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Modified bentonite-derived materials as catalysts for selective catalytic reduction of nitrogen oxides

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In the last few years, cationic layered clays, including bentonites have been investigated as potential catalysts for SCR DeNO$_x$ systems. In this work, bentonite as the representative of layered clays was modified in order to obtain an alternative, low-cost NH_3–SCR catalyst. Samples of raw clay were activated with HCl or HNO_3, treated with $C_2H_2O_4$ and subsequently pillared with alumina by the ion-exchange. Afterwards, the modified materials were impregnated with iron and copper. The obtained catalysts were characterized by XRD and FT-IR. SCR catalytic tests carried out over analyzed samples indicated the conversion of NO of approximately 90% for the most active sample. The type of acid used for modification and the type of active phase strongly influenced the catalytic properties of the analyzed materials.

Keywords: pillared bentonite, acid activation, alumina, iron, copper, selective catalytic reduction, NO, DeNO$_x$

1. INTRODUCTION

Nitrogen oxides (NO$_x$) generated by fuel combustion in stationary and mobile sources are ones of the most harmful pollutants of the environment. The currently valid EU directive 2010/75/EU restrictively limits the permitted amount of NO$_x$ emitted with the exhaust gases (Motak, 2008; Regulation (EC) No 595/2009). The most efficient industrial technology applied for nitrogen oxide abatement is selective catalytic reduction (SCR). The process is based on NO$_x$ elimination by the reducing agent (usually ammonia) and their conversion into nitrogen and water vapor. Despite the fact that the industrial catalyst, V_2O_5–TiO_2 promoted with WO_3 or MoO_3 provides high NO conversion, it has some considerable limitations. First of all, the system exhibits satisfactory catalytic properties only in the narrow temperature window (300–400 °C). Therefore, it is applied in the "high-dust" position, where it undergoes deactivation by SO_2 or fly ash very quickly. On the other hand, location of the catalyst at the "tail end" position or downstream of the electrostatic precipitator requires additional heating of the gases and increases the overall costs of the process. The commercial catalyst is also relatively expensive. Moreover, vanadium compounds are harmful for the environment and their utilization is complicated (Motak, 2008; Wierzbicki et al., 2015). In view of the above, novel, effective and low-cost catalysts need to be found in order to improve the activity in the low temperature range (< 250 °C) and the resistance to SO_2 and other poisonous compounds present in flue gases.

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In recent years, many new materials have been intensively studied as the potential SCR catalysts, including supported metal oxides, exchanged zeolites, hydrotalcite-derived materials, modified vermiculites, activated carbons or activated coke (Chmielarz et al., 2010; Li et al., 2018; Rutkowska et al., 2017; Samojeden and Grzybek, 2016; Ziemiański et al., 2017). Other interesting precursors of new NH_3–SCR catalyst are layered cationic clays. It is especially due to their special properties, including high specific surface area, ion-exchange properties and stability in high temperature (Chmielarz et al., 2003; Chmielarz et al., 2004; Grzybek, 2007; Piwowarska et al., 2008). The materials are layered aluminosilicates, widespread in nature. Their building blocks consist of Si(O,OH) tetrahedra and $M(O,OH)_6$ octahedra (where M – Al^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}). The layers are negatively charged and the whole structure is balanced by interlayer cations (e.g. Na^+, Ca^{2+}). The representative example of cationic clays is bentonite, in which the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer takes place. Its main phase is montmorillonite, which is the di-octahedral low charged clay of the smectite group. Additionally, there are some amounts of quartz, cristobalite, pyrite, mica and kaolinite present in the material. The majority of bentonites are developed from weathering of volcanoclastic rocks (Kaufhold et al., 2002). The catalytic potential of these aluminosilicates is caused by the presence of considerable amount of both Brönsted and Lewis acidic centers, which are the external OH^- groups and Al^{3+} ions in the tetrahedral sheet, respectively (Church and McCarthy, 2008; Kaufhold et al., 2002). What is more, it is possible to easily induct redox properties to the materials by the introduction of transition metal cations, e.g. Cu^{2+}, Fe^{2+} or Ag^+ (Chmielarz et al., 2003; Chmielarz et al., 2004; Vaccari, 1998).

