C, followed by its decrease [29].
(iv) In most cases copper was recognized as a promising active material [26,29].
(v) If comparison of hydrocarbons and ammonia was made, it was found that the former were unfortunately less active than the latter [26,27].

In conclusion, all preparation steps leading to pillared clay promoted with active material influence SCR activity and selectivity. The following steps are of crucial importance:

- Intercalation on several reasons. Firstly, because it increases specific surface area, secondly it introduces new acidic sites and thirdly, because some types of pillars (e.g. TiO_2) lead to catalysts resistant to water and SO_2;
- Acidic pretreatment before pillaring. The reason is as yet not clear, and
- Appropriate choice of active material. As most promising the following were identified: oxides of V or Fe for SCR-NH_3 and Cu for SCR-hydrocarbons.

4. Mechanistic considerations

Mechanism of SCR-NH_3 reaction was discussed in several articles. A good review of the literature up to 1998 was given by Parvulescu et al. [34] for vanadia either unsupported or supported on TiO_2, or chromia or zeolites. Recently, Busca et al. [35] reexamined some aspects of mechanism for both oxide catalysts and protonic zeolites. As discussed by Parvulescu et al. [34], there are arguments in favor of both Eley–Rideal and Langmuir–Hinshelwood mechanisms. According to this review, for oxide-based catalysts NH_3 is activated on the surface on both Lewis and Broensted sites. However, the work of Busca et al. [35] indicates, that coordinated ammonia is present on reducible sites and this is the main surface species. Either gas or weakly sorbed NO is believed to be involved in the reaction. The situation is different for protonated zeolites where both NH_4^+ and coordinated NH_3 species may play a significant role. For the former, highly oxidizing NO_2 species are necessary for the reaction to proceed while the latter are highly reactive with NO.

It seems that there is a more or less general agreement that two factors play a very important role in DeNOx reaction (both with ammonia [36,37] and hydrocarbons [38]): acidity and redox properties.

Pillared clays unpromoted or promoted with different active materials exhibit two types of acidity. Lewis sites are connected with pillars and some active materials (e.g. Fe^{3+} [39]). Broensted sites may arise from two sources. The first are structural hydroxyl groups in clay layers. The second source of protons may be connected with cationic oligomers that upon heating decompose and form oxide pillars. Some active materials also add to Broensted acidity, e.g. V_2O_5, as confirmed for VO-exchanged TiO_2-pillared clays by Long and Yang [10].

4.1. The influence of acidic properties

4.1.1. Ammonia as a reducing agent

The important role of acidity for modified layered clays is generally accepted. It was supported by:

- Chen et al. [4] who found a correlation between Broensted acidity for delaminated Fe_2O_3-pillared montmorillonite and activity.
- Long and Yang [10] who studied VO^{2+}-exchanged TiO_2-pillared montmorillonites and found that the increase in Broensted acidity with vanadium content was consistent with the increase in activity at lower temperatures (ca. 200 °C).
- Perathoner and Vaccari [27] for Cu^{2+}-promoted Al- or Fe/Al-pillared clays.
- Khalfallah Boudali et al. [40,41] who compared titanium-pillared or sulfated titanium pillared montmorillonite either unpromoted [41] or promoted with V_2O_5 [40]. For sulfated titanium pillared clays, acidity as well as activity were correlated to S/Ti atomic ratios (as obtained from XPS). IR investigations pointed to both Lewis and Broensted sites present, but the increase upon sulfation produced mainly the latter [41]. Higher NO conversions (with ammonia) were also found for more acidic S-containing samples when used as supports for V_2O_5 [40]. Similar effect was connected with the sulfation of Fe-exchanged TiO_2-pillared clay [42].

However, it must be mentioned, that higher density of adsorbed ammonia which is due to higher acidity was invoked as a possible reason for the formation of N_2O, as suggested by Boudali [40].

