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Selective catalytic reduction of NO with ammonia over porous clay heterostructures modified with copper and iron species

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Abstract

Porous clay heterostructures (PCH), obtained on the basis of synthetic saponite, were modified with copper and iron ions by an ion-exchange method and tested as catalysts for the selective reduction of NO with ammonia (NH_3-SCR). Transition metal ions were introduced into H^+ and NH_4^+ forms of PCH. The catalysts were characterized with respect to their texture (BET), composition (EPMA), coordination of transition metals (UV–vis-DRS) and surface acidity (FT-IR, NH_3-TPD). The PCH-based catalysts have been found to be active, selective and stable in the NH_3-SCR process. The Cu-containing catalysts effectively operated at temperatures significantly lower than the Fe-modified samples. The catalyst obtained by exchanging copper ions in the ammonium form of PCH was considerably more active compared to the sample obtained from H^+-PCH.

Keywords: $DeNO_x$; Ammonia; UV–vis-DRS; NH_3-TPD; PCH-NH_3

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1. Introduction

Cationic layered clays are very interesting materials for catalysts and adsorption. Clays may be modified by an introduction of metal oxide pillars between the layers to obtain microporous materials. A large number of metal oxides such as Al_2O_3, TiO_2, and ZrO_2, have been successfully incorporated into different types of smectites (e.g. [1,2]). Pillared clays modified with transition metals have been found to be active and selective catalysts of the NO reduction with ammonia (e.g. [3,4]). Unfortunately, the structure of pillared smectites is not stable at temperatures higher than 500 °C, and therefore an overheating of such catalysts may result in a partial destruction of their pillared structure. In 1995 Galarneau et al. [5] proposed a different way to obtain thermally stable porous materials from cationic layered clays. The synthesis of such material consists of the following steps: (i) cationic templates and neutral amine co-templates are intercalated in the interlayer space of host clay forming micelle structures; (ii) the silica pillars are created by in situ polymerization of a silica source around the micelle structures; (iii) the organic templates are removed from the material by a classical calcination, producing materials with a high surface area and combined micro- and mesoporous structure. This new class of materials is called porous clay heterostructures (PCH). The negative charge of the clay layers is compensated by protons formed during the decomposition of the organic templates. Protons can migrate into unoccupied position in the clay layers (octahedral vacancies in dioctahedral clays or defects in trioctahedral clays) and in consequence reduce a CEC potential of the PCH. This effect can be limited by exchanging the protons for NH_4^+ cations, which are too large to migrate into the clay layers.

2. Experimental

Synthetic saponite (Kunimine Industries Co.) characterized by the chemical formula of $(Na_{0.49}Mg_{0.14})^{+0.77}$ $[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})(OH)_4O_{20}]^{-0.77}$ was used as the starting material for preparing the PCH. Three grams of clay were added to 50 ml of a solution of the surfactant (hexadecyltrimethylammonium chloride) and stirred at 50 °C for 24 h. After the exchange reaction, the intercalated clay was separated from the solution and washed with demineralised water until pH of 7 was reached. Subsequently, the modified clay was added to a neutral

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amine (dodecylamine) and a silica source (tetraethylorthosilicate). The mixture was allowed to react for 4 h under continuous stirring at ambient temperature. Then, the modified saponite was separated from the solution, dried at room temperature and calcined at 550 °C for 6 h. A part of the PCH was treated with ammonia to obtain the NH_4^+ form of the material. The modification of PCH was performed in a flow reactor at temperature 200 °C using a gas mixture containing 1 vol.% of NH_3 diluted in He. A detailed description of the procedure used for the PCH synthesis as well as the ammonia treatment was presented in our pervious papers [6,7].

Transition metal ions ($Cu^{2+}$and Fe^{3+}) were introduced into the PCH and PCH-NH_3 supports by an ion-exchange method using aqueous solutions (0.02 M) of $Cu(NO_3)_2 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$. The modified samples were dried at room temperature and afterwards calcined in air at 450 °C for 3 h.

Textural parameters of the samples were determined by N_2 sorptions at −196 °C using a Quantachrome Autosorb-1-MP automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 200 °C for 16 h. The surface area was determined using the BET equation, while the micropore volumes of the samples were calculated using the *t*-method of DeBoer.