Both the surface acidity and the specific surface area of the clay can be greatly enhanced by acid activation. Motak (2008) carried out research over the surface properties of acid activated montmorillonite and its catalytic performance in NH_3–SCR. It was proven that pre-treatment with HCl solution considerably increased the specific surface area of the material. The effect was probably caused by the partial delamination of the clay. Moreover, activated materials subsequently impregnated with copper exhibited increased NO conversion in comparison to the samples non-treated with acid.

Another kind of modification is intercalation (pillaring) of cationic clays. In general, the process is based on the insertion of guest metal oxide species in the interlayer space of the solid, in order to obtain pillared interlayered clays (PILCs). Practically, the material stays in contact with the pillaring solution of bulky inorganic polyoxycations (precursors of the pillars) for a certain amount of time and the precursors are introduced into the interlayer space via ion-exchange. Calcination of the materials results in the formation of three-dimensionally or disordered (delaminated) microporous structure (Grzybek, 2007). The condition of successive pillaring is larger dimension of the introduced cation, in comparison to the original one. What is more, intercalated layered aluminosilicates are confirmed to have considerably larger specific surface area. The influence of pillaring with alumina, titanium oxide and zirconium oxide on the final structure and catalytic activity in NH_3–SCR of montmorillonites was intensively studied over the past few years (Chmielarz et al., 2014; Grzybek, 2007; Ma et al., 1996). XRD analysis carried out for the pillared clays indicated a shift of (0 0 1) reflectance to lower values of 2θ, which means the successful introduction of metal oxide pillars into the interlayer space and increase of the distance between the layers. Additionally, pillaring resulted in the considerable increase of S_{BET}, from 38 $m^2\ g^{-1}$ to even 279 $m^2\ g^{-1}$. Catalytic tests carried out for intercalated materials containing copper or iron as an active phase indicated high level of NO conversion of 95%, especially in the low-temperature range (< 250 °C) and N_2 selectivity over 90% for all the analyzed materials. Alternative class of pillared materials are porous clay heterostructures (PCH) that are prepared by the intercalation of pure silica or silica-containing pillars into the interlayer space using surfactant as the structure-directing agent (Chmielarz et al., 2018). Afterwards, different types of pillars (Si, Al, Ti, Zr) can be introduced into the clay structure. The final materials exhibit high acidity, therefore they are considered as promising catalysts in many processes, for example NH_3–SCR (Chmielarz et al., 2007).

Many kinds of metals have been investigated as active phase in SCR. Noble metals are considered to be very active when hydrocarbons are used as the reducing agent (Burch et al., 2002; Koh et al., 1997;

Ohtsuka and Tabata, 1999; Richter et al., 2004). However, due to their high cost and easy deactivation, transition metals seem to be more efficient and economic (Captain et al., 1998; Smirniotis et al., 2001; Thirupathi and Smirniotis et al., 2001; Zhang et al., 2004). Among d-electronic metals, copper and iron are confirmed to exhibit the highest activity in NH_3–SCR. The catalytic performance can be even increased when zeolites (Chmielarz et al., 2004; Fu, 2014; Koh et al., 1997; Ohtsuka and Tabata, 1999; Richter et al., 2004) or layered clays (Chmielarz et al., 2003; Gil, 2010; Motak, 2008; Vaccari, 1998) are used as the catalyst support.

In view of the above, the subject of this work was to study the influence of the type of acid (HCl or HNO_3) and intercalation with Al_2O_3 pillars on the structural properties of bentonite. Materials were subsequently impregnated with iron and copper and tested as NH_3–SCR catalysts.