4.1.2. Hydrocarbons as reducing agents

For DeNOx with hydrocarbons the role of acidity was proven by:

- Bahamonde et al. [24] who related that Pd, Pt or Rh supported on pillared montmorillonite had acidity higher by a factor 2–3.5 than Pd supported on ZrO_2. Activities in DeNOx (CH_4) were higher for Pd promoted pillared clays than zirconia promoted with Pd; on the other hand, the role of other factors, such as S_{BET} and porosity was not excluded.
- Li et al. [6] for reduction of NO with ethene on Cu^{2+} exchanged Al-pillared laponite or Ti-pillared montmorillonite where Lewis sites were found to be important.
- Valverde et al. [29] for Cu–Ti-montmorillonite for C_3H_6 as a reducing agent. Additionally, the distribution of Cu^{2+} and CuO was found to depend on the preparation method and affect the activity. The relevance of this lies in the fact that Cu^{2+} form strong Lewis sites.

In conclusion, for SCR-NH_3 most of the authors seem to agree that Broensted acidity plays the main role. However, it could be argued that pillared clays contain also Lewis sites and in some works they are also postulated as additional reaction centers. Moreover, for other types of catalysts, either oxidic (e.g. V_2O_5–TiO_2) or zeolites, recent work of Busca et al. [35] pointed out to the important role of Lewis sites.

For SCR-hydrocarbons mainly Lewis sites are believed to be responsible for the reaction.

Therefore, the matter needs some clarification, especially where ammonia as a reducing agent is concerned.

4.2. *The role of redox properties*

The role of redox properties for clay catalysts was discussed by:

- Yang et al. [26] who compared Cu promoted titania pillared montmorillonite with Cu-ZSM-5 in reduction of NO with C_2H_4 and ascribed higher activity of the former to a weaker Cu^{2+} bonding to clay than ZMS-5 which makes redox cycle easier.
- Valverde et al. [29] for Cu or Ni–Ti–montmorillonite who indicated a correlation between activity and reducibility of copper species expressed by the maximum temperature in TPR.

Redox properties and the form of active material are strongly connected which was observed before for different systems. Long and Yang [10] compared V-containing catalysts based on titania pillared clays and ZSM-5 and ascribed the higher activity of the former to different forms of V present.

However, the proper form of active material has not been established as yet, as exemplified by the experimental results for V-promoted montmorillonites [9,43].

Chae et al. [43] compared SCR activity of V_2O_5 on different supports (SiO_2, Al_2O_3, TiO_2, TiO_2-pillared montmorillonite) and correlated it to the structure of V_2O_5 as elucidated by Raman spectroscopy, ^{51}NMR and XRD. TOF changed depending on the type of V species; the activity increased in a sequence: crystalline V_2O_5 (inactive) < monomeric vanadyl < polymeric vanadyl. Higher activity of titania-pillared montmorillonite was ascribed to higher formation of polymeric species. It was influenced by higher S_{BET} (of pillared montmorillonite in comparison to TiO_2), as well as different interactions of V species with the support, which is too weak for SiO_2 and too strong for Al_2O_3. On the other hand, Serwicka and Bahranowski [9] ascribed higher activity of vanadium promoted titania-pillared montmorillonite to monomeric and not polymeric species. However, it must be mentioned that the catalysts in this case were prepared differently and the authors claim that V sites were anchored exclusively to Ti-pillars.

4.3. *Surface intermediates*

The complete mechanism of the reaction on layered clays was considered only in a few works and a generalization is difficult. The comparison is rather difficult because the studied catalysts varied in several properties: (i) the type of starting material—montmorillonite, saponite, laponite, hydrotalcites, etc., (ii) different types of pillars, which introduce new additional oxides into the system, changing acidity and/or leading to different textures and (iii) initial (or final) modification, e.g. acidic treatment leading to the formation of new acidic sites.

However, on the basis of the already known experimental facts some mechanistic hypothesis are discussed in literature. Among the more detailed works, those of Sirilumpen et al. [44], Valverde et al. [45], Chmielarz et al. [18,46], Li et al. [6] and Long et al. [39,42] are worth mentioning. Experimental arguments are based on infrared spectroscopy [6,18,39,42,44,45], temperature programmed desorption TPD [46] and temperature programmed reaction TPR [18,3,46]. The studies were carried out on different pillared clays: Cu^{2+} promoted Al-pillared laponite [6,44], Cu^{2+} promoted Ti-pillared montmorillonite [45,46], Ti- or Al-pillared montmorillonite promoted with Co^{2+} [46], Co^{2+}-promoted titania pillared montmorillonite [46], Fe^{3+}-promoted titania pillared montmorillonite [42] and carbonaceous-montmorillonite nanocomposite promoted with Mn oxides [18].