Transition metal loadings were determined by electron microprobe analysis performed on a JEOL JCXA 733 superprobe (electron probe microanalysis, EPMA).

The UV–vis-DRS spectra of the samples were recorded on a Nicolet Evolution 500 spectrophotometer. The measurements have been performed in the range of 200–900 nm with a resolution of 2 nm for the samples (2 wt.%) diluted in KBr.

The total surface concentration of acid sites was determined by a temperature programmed desorption of ammonia (NH_3-TPD). The measurements were carried out in a flow microreactor system equipped with a QMS detector (VG QUARTZ). Sorption of ammonia was performed for the outgassed sample at 70 °C in a flow of a gas mixture containing 1 vol.% of NH_3 in helium. Then, the catalyst was purged in a helium flow until a constant baseline level was attained. Desorption was carried out with a linear heating rate (10 °C/min) in a flow of pure helium (20 ml/min).

The nature of the surface acid sites was studied by FT-IR measurements of the samples preadsorbed with pyridine. Transmission IR spectra were recorded using wafers in the form of self-supporting pellets of the catalyst powder. The pellet was placed in a IR cell equipped with KBr windows properly designed to carry out spectroscopic measurements at different temperatures. The cell was connected to a vacuum line allowing all thermal treatments and adsorption–desorption experiments to be carried out in situ. Prior to pyridine adsorption, the sample was outgassed overnight at 200 °C under vacuum. Then the cell was cooled to room temperature and the catalyst was allowed to react with pyridine for 1 h. FT-IR spectra were recorded on a Nicolet 20SXB spectrometer at different desorption temperatures. Two hundred scans were taken with a resolution of 4 cm^{-1}.

The modified PCH samples were studied as catalysts of the selective catalytic reduction of NO with ammonia (NH_3-SCR). The catalytic experiments were performed in a fixed-bed flow reactor. The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG QUARTZ) connected directly to the reactor outlet. Prior to the reaction, each sample (100 mg) was outgassed in a flow of pure helium at 450 °C for 30 min. The following composition of the gas mixture was used: $[NO] = [NH_3] = 0.25\%$, $[O_2] = 2.5\%$. Helium was used as a balancing gas at a total flow rate of 40 ml/min. The intensity of the mass lines corresponding to all reactants and products were measured at a given temperature at least for 30 min after the reaction had reached a steady state. The sensitivity factors of analysed lines were calibrated using commercial mixtures of gases.

The influence of H_2O on the course of the NH_3-SCR reaction was studied by a periodical addition of water vapor into the reaction mixture. In the gas supplying system there were two separated helium lines, first with pure helium and second with He constantly flowing through the saturator kept at 0 °C. Water vapor concentration in the reaction mixture was measured as 0.30 vol.%. The helium (used as a balance gas) was switched by means of a four-port valve from dry to wet in intervals of 30 min. All the gas lines were heated in order to prevent condensation of water.

The influence of SO_2 on the performance of the catalysts were studied by their treatment (60 min) in the flow (20 ml/min) of gas mixture containing 0.2 vol.% of SO_2 in helium and subsequent catalytic test at constant temperature (400 °C). The results of catalytic measurements performed over the SO_2-treated catalyst were compared with those obtained for the fresh sample.

3. Results and discussion

Table 1 summarises the texture parameters of the PCH samples, transition metal loadings and surface concentration of

Table 1
Texture parameters, transition metal loading and surface acidity of PCH-based samples

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{micro}/V_{tot}	Transition metal content (wt.%)	Concentration of acid sites (μmol/m^2)
PCH	903	0.743	0.602	0.81	–	0.022
PCH-NH_3	855	0.717	0.581	0.81	–	–
PCH-Cu	832	0.696	0.563	0.81	0.59 (Cu)	0.047
PCH-NH_3-Cu	800	0.675	0.539	0.80	1.43 (Cu)	0.137
PCH-Fe	840	0.702	0.560	0.80	1.43 (Fe)	0.053
PCH-NH_3-Fe	783	0.679	0.527	0.78	1.41 (Fe)	0.049

acid sites determined by the NH_3-TPD measurements. It was assumed that one ammonia molecule reacts with one acid centre. The parent PCH material was characterized by a very high surface area, which exceeded 900 m^2/g, and a combined micro- and mesoporosity. The treatment of PCH with ammonia as well as an introduction of transition metal ions has no significant influence on its textural parameters. It should be noticed that significantly higher amount of copper ions were introduced to the ammonia modified support (PCH-NH_3) compared to parent PCH. This behaviour was not present in the Fe-containing samples. Furthermore, the introduction of transition metal ions into the PCH materials increased the concentration of acid sites.