2. MATERIALS AND METHODS

2.1. Catalyst preparation

The supports of the catalysts based on bentonite were prepared according to two routes:

(1) bentonite → acid activation with HCl → acid activation with $C_2H_2O_4$ → pillaring with Al–polycations → impregnation with Cu or Fe;

(2) bentonite → acid activation with HNO_3 → acid activation with $C_2H_2O_4$ → pillaring with Al–polycations → impregnation with Cu or Fe.

The samples of bentonite were dispersed in a solution of HCl (0.8 M) or HNO_3 (0.8 M) with the ratio of clay mass to acid solution of 1g/10 cm^3 and stirred at 95 °C for 2 h. The samples were separated by filtration and washed with distilled water. The thermal treatment included drying at 120 °C for 24 h and calcination at 350 °C for 2 h. Subsequently, the next acid activation with organic acid ($C_2H_2O_4$) was performed. Previously activated samples were dispersed in the oxalic acid (0.12 M) and stirred at 80°C for 2 h. Further steps included filtration, washing several times with distilled water and drying for 24 h at 70 °C. The samples were labelled as BentAlHCl or BentAlHNO_3.

Subsequently, acid activated samples were pillared with Al–polycations. The aluminium hydroxy-oligometric solution was prepared by slow addition of 0.4 M NaOH to 0.4 M solution of $AlCl_3$ under constant stirring, until OH/Al ratio of 2.5 was reached. Then, the pillaring solution was left to age in room temperature for about 96 h. In the next step, an appropriate amount of the obtained mixture was added to the suspension containing 1% m/m of activated bentonite in distilled water. The final Al/clay ratio was 12 mmol of Al per 1 g of bentonite. The obtained suspension was left to react for 24 h. Then, modified samples were separated, washed with distilled water to remove chloride ions and dried at 120 °C for 24 h. Finally, the obtained samples were calcined at 350 °C for 12 h.

The next step of the preparation included incipient wetness impregnation with aqueous solution of $Cu(NO_3)_2$ or $Fe(NO_3)_2$. The calculated and predicted amount of active phase was 5% m/m in respect to the mass of the support. The materials were subsequently dried for 24 h at 120 °C and calcined at 350 °C for 2 h.

2.2. Catalyst characterization

The mineralogical compositions of the samples were determined with XRD analysis. The measurement was carried out using PANalytical-Empyrean diffractometer equipped with K_αCu LFF HR (λ = 1.5206 Å) radiation source. The 2θ spectrum of the diffractometer ranged from 5 to 90° with the step size of $0.02°min^{-1}$.

Fourier-transform-infrared spectra (FT-IR) were obtained with a Thermo Nicolet 380 FT-IR spectrometer in the region of 4000–400 cm^{-1}, registered with a resolution of 4 cm^{-1}. In order to carry out the measurement, samples were mixed with KBr at the ratio of 1:100 and pressed into disks.

Catalytic measurement

Catalytic NH_3–SCR tests were performed at atmospheric pressure in a fixed-bed flow reactor containing 0.2 g of the catalysts. The reaction gas mixture contained 800 ppm of NO, 800 ppm of NH_3, 3.5 vol.% of O_2 and balance He with the total flow of 100 cm^3 min^{-1}. The concentrations of NO and N_2O were analyzed using an FT-IR detector (ABB 2000 AO series). During the reaction, the reactor was heated to the appropriate temperature (150–200–250–300–250 °C, 10 °C/min. The temperature inside the reactor was measured with a thermocouple with an electronic temperature controller (Lumel RE19). NO conversion was calculated according to Equation (1):

$$\text{NO}_{\text{conversion}} = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \cdot 100\% \tag{1}$$

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies of modified bentonite

The results of structural studies of the modified bentonites are shown in Figs. 1 and 2. For the XRD pattern of natural bentonite, the reflection observed for $2\theta \sim 7.30°$ arose from (0 0 1) basal spacing, which was calculated for 12.30 Å. The reflections observed at $2\theta \sim 19.5°$ and 61–62° correspond to the diffraction from (1 0 0) layers of montmorillonite phase present in the bentonite structure (Church and McCarthy, 2008). The XRD pattern of samples pre-treated with acid show poorer crystallinity, confirmed by less intense reflections in comparison to the parent clay.

