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Montmorillonites modified with polymer and promoted with copper as DeNO$_x$ catalysts

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Abstract

Clays modified with polymer and promoted with copper cations were studied in selective catalytic reduction of NO with ammonia. The modification with polymer and promotion with copper did not influence the layered structure of pillared clays. Specific surface areas of the catalysts were between 22 and 98 m^2/g, lower or much lower than for pillared supports. The following elements of the preparation influenced positively NO conversion: acidic pretreatment (or the choice of acidic clay), modification with polymer and copper promotion. The most active catalyst was based on acidic clay modified with polymer and promoted with copper. Selectivity to N_2 did not deteriorate after polymer modification.

Keywords: Montmorillonite; Polymer modification; Copper; SCR

1. Introduction

Environmental pollution with nitrogen oxides forms constant challenge for researchers. The amount of NO$_x$ emitted in the last 10 years decreased but they still form a major danger to the environment. Currently the only method of NO$_x$ removal on industrial scale is selective catalytic reduction with ammonia carried out on vanadia catalyst supported on titanium oxide [1]. It is an active and selective catalyst with high resistance to nitrogen oxides and sulfur dioxide but not without certain shortcomings. First of all, it is expensive. Secondly, its optimum window is between 523 and 673 K while no good solution was found yet for lower and higher temperatures. Therefore, new catalysts are still searched, either using ammonia or hydrocarbons as reducing agents [2]. One of the types of the studied catalysts are modified layered clays [2–22]. It was shown in literature that some pillared clay catalysts showed activity higher than the commercial vanadia–titania systems [3,4,12–15]. Montmorillonites are especially interesting because of several modification possibilities. Both chemical i.e. activity, selectivity and acidic/basic, and textural properties may be changed through appropriate preparation procedure. Typical preparation steps used to tailor chemical and physical structure of layered clays are acidic/basic treatment, intercalation of hydroxycations called pillaring and promoting with transition metal oxides/hydroxides. It was pointed out lately [16–20,23] that there is a possibility of forming hybrid carbonaceous–clay systems, either through in situ polymerization of small organic molecules or sorption of polymer, followed by carbonization and activation. The application of such systems in SCR is rather seldom.

Chmielarz et al. [16–18] presented catalytic SCR (NH_3) tests for the following catalysts: acidic pretreated montmorillonite pillared with zirconium hydroxycations unpromoted or promoted with polymer, with the addition of manganese. Catalysts pretreated with acid were ca. twice more active than non-treated ones before pillaring. All used preparation steps—acidic treatment, pillaring and carbon deposition led to the increase in NO conversion.

On the other hand, Grzybek et al. [19] proposed as supports montmorillonites which were an industrial waste. The mentioned materials were used in industry as sorbents for cleaning edible oils of organic compounds. After prolonged application, they were deactivated by irreversible sorption of carbon species. After preparation procedure, consisting of carbonization and promotion of manganese and/or iron oxides/hydroxides, the obtained materials proved to be active and selective in SCR (NH_3) at low temperature region (below 473 K).

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The subject of the work was to study the influence of different preparation parameters of montmorillonites (treated as supports for copper species) on DeNO$_x$ catalytic properties. The following preparative elements were compared in SCR: (i) polymer treated versus untreated; (ii) differently pillared (Zr or Al) or non-pillared; (iii) with or without acidic pretreatment, as well as acidic clays.

Copper species were chosen because this active material was found before to have a promising SCR behavior for zeolites [24–26] (e.g. Cu-ZSM5), active carbons [27] or clays [21,22,28]. Yang et al. [28] showed that TiO$_2$-pillared Cu promoted clay could by used for NO reduction with hydrocarbons. It was found, however, that C_2H_4 was interior to NH_3. In articles [21,22] Chmielarz et al. studied as SCR (NH_3) catalysts montmorillonites pillared with alumina, zirconia or titania doped with copper, cobalt or iron. The best catalysts were pillared with titania and promoted with copper cations (100% NO conversion at 523 K), while other studied samples either did not reach 100% conversion or reached it at much higher temperatures.

2. Experimental

2.1. Catalysts

The supports for the catalysts were prepared according to route 1 or route 2:

- route 1: starting clay (Mt or K5) → pillaring → MtAl, MtZr, K5Al;
- route 2: montmorillonite (Mt) → acidic pretreatment → MtH.