The chemical nature of the transition metal containing PCH materials was studied by UV–vis-DR spectroscopy. Fig. 1A shows the results obtained for the Cu-containing catalysts. The spectra consist of three maxima centered at about 260, 360 and 520 nm. The first peak is attributed to charge-transfer between mononuclear Cu^{2+} ion and oxygen. The maximum at about 360 nm can be ascribed to charge-transfer between Cu^{2+} and oxygen in oligonuclear $[Cu–O–Cu]_n$ species [8], while the peak at about 520 nm can be related to the d–d transition of Cu with an octahedral environment in CuO [8]. The difference in the intensity of the spectra recorded for the PCH-Cu and PCH-NH_3-Cu is caused by differences in the transition metal loading. The distribution of copper among these species was determined on the basis of the areas of the deconvoluted peaks. For the PCH-Cu sample, about 20% of copper is present in the form of

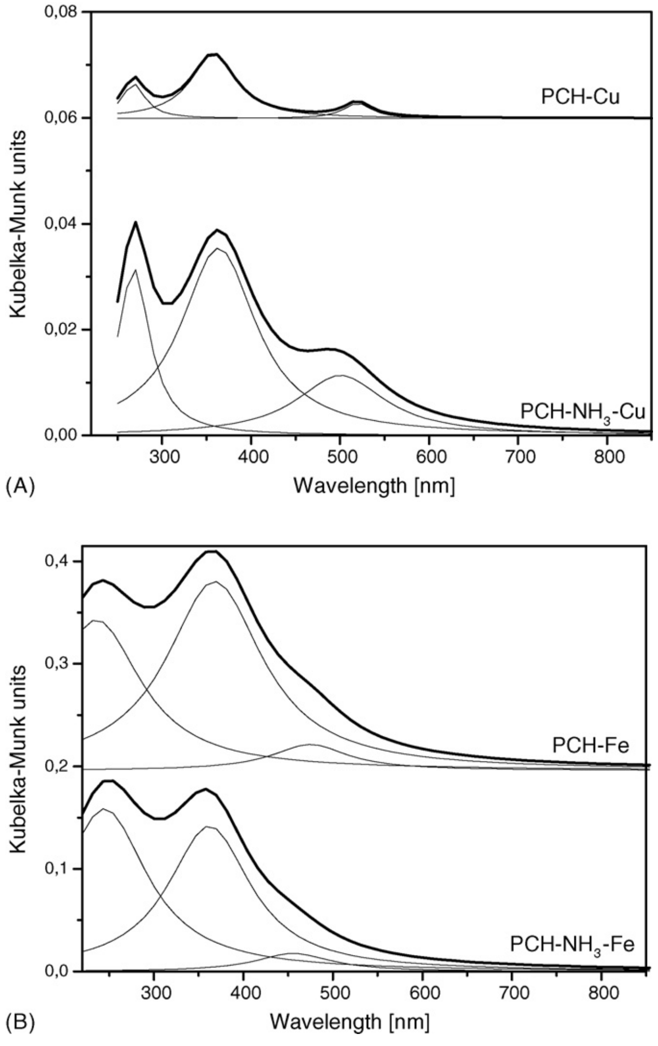

Fig. 1. UV–vis-DR spectra of the PCH-based catalysts.