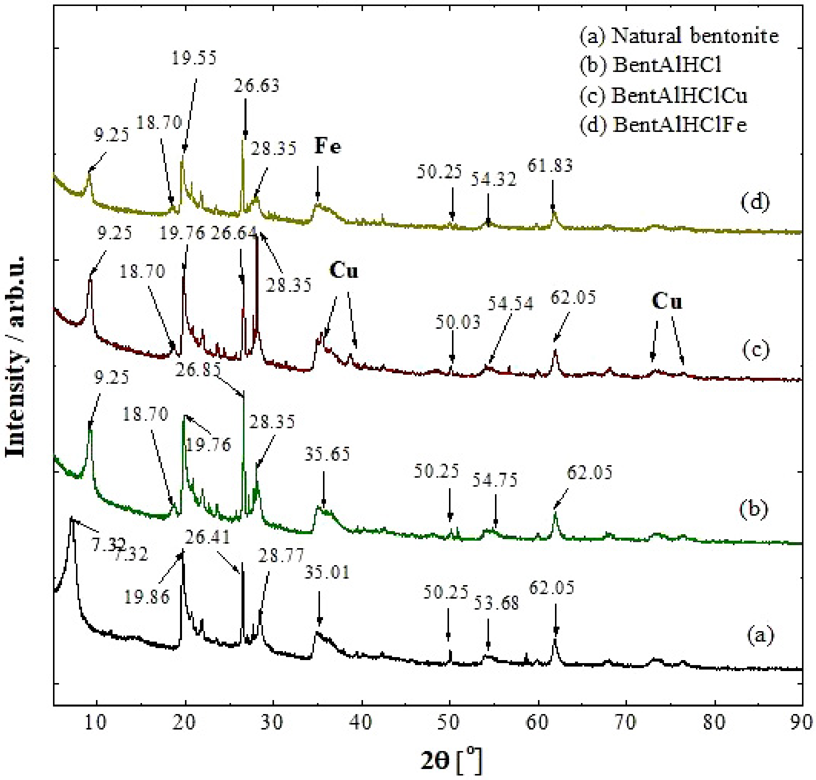

Fig. 1. The XRD patterns of the natural bentonite (a) and bentonite pre-treated with HCl + modified with Al pillars (b) and modified bentonite impregnated with cCu (c) or Fe (d)