The NO intermediates are still not clearly identified. Sirilumpen et al. [44] and Li et al. [6] found different nitro and nitrate species, as well as nitrous oxide [44] as intermediates. Valverde et al. [45] registered monodentate and bidentate nitrate species. These articles stress the importance of redox cycle, Sirilumpen et al. [44] through the formation of Cu^+ from Cu^{2+}–O–Cu^{2+} by oxygen removal and Li et al. [6] for Cu^{2+} bonded to Al-pillars and Valverde by the action of hydrocarbon (C_3H_6) which chemisorbs competitively with NO, removes NO_3^- from adsorption sites and reduces Cu^{2+} to Cu^+/Cu^0 thus enabling the formation of N_2 and CO_2. Chmielarz et al. [18,46] indicated, that the amount of chemisorbed NO was significantly lower than that of the reducing agent (ammonia). Two forms of chemisorbed NO were detected: one relatively weakly sorbed, which desorbed below 250 °C and other, stable to ca. 450 °C. It was found that only a very small fraction of NO was oxidized to NO_2 and the relative importance of such species was postulated to be low. In this case two routes were proposed: reaction of chemisorbed ammonia with (a) NO dominating at low-temperature region and additionally (b) surface nitrate anions at higher temperatures [18,46].

On the other hand, there is much less controversy regarding the role of reducing agents. Ammonia is chemisorbed on the surface, either on Lewis and/or Broensted sites and hydrocarbon is activated on surface sites. The more detailed model of Long and Yang [39] assumed that two NH_3 molecules adsorbed on neighboring Broensted or Lewis sites and reacted with one molecule of NO_2 formed from oxidation of NO with oxygen. So formed active intermediate finally reacted with NO forming N_2 and H_2O. Thus the reaction mechanism was similar to that postulated for Cu-ZSM-5 and H-ZSM-5 by Komatsu et al. [47] and Eng and Bartholomew [48]. On the other hand, Chmielarz et al. [46] argued that the formed active complex reacted subsequently with one NO molecule.

Thus it could be concluded that:

- the reducing agent is adsorbed on the surface;

- NO is adsorbed in several forms. Both species, weakly and strongly adsorbed, are present.

However, there are still several controversies regarding the complete mechanism of DeNOx on layered clays:

- The precise role of Broensted and Lewis acidity is unclear. It needs to be established if the intermediates involve coordinated ammonia and Broensted sites play a minimal role as postulated by Busca et al. [35] for oxide catalysts, or protonation is necessary as for zeolitic structures;
- What is the role of more strongly adsorbed NO species;
- How dispersion of active material affects the number of possible processes;
- Although the necessity of both redox and acidic sites is recognized and obviously some balance is necessary, no proper definition of such balance was established as yet.

5. Poisoning

The applicability of new systems for DENOx is directly linked with their behavior towards substances other than nitrogen oxides, present in outgases.

5.1. Ammonia as a reducing agent

One of the most interesting characteristics of some promoted pillared clays is their high resistance against poisons such as water vapor and/or sulfur dioxide for selected compositions and for certain range of temperatures [e.g. 11–13,49,50]. The described behavior is not a general feature because it depends on the structure of the catalysts, resulting from pillaring and type and/or distribution of active material. Both negative and positive examples were registered in literature. Nevertheless, even if deterioration was found, in some cases either its extent was minimal (cp. e.g. [19]) or the activity was lower but stable as a function of time [4].