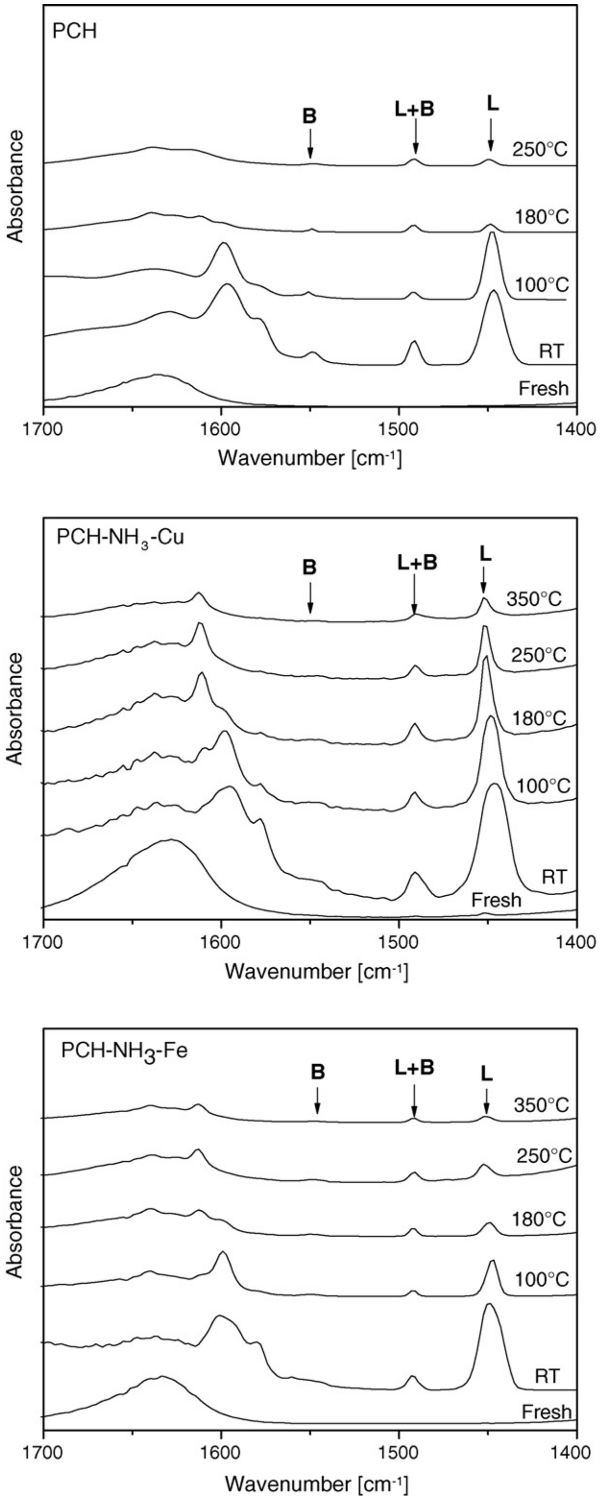

Fig. 2. FT-IR spectra of the PCH-based catalysts preadsorbed with pyridine. L and B bands related to the presence of Lewis and Brönsted acid sites.

separated Cu^{2+} cations, 70% in oligomeric $[Cu–O–Cu]_n$ species and 10% in bulky CuO clusters. A slightly different distribution of copper species was found for PCH-NH_3-Cu. 22% of copper is present in the form of isolated Cu^{2+} cations, 57% in oligomeric $[Cu–O–Cu]_n$ species and 21% in bulky CuO clusters.

Three UV–vis-DR bands can be distinguished for the Fe-modified samples (Fig. 1B). The peak, centred at about 240 nm is related to isolated Fe^{3+} cations, while the band, at about 360 nm corresponds to oligonuclear $(FeO)_n$ species [9]. The small peak at 460–480 nm can be assigned to symmetrical and spin forbidden d–d transitions of Fe^{3+} [10]. The distribution of iron among these species is very similar for the both Fe-containing catalysts. In the case of PCH-Fe, about 58% of iron is present in the form of isolated Fe^{3+} cations and 42% in oligonuclear $(FeO)_n$ species, while for the PCH-NH_3-Fe sample the distribution of Fe among these species is 54% and 46%, respectively.