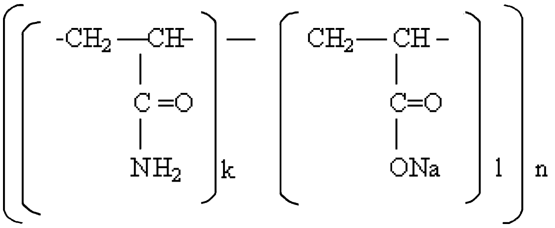
The starting clays were montmorillonite (designation Mt) sedimented from bentonite from Milowice, and commercially available acidic montmorillonite K5 (producer Sigma–Aldrich GmbH). The % composition of the starting motmorillonites Mt and K5 was (respectively): SiO$_2$(56.3; 65.0); Al$_2$O$_3$ (23.2; 19.0); Fe$_2$O$_3$ (3.0; 4.8); CaO (0.1; 0.2); MgO (0.8; 2.4); Na$_2$O (0.3; 1.6); K$_2$O (2.6; 1.5) [29,30]. The materials contain relatively high amounts of Fe$_2$O$_3$, which is known to be catalytically active at SCR. This may explain why all supports, as shown further in the text, exhibit ca. 3–35% conversions, depending on temperature.

Pillaring was carried out with: (i) Al-polycations (designation "Al") with chlorhydrol according to the procedure described by Vaughan [31] or (ii) zirconium polycations (designation "Zr") prepared from ZrOCl$_2$ as proposed by Yamanaka and Brindley [32].

Acidic pretreatment of Mt was carried out with 20% HCl solution at boiling temperature for 1 h. Activation time was chosen based on previous experiments [33].

The next step of preparation was (i) either impregnation with aqueous solution of copper nitrate(V) or (ii) a treatment with polymer, followed by impregnation with aqueous solution of Cu(NO$_3$)$_2$.

The polymer treatment was carried out similarly as described in detail in [33]: an aqueous suspension of the support and 3% aqueous solution of polymer were contacted for 48 h at room temperature under constant stirring. After sorption water was removed by evaporation and montmorillonite was carbonized at 773 K for 30 min. The polymer used was polyacryloamide (commercial name Gigtar, produced by Zakłady Azotowe, Tarnów, Poland):



$$\left[\left(-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right)_k-\left(CH_2-\underset{\underset{ONa}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right)_l\right]_n$$

Copper species – in each case 5 wt.% – were introduced by incipient wetness technique.

Before reaction all samples were calcined in situ.

3. Characterization

The characterization of the samples included: (i) elemental analysis C (content) using Elemental Analyser Vario-EL (Elementar-Analyser Systeme GmbH, Hanau); (ii) structure by X-ray diffraction XRD using Philips PV 3020 X' Pert and Cu Kα radiation (line = 0.15418 nm). Clay samples were prepared by settling a suspension of montmorillonite onto a glass slide, similarly as described in [23]. All clay mounts were dried. No calcinations was carried out; (iii) S_{BET} by nitrogen sorption at 77 K using a volumetric method (Micromeritics ASAP 2000). Prior to sorption the samples were outgassed at 453 K for several hours; and (iv) surface composition by X-ray photoelectron spectroscopy XPS using Hemispherical Energy Analyzer PHOIBOS 150 MCD (SPECS GmbH). The main Si 2p peak at 103.1 eV was used as an internal standard to calibrate binding energies. The areas of main peaks Cu 2p$_{3/2}$, Al 2p, Si 2p and O 1s and sensitivity factors of Scofield were used to determine surface composition.

Catalytic properties in NO reduction with ammonia (NO conversion and N$_2$O formation) were studied under the following conditions: mass of catalyst 200 mg; reaction mixture: 800 ppm NO, 800 ppm NH$_3$, 3% O$_2$, He; flow: 100 ml/min. The experiment was carried out as follows: first catalysts were calcined on-line at 773 K in helium (100 ml/min) for 30 min. Then temperature was decreased under helium to 423 K and gas flow was switched to the reaction mixture. After 60 min on-line, temperature was raised by 50 K and next experimental point was measured, followed again by the same procedure. Experimental points were taken at 423, 473, 523, 573 and 623 K. NO and N$_2$O concentrations were measured at the outlet of the reactor by NDIR (Hartmann and Braun) every 10 min for each experimental temperature.