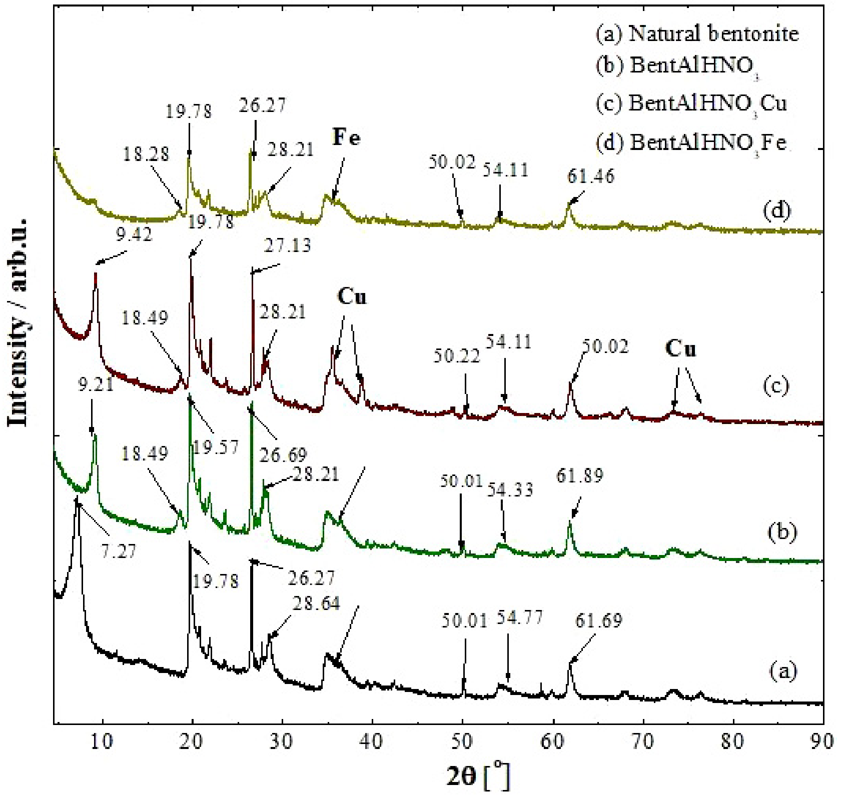

Fig. 2. The XRD patterns of the natural bentonite (a) and bentonite pre-treated with HNO_3+ modified with Al pillars (b) and modified bentonite impregnated with Cu (c) or Fe (d)

This result can be explained by the presence of layers activated with hydrogen ions or the irregular placement of both non-activated and activated layers (Church and McCarthy, 2008). Additionally, regardless to the type of acid used for the activation procedure, the pattern is similar for both samples. The reflections observed at $2\theta \sim 9°$ suggest that some fraction of the clay was not pillared with Al-polycations. However, the small peak at $2\theta \sim 18.70°$ confirms the presence of Al in the interlayer space (Chmielarz et al., 2003). The reflections observed at $2\theta \sim 26.5°$ and 28.5° are caused by the presence of quartz and crystobalite impurities in the clay, respectively (Chmielarz et al., 2004). The presence of Cu or Fe introduced into the modified bentonite via impregnation is confirmed for example by the reflections at $2\theta \sim 35°$, 75° and 35°, respectively (Ahmed et al., 2012). What is more, incorporation of the transition metals did not change the basal spacing of montmorillonite phase present in the samples.

The average particle size of copper oxide and iron oxide incorporated into modified bentonite were calculated with Debye–Scherrer's formula (Eq. (2)).

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} \tag{2}$$

The results of calculations are shown in Table 1.

It is clearly visible that in case of the samples functionalized with copper, bigger crystals were obtained while the clays were modified with HNO_3. Therefore, it can be expected that nitric acid increased the porosity and access to the interlayer space of the sample more than hydrochloric acid. Therefore, bulky and aggregated metal oxides could be successfully deposited in BentAlHNO_3. The samples modified with iron showed the opposite trend – except for FeO, all the oxides exhibited bigger particle size for the clays modified with HCl. The observation suggests that probably iron species were deposited on the external surface of the clay in case of materials modified with HNO_3 and in the interlayer space for those that were treated with HCl.

Table 1. The average particle size of Fe or Cu oxide crystals deposited on the modified bentonite

Sample	Metal oxide	Particle size [nm]
BentAlHClCu	CuO	31.4
	Cu_2O	38.3
BentAlHClFe	FeO	28.6
	Fe_2O_3	46.3
	Fe_3O_4	104.23
BentAlHNO$_3$Cu	CuO	55.8
	Cu_2O	48.4
BentAlHNO$_3$Fe	FeO	38.5
	Fe_2O_3	38.1
	Fe_3O_4	66.0

3.2. FT-IR studies of acid-activated bentonite

FT-IR spectra of natural and acid activated bentonite are presented in Fig. 3. The absorption band observed at 3635 cm^{-1} corresponds to the stretching vibrations of structural OH groups of montmorillonite. Bands present at 929 cm^{-1}, 845 cm^{-1} and 526 cm^{-1} are due to the presence of Al–O–Si bending vibrations, respectively. The band at 1040 cm^{-1} observed for natural bentonite is ascribed to the stretching vibrations of Si–O groups in the in-plane tetrahedral sheets (Kaufhold et al., 2002; Madejová et al., 2003; Madejová et al., 2006; Tyagi et al., 2006). Absorption bands at 642 and 634 cm^{-1} correspond to the coupled Al–O and Si–O out-of-plane vibrations, respectively (Church and McCarthy, 2008). An alternative explanation