The nature of acid sites was studied by pyridine adsorption. Fig. 2 presents the FT-IR spectra in the region of 1400–1700 cm^{-1} after the adsorption of the probe molecule on the PCH-based catalysts. The spectra recorded for the samples after the sorption of pyridine at room temperature (RT) contain three well resolved maxima at about 1545, 1490 and 1450 cm^{-1} related to the chemisorbed forms of pyridine. The bands at 1545 and 1450 cm^{-1} are assigned to pyridine adsorbed on the Brönsted and Lewis acid sites, respectively. The peak at 1490 cm^{-1} is attributed to the adsorbed pyridine species on both Brönsted and Lewis acid centres. The Brönsted acidity is related to the protons compensating negative charge of saponite layers. The protons were formed during thermal decomposition of the surfactant cations. The Lewis acid sites exist in PCH, due to the presence of aluminium in the tetrahedral sheet of saponite clay (host clay of PCH). It should be noticed that the intensity of the bands assigned to the presence of Brönsted and Lewis acid centres decreases with an increase in desorption temperature. The modification of the PCH with transition metal ions causes an increase in the Lewis acid sites and a decrease in the Brönsted acid sites. This effect can be related to the electron acceptors behaviour of the transition metal cations which give rise to additional Lewis acid centres. The reduction in Brönsted acid sites is reasonable as these sites are replaced by transition metal cations. It should be noticed that the transition metal containing samples are characterized by significantly stronger Lewis acid centres than the pure PCH support. Therefore, it could be concluded that pyridine is more strongly bonded to transition metals, especially copper, compared to aluminium in the tetrahedral sheet of the saponite clay.

The modified PCH samples were tested as catalysts for the selective reduction of NO with ammonia (NH_3-SCR). N_2 and N_2O were the only detected N-containing products in the NH_3-SCR process. Fig. 3 presents the results of the catalytic studies. For PCH-NH_3-Cu, the maximum of the NO conversion (92%) was reached at temperature around 330 °C. The PCH-Cu catalyst was found to be less active in the low temperature region, however at higher temperatures ($T > 370$ °C) its catalytic performance is very similar to that presented by PCH-NH_3-Cu. The significant differences in activity of these catalysts are probably related to loading and distribution of copper species. It should be noticed that PCH-NH_3-Cu contains