4. Results and discussion

From elemental analysis it may be observed that although the procedure of polymer modification is identical in all cases, the C content distinctly differs both for supports and copper-promoted catalysts and forms the following sequence:

- supports: MtHG (2.88) > MtZrG (2.35) > K5AlG (0.58) > MtAlG (0.42);
- catalysts: MtHGCu (2.55) > MtZrGCu (2.42) > MtAlGCu (0.77) > K5AlGCu (0.65).

The observed differences may be caused by several parameters. The supports differ in the type of the starting material, acidity and the type of pillars. It was found before [33,34] that acidity and type of pillars influenced the interaction of polymer with pillared montmorillonite. From TPD (surface oxides), acidity measurements by TPAD and XPS studies it was postulated that polymer molecule was attached to the acidic surface group through its basic NH_2 group [33,39]. Depending on the way of carbonization (slow increase of temperature to 500 °C or a direct introduction into preheated reactor), there was stronger or weaker competition between desorption of the polymer molecule or its pyrolysis [34]. Acidity was an additional factor, as it was the source of more acidic sites. It was postulated additionally that cracking of adsorbed polymer either preceded carbonization or competed with it, resulting in smaller deposits than for non-acidic montmorillonites [33]. The fourth factors are different pillars. They may also influence the interaction of polymer with pillared montmorillonite, because they are different in size and lead to different specific surface areas (and also porosities). This may influence the penetration of the inner structure by polymers [35].

The values of $d_{0\,0\,1}$ calculated from the first low-angle diffraction maximum give information on the interlayer distances in clays. They were 1.2 for Mt and MtH, indicating that acidic treatment did not change the interlayer distance. For MtZr and MtAl, $d_{0\,0\,1}$ was 2.0 and 1.8, respectively, and for ZMtZrG, MtAlG and MtAlGCu 1.8 or 1.9 nm. K5Al, K5AlG and K5AlGCu showed $d_{0\,0\,1}$ of 1.6 nm. Thus, the introduction of polymer, its carbonization and the promotion with copper do not influence the structure of the pillared clays.

Specific surface areas were measured for the starting montmorillonites Mt and K5 (40 and 164 m^2/g, respectively), for supports MtH, MtZr, MtAl and K5 Al (160, 114, 204 and 128 m^2/g, respectively), as well as for catalysts promoted with polymer and copper: MtHGCu, MtZrGCu, MtAlGCu and K5AlGCu (81, 53, 22 and 98 m^2/g, respectively).

Acidic clay K5 and acid-pretreated clay MtH have higher surface areas than untreated montmorillonites, in agreement with previous observations. The increase in specific surface area caused by acidic treatment may arise from a partial delamination caused by a partial destruction of clay layers caused by the washing out of Al-oxides and the formation of silica insoluble in HCl solution. The total delamination of clay structure was observed by Mahboub et al. [36] and proven by the disappearance of XRD peaks (the sample became totally XRD amorphous) as well as sorption studies. On the other hand, Temuujin et al. [37] showed that the extent of the destruction of clay layers depended on the duration of acidic treatment. For shorter treatment times, the position of XRD 0 0 1 reflex did not change but S_{BET} increased. It was concluded that there was only partial destruction of clay layers.

Pillaring increased S_{BET} for MtZr and MtAl in comparison to Mt, in good agreement with previous observations. For K5Al no such effect was observed which is rather difficult to explain. The sample was pillared which is proven by the change in $d_{0\,0\,1}$ distance from 1.3 nm for K5 to 1.6 nm for K5Al. Possibly the rearranged structure is only partly accessible to nitrogen molecules.

No measurements were carried out for the samples promoted with polymer and carbonized (before copper introduction), because the systems prepared similarly as in this work were already thoroughly discussed in literature [33,34]. It was shown that carbon deposits of nanometer or sub-nanometer size were introduced into the porous structure, partly restricting it and resulting in the decrease of S_{BET}. The total effect depended both on the starting montmorillonite (acidic or not) and the type of pillars. For non-modified starting clays carbon deposits were found to be bigger and penetrated the system to a smaller extent than for acidic clays. When zirconia pillars were present more carbon was deposited on the outer surface of montmorillonite particles than in case of alumina-pillared systems [35].