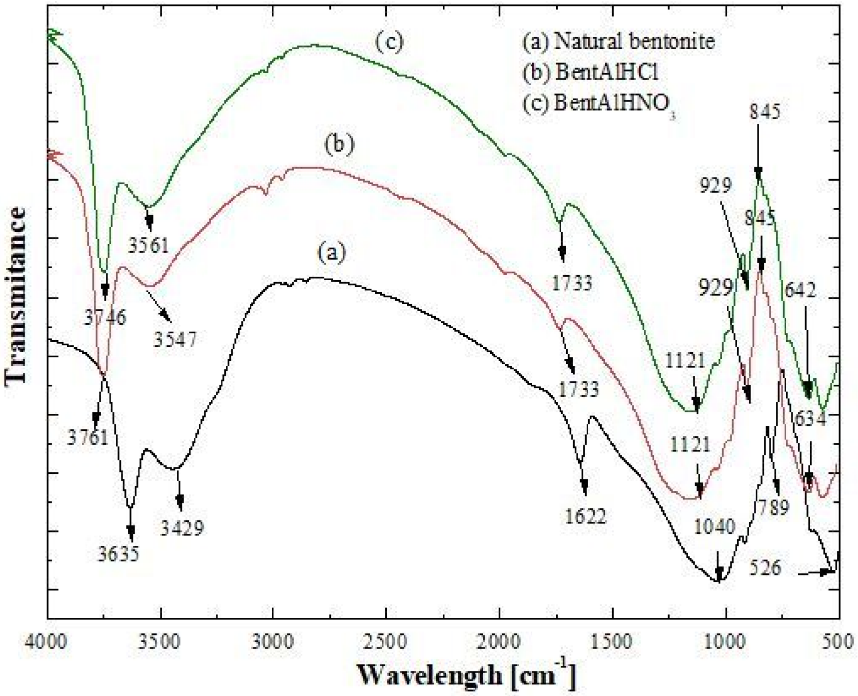

Fig. 3. IR spectra of the natural bentonite (a) and bentonite activated with HCl (b) or HNO_3 (c)

of the presence of these bands is the plane deformation of M–O–Si vibrations, where M = Mg or Al (Santos et al., 2015). Hence, the analysis indicated that montmorillonite is the dominant phase of bentonite which stays with agreement with the XRD measurement. The band at 3429 cm^{-1} observed for natural bentonite is assigned to H_2O that occurs naturally in the material. For acid activated samples, the bands assigned to water molecules are shifted to 3517 cm^{-1} and 3524 cm^{-1}, which suggests the overlapping of asymmetric and symmetric H–O–H stretching vibrations (Church and McCarthy, 2008). Treatment with acid influenced the fundamental vibrations of Si–O and OH groups in comparison to the non-modified samples. For instance, the stretching vibration band characteristic for montmorillonite was shifted up to 3746 cm^{-1}. What is more, a slight shift of the band at 1040 cm^{-1} also indicated differences in the structure in comparison to the parent clay. Lack of the band at 789 cm^{-1} suggest the exit of octahedral cations to the tetrahedral layers (Santos et al., 2015).

3.3. Catalytic tests

Acid treated and Al-pillared bentonites were tested as catalysts of selective catalytic reduction of NO with ammonia (NH_3–SCR). The desired products of these reaction are N_2 and H_2O, while N_2O is the side-product.

Catalytic activity of all the modified bentonites is presented in Fig. 4. The samples activated with HNO_3 exhibited significantly higher catalytic activity in NO reduction than materials treated with HCl, regardless of the type of active phase. Moreover, considering the whole temperature range of the catalytic tests, bentonites that contained Fe showed much better catalytic performance in comparison to the samples with Cu. However, in case of the T_{50}, which is the temperature of 50% conversion of NO, both BentAlHNO$_3$Cu and BentAlHNO$_3$Fe samples showed similar results (about 190 °C). The highest catalytic activity of 90% at about 300 °C was detected for BentAlHNO$_3$Fe. Moreover, the NO conversion did not decrease with the increasing temperature, which means that the reaction reached its equilibrium. It can be assumed that this catalyst has a strong potential to be the substitute of the commercial system based on vanadium oxide that reaches the maximum of NO conversion at about 300–450 °C (Lietti et al., 1999; Peng et al., 2015).