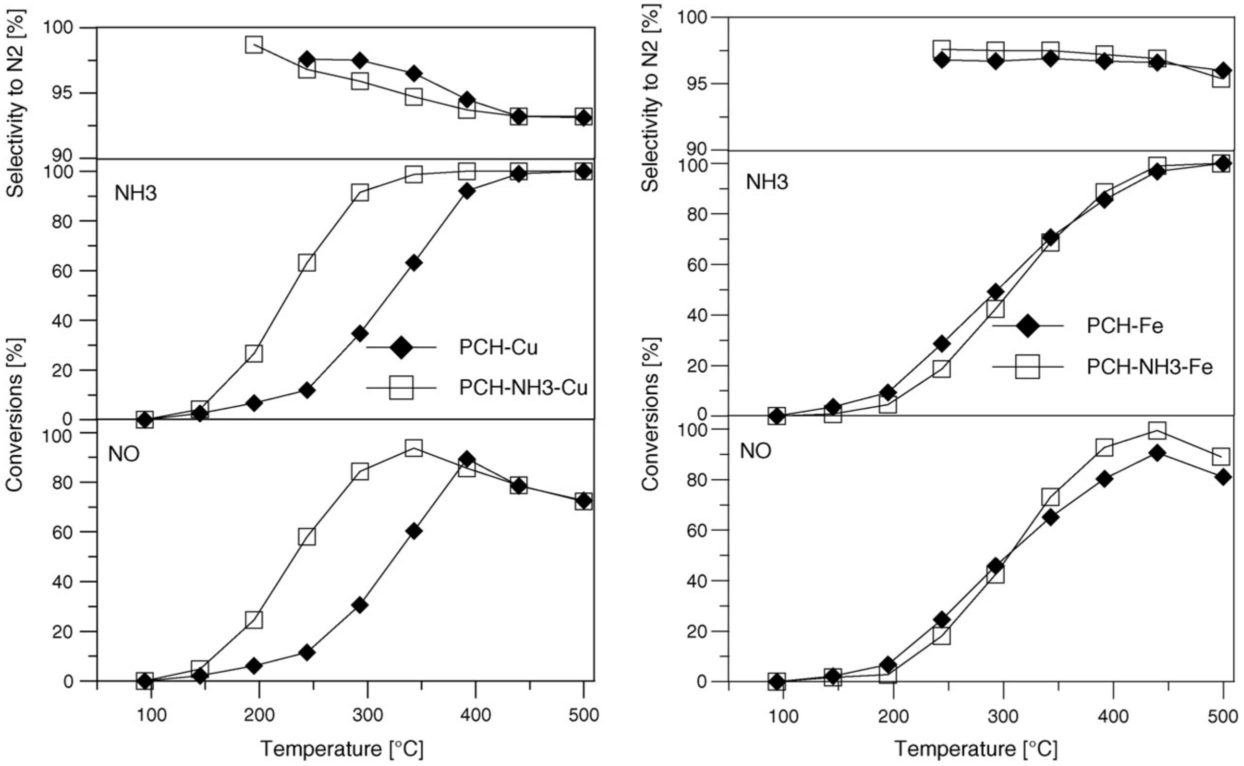

Fig. 3. Results of the activity tests for the PCH-based catalysts in the NH_3-SCR process.

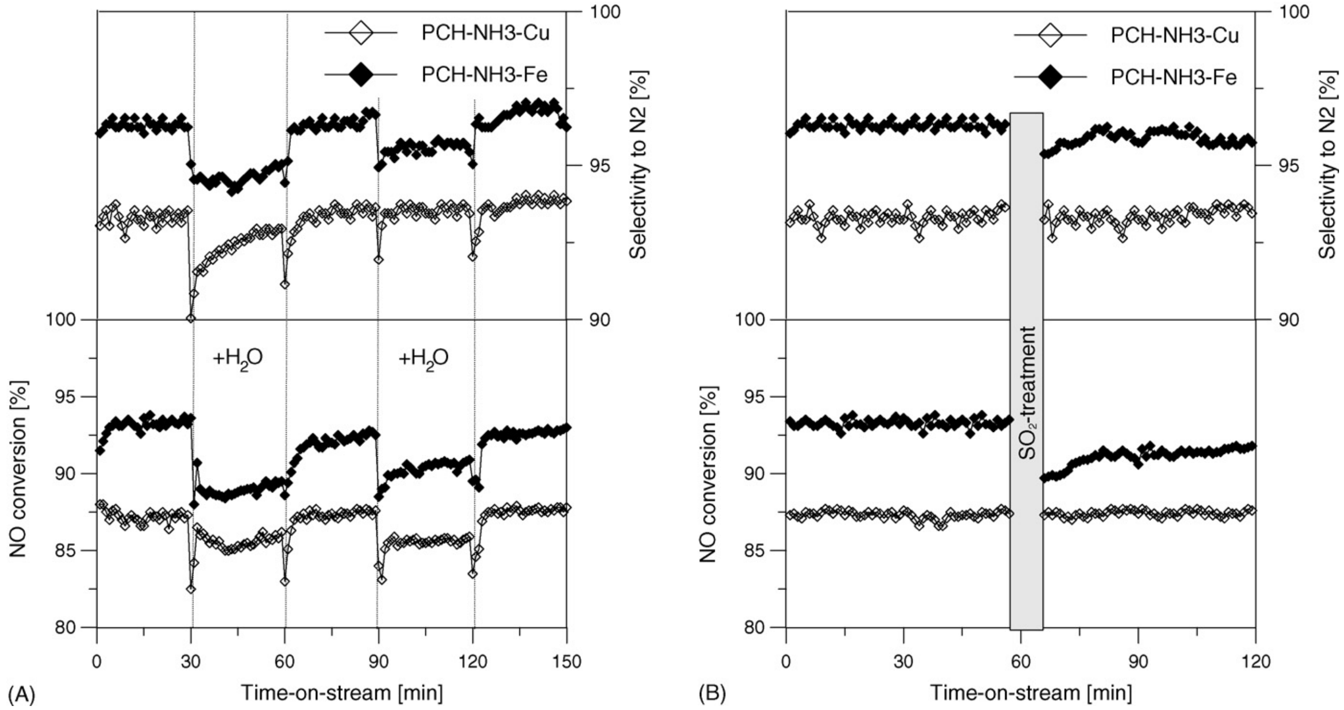

Fig. 4. Study of the influence of H_2O and SO_2 on the catalytic performance of PCHs modified with copper and iron.