The end effect of modification with polymer and copper was a considerable decrease in specific surface area. The highest (%) decrease was in case when non-acidic clay pillared with alumina was used and the smallest for acidic pillared clay K5Al.

Binding energies BE of Al 2p, O1s and Cu $2p_{3/2}$ and surface composition as atomic ratios of Al/Si, O/Si and Cu/Si are summarized in Table 1. BE registered for Al 2p and O 1s are typical for clays. Binding energy of Cu $2p_{3/2}$ is between 935.1 for MtZrGCu and 936.1 for MtAlGCu. Cu$2p_{3/2}$ peaks are for all samples accompanied by an extensive satellite which indicates that copper is present as Cu^{2+}. Farquhar et al. [38] studied copper sorption from $Cu(NO_3)_2$ + $NaNO_3$ aqueous solution on a model clay mineral (muscovite mica) and found Cu $2p_{3/2}$ at 934.7 eV. By comparison comparison with XPS spectra of $Cu(NO_3)_2$, CuO

Table 1
Binding energies and surface composition of the studied catalysts

Samples	MtZrG	MtZrGCu	MtAlCu	MtAlG	MtAlGCu	K5AlCu	K5AlG	K5AlGCu
Binding energy (eV)								
Al 2p	75.5	75.0	75.0	75.1	75.0	75.02	75.1	75.0
O 1s	532.4	532.1	532.6	532.4	532.4	532.4	532.5	532.4
Cu $2p_{2/3}$	–	935.1	936.1	–	936.1	935.7	–	935.8
Composition (at%/at%)								
Al/Si	0.48	0.405	0.419	0.579	0.405	0.365	0.636	0.422
O/Si	3.31	3.064	3.33	2.78	3.06	2.89	2.92	2.99
Cu/Si	–	0.066	0.113	–	0.083	0.048	–	0.1

and $Cu(OH)_2$ at BE of respectively 935.1, 933.1 and 934.1 eV, it was concluded that copper state was between CuO and $Cu(OH)_2$. However, the content deposited in this case on the surface was very low. On the other hand, Choung and Nam [39] studied Cu deposited on mordenite and stated that Cu(II) would be expected within 934.41–934.95 eV with satellite around 943.6 eV, while Cu(I) could be anticipated at 932.78 eV.

The binding energy of Cu $2p_{3/2}$ for MtZrGCu coincides with that of copper nitrate as given by Farquhar et al. [38]. This is in good agreement with the presence of nitrogen oxides which were observed on-line during calcination. They are formed by decomposition of $Cu(NO_3)_2$ to $Cu(OH)_2$. However, the position of the Cu $2p_{3/2}$ peak for other samples lies between 936.1 and 935.1 eV. The differences in BE may arise from the so-called double charging which is often observed for fairly heterogenous samples, especially containing bigger aggregates of non-conducting active material on non-conducting support. Thus, the observed differences in binding energies may suggest bigger aggregates.

The comparison of composition allows the following conclusions:

- Al/Si is: MtZrGCu<MtZrG; MtAlGCu < MtAlG; K5AlGCu < K5AlG. Taking into account that XPS probes only 2–20 monolayers, it seems to suggest that copper is placed 'on-top' but rather Al-rich part are chosen than Si-rich. This is perhaps not quite suprising, taking into account that Al-OH groups form Brønsted acidic sites on montmorillonites.
- Cu/Si ratios are between 0.05 and 0.11 and there is no clear tendency, due to very different preparation conditions used.

Fig. 1 compares NO conversion and N_2O formation for montmorillonites pillared with alumina or zirconia promoted with copper, polymer, or polymer and copper, while Fig. 2 compares catalysts based on montmorillonites with higher acidity, MtH with acidity increased by pretreatment with HCl and commercial acidic clay K5.