Among positive examples, those described by Long and Yang [11,12] and del Castillo et al. [50] are worth mentioning:

- Long and Yang [11] studied the effect of 8% H_2O and 1000 ppm SO_2 on NO conversion for V_2O_5 promoted titania pillared clays. At low temperatures (below 573 K), NO conversion was decreased by the presence of sulfur dioxide and water vapor but above 623 K, activity was slightly higher than that for a reaction mixtures not containing these poisons. Additionally, selectivity to N_2 was improved in the presence of SO_2 and H_2O.
- Long and Yang [12] found that in the presence of H_2O and SO_2 Fe- or Ce–Fe-promoted-TiO_2-pillared montmorillonite [12,13] exhibited activity about two to three times higher (respectively) than a commercial catalyst.
- Del Castillo et al. [50] tested titanium pillared clays untreated or sulfated either with $(NH_4)_2SO_4$ or H_2SO_4 in DeNOx reaction both in the presence and absence of SO_2 in the reaction mixture. The sample pretreated with H_2SO_4 showed higher resistance towards SO_2 at 673 K than untreated pillared clay.

The possible reason for the improvements of activity may be attributed to the increase in acidity, which is believed to be one of the key features in the reaction mechanism. The improvement of selectivity may arise from the suppressed oxidation of reducing agent (ammonia).

5.2. Hydrocarbons as reducing agents

The influence of poisons was tested only for selected catalysts. In the most cases, SO_2 and/or H_2O had a negative effect on activity although it should be mentioned that titania pillared clay promoted with copper was more resistant to water and sulfur dioxide in DeNOx (C_2H_4) than most often studied Cu-ZSM-5 [6,26]. Also for Cu^{2+}-promoted Al_2O_3-pillared laponite and ethene as reducing agent deactivation was observed at lower temperatures (up to 450 °C) but at 500 °C the poisoning effect was small.

Competitive adsorption is most often quoted as a possible reason for poisoning. This phenomenon may be a reason why more polar reductants (alcohols, acetone) were more efficient in wet streams [25]. Another possibility may be that water influences DeNOx activity by changing the acidity of the catalysts [6].

6. Other layered clays

The second class of layered clays are anionic clays also called hydrotalcites or sometimes, layered double hydroxides. They are either natural materials or may be prepared synthetically. The structure of hydrotalcites is derived from layered $Mg(OH)_2$ and may be described by a formula $[M(II)_{1-x}M(III)_x(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$ with M(II), M(III) and A^{n-} denoting divalent or trivalent cations and interlayer anion compensating the layer charge (e.g. [3,9]). Hydrotalcites attract broad attention because their thermal decomposition results in mixed oxides with high dispersion and unique catalytic properties [3]. There are several articles in the literature dealing with the possible application of hydrotalcites in environmental protection. Recently, much interest has been focused on DeNOx reaction, as well as N_2O removal. Hydrotalcites or mixed oxides derived from hydrotalcites were studied as catalysts for: (a) NO reduction with ammonia (Mg/Cr/Al and Mg/Fe/Al oxides [51], Cu/Mg/Al [52,53]), (b) NO reduction with hydrocarbons [3,54–57] or (c) decomposition of N_2O [58–62].

7. Concluding remarks

Cationic layered clays are an interesting class of materials, which may be modified in different ways, resulting in materials with differing texture, acidity and chemical (redox) properties. Several attempts have been made to use cationic layered clays as DeNOx catalysts. It has been found that some modifications led to the materials with activity higher or comparable to that of the currently used industrial vanadia–titania systems. The most promising catalysts seem to contain titania pillars and vanadium, iron or copper oxides as active materials.

The additional advantage of the layered clays lies in the possibility of tailoring the catalysts to high resistance to water and sulfur dioxide. In some cases (certain compositions and temperatures), activity was found to be higher when these poisons are present than without them. Attempts have been made to apply reductants other than ammonia (hydrocarbons, carbon monoxide, hydrogen). The obtained results indicate a possibility to form a catalyst with features better than Cu-ZSM-5 currently recognized as one of the most promising materials.

There is still no general agreement concerning the mechanism of DeNOx reaction on pillared clays. Both the problem of NO intermediate species and the main acidic sites necessary for the reaction are still under discussion. It is recognized that a certain balance between redox and acidic properties is necessary although no proper definition of such balance was established as yet.

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