about five times more copper in the form of bulky CuO clusters comparing to PCH-Cu. Such species are more easily reduced that isolated Cu^{2+} ions and [Cu–O–Cu] oligomers [11,12]. Therefore, it could be suggested that bulky CuO clusters are responsible for the activity in the low temperature range. A decrease in the NO conversion observed in the high temperature range is caused by the oxidation of ammonia by oxygen. The Fe-containing catalysts effectively operated at temperatures significantly higher than PCHs modified with copper. The NO conversions as well as the selectivities towards N_2 obtained for both Fe-modified PCHs are very similar, however PCH-Fe is slightly more active in the low temperature region ($T < 310$ °C), while the PCH-NH_3-Fe catalyst is more effective at higher temperatures.

The influence of water vapor on the catalytic performance of PCH-NH_3-Cu and PCH-NH_3-Fe was studied by periodical catalytic tests with dry and wet reaction mixture (Fig. 4A). After the exchange from dry to wet reaction mixture, the NO conversion measured over the PCH-NH_3-Cu and PCH-NH_3-Fe catalysts decreased by about 2% and 3.5%, respectively. However, it should be noticed that for both the catalysts the exchange from wet to dry reaction mixture resulted in obtaining previous levels of the NO conversions. An introduction of water vapor into the reaction mixture caused slight decrease in the selectivity towards nitrogen. However, this effect was fully reversible and after exchange from wet to dry reaction mixture, the selectivity to N_2 increased to the previous level. Therefore, it could be conclude that the PCH-based catalyst are resistant for H_2O poisoning.

Fig. 4B presents results of the studies of SO_2 influence on the performance of the catalyst. After 60 min of the catalytic test performed at 400 °C, a flow of the reaction mixture was exchanged for a flow of SO_2 (0.2 vol.%) diluted in helium. The treatment with SO_2 was performed at 400 °C for 60 min. Then, a flow of the SO_2-containing mixture was exchanged for a flow of reaction mixture. The catalytic test was performed at 400 °C for additional 60 min. After treatment the PCH-NH_3-Fe catalyst with SO_2, the NO conversion decreased only by 1.5%, while selectivity to N_2 decreased by about 1%. Any deactivation effect of SO_2 was detected for the PCH-NH_3-Cu sample.

4. Conclusions

Porous clay heterostructure (PCH) material, obtained by a surfactant-directed assembly of silica species in the interlayer space of synthetic saponite, is characterized by a high surface area and a combined micro- and mesoporous structure. The classical ion-exchange method, used for the introduction of transition metals, resulted in higher amounts of copper in the ammonium form of PCH compared to protonic form. This effect was not observed for the Fe-containing samples. Transition metals in the PCH materials were present in various forms. In the copper-containing catalysts, isolated Cu^{2+} cations and oligonuclear [Cu–O–Cu] species dominated, while bulky CuO clusters were present in a significantly lower quantity. For the Fe-containing samples, transition metal was found in the form of isolated Fe^{3+} cations and oligonuclear $(FeO)_n$ species. The distribution of transition metals in these species is different for the ammonia treated and non-treated PCH materials. Lewis and Brönsted acid sites were found in the parent PCH support. Lewis acid sites are related to the presence of aluminium in the tetrahedral sheets of saponite clay, while Brönsted acid sites are related to the protons compensating negative charge of saponite layers. An introduction of transition metals generated additional strong Lewis centres and reduced the Brönsted acidity.

The catalysts based on the PCH support have been found to be active, selective and stable in the NH_3-SCR process. The Cu-containing catalysts are more effective at lower temperatures than PCHs modified with iron. The Cu-containing catalyst obtained from the ammonium form of PCH was significantly more active compared to the sample prepared by the modification of the protonic form. At higher temperatures the NO conversion decreased due to oxidation of ammonia by oxygen.

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