From catalytic experiments it may be concluded that:

(i) For zirconia or alumina pillared Mt montmorillonite, the introduction of carbon species leads to small changes in NO conversion (cp. MtAl versus MtAlG and MtZr versus MtZrG), at lower temperatures. For Al-pillared samples (MtAl and MtAlG) NO conversion is slightly inferior for carbon-doped supports. Carbon-promoted Zr-pillared montmorillonite (MtZrG) shows NO conversion within experimental error the same as for non-promoted one at lower temperature. On the other hand, at the highest studied temperature (623 K) MtZrG is more efficient than MtZr. For acidic catalysts MtH and K5 NO conversion is higher for samples modified with polymer than for non-modified ones. The possible reason of the different behavior of Mt, MtH and K5 sample undoped or doped with carbon may be the different distribution of carbon deposits, as well as some restrictions in texture caused by carbon introduction. It was shown before that both these parameters are influenced by the type of pillars—in case of zirconia pillars most carbon was deposited on the outer surface of support grains [35] while for alumina pillared clays carbon deposits entered micropores, partially blocking or narrowing them [39]. Taking into account, as found by Grzybek et al. [34], that acidic surface groups are anchoring places for the introduced polymer, the modification of K5Al and MtH, which are more acidic than Mt, should result in more even carbon distribution and thus less restricted systems.

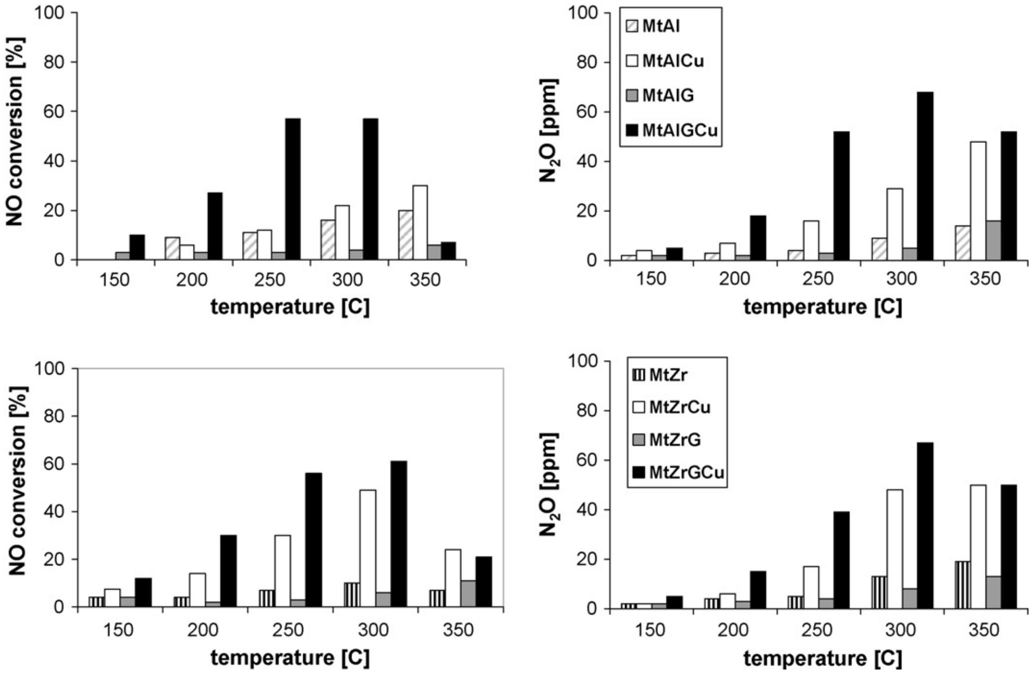


Fig. 1. NO conversion and N_2O formation for montmorillonites pillared with alumina or zirconia promoted with copper, polymer or polymer.

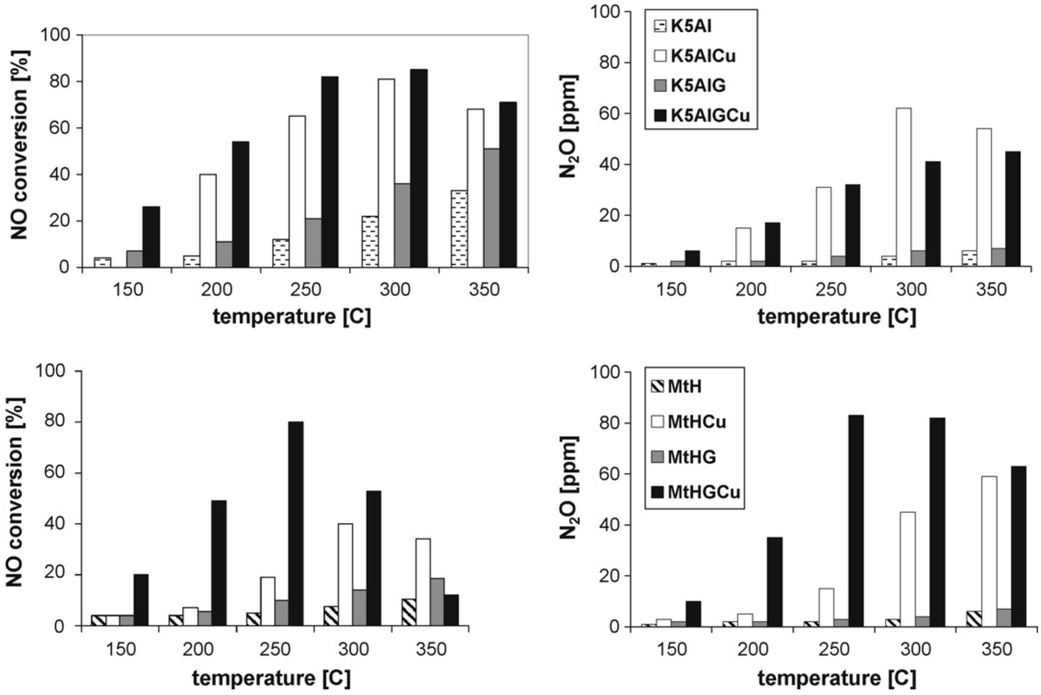


Fig. 2. NO conversion and N_2O formation for catalysts based on montmorillonites with different acidity.

(ii) N_2O is not formed on supports either promoted with carbon or unpromoted. The registered values are between 5 and 20 ppm i.e. they lie within experimental error.

(iii) The addition of copper increased NO conversion. The extent of the improvement depended on temperature, as well as on the preparation conditions.

In all cases conversion went through a maximum as a function of temperature. At higher experimental temperatures (623 K, and in case of MtHGCu at 573 K) conversions decreased. The literature studies indicate that the main reason is the increased oxidation of ammonia which starts prevailing over NO reduction.

At temperatures from 423 to 573 K the highest conversions for a series based on a certain type of a support (MtAl, MtZr, MtH, K5Al) were in all cases obtained for the samples modified both *with polymer and copper species*. The comparison with catalysts non-modified with polymer indicates *the positive role of this preparative step*. Let us compare NO conversion at 523 K for sample with or without modification with polymer. For polymer-treated samples the gain in conversion was 17% (MtHGCu versus MtHCu) to 61% (K5AlGCu versus K5AlCu). Carbon may play a certain role as a reductant but its major role may be excluded. It is obvious from the comparison of the samples with and without polymer treatment and without the addition of copper-MtAl versus MtAlG, MtZr versus MtZrG, MtH versus MtHG, and K5Al versus K5AlG, as well as the appropriate samples containing copper. The relative gain in NO conversion is higher or much higher for GCu than G series when compared to MtAl, MtZr, MtH or K5Al. Thus, it may be assumed that polymer influences the structure of the introduced copper aggregates. More experimental data are, however, necessary to clarify this point.

The introduction of copper leads to the increase in N_2O formation, thus copper oxides are the source of additional N_2O. The increase is, however, not very high and strongly dependent on the preparation procedure. The best selectivity to N_2 was observed for K5-series. The effect may be partly related to acidity. However, some other effects may also influence N_2O production. It is demontrated by two acidic montmorillonite-based samples (MtHCu and K5AlCu) which show different amounts of N_2O in the products. On the other hand, for MtZrGCu or MtAlGCu catalysts, which differ in the type of pillars, the N_2O formation is similar (within experimental error ca. 20 ppm) when compared with appropriate samples without polymer treatment.

On the whole it may be concluded that treatment with polymer, carbonization and the introduction of copper oxides improves activity and does not decrease selectivity.

5. Conclusions

Clays modified with polymer and promoted with copper oxides were studied. Several elements of preparation were tested: pretreatment (acidic), pillaring, modification with polymer (followed by carbonization) and the promotion with copper oxides/hydroxides. The following elements of preparation influenced positively NO conversion in SCR: acidic pretreatment and modification with polymer before impregnation with copper. For appropriate clays the sequences in NO conversion were:

- Mt: MtHGCu > MtAlGCu > MtAlCu and MtZrGCu > MtZrCu;
- K5: K5AlGCu > K5AlCu.

Selectivity to N_2 was either similar for polymer and copper-modified catalysts or was improved in comparison to those untreated with polymer.

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