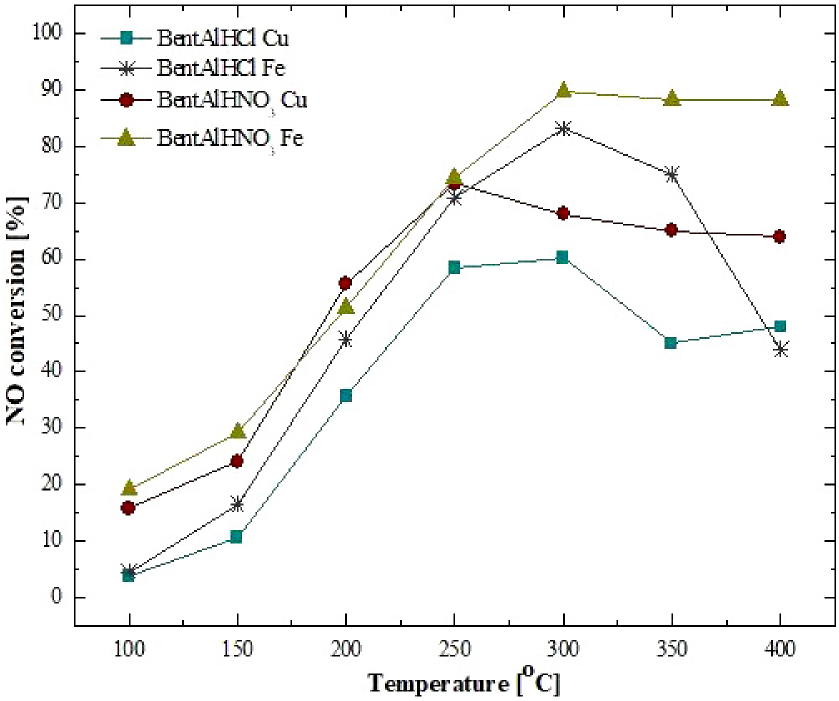

Fig. 4. Catalytic activity comparison of BentAlHCl Cu, BentAlHCl Fe, BentAlHNO3 Cu, BentAlHNO3 Fe samples. Reaction conditions: NO – 800 ppm, NH_3 – 800 ppm, O_2 – 3.5 vol.%, balance He

In case of bentonites, a similar, or even lower temperature range is taken into account. Hence, it is possible that after addition of the promoters that may provide better stability and selectivity to N_2, the commercial catalyst could be replaced by bentonite-based system. What is more, for T_{50} of BentAlHNO$_3$Fe and another commercial zeolite-based catalysts, Cu–SSZ and Cu–SAPO, similar results (about 190 °C) were obtained (Ma et al., 2013).

BentAlHClCu showed relatively poor catalytic activity, exhibiting maximum NO conversion of 42% at 250 °C. The reason of lower catalytic activity of this sample might be weaker interaction of HCl with the support, in comparison to HNO_3. Consequently, the cations present in the octahedral layers of bentonite were not successfully leached on the tetrahedral layers. Thus, it can be assumed that the activation treatment of layered clays is mainly related to the transfer of catalytically active species from octahedral sheets (not available for gas molecules) to easily accessible, external tetrahedral sheets. In case of the samples modified with iron, the results of catalytic tests are in agreement with XRD analysis. When the sample was activated with HNO_3, the obtained crystallites were smaller than in case of materials treated with HCl. According to the literature, SCR reaction is catalyzed mostly by small and well-dispersed metal particles. Consequently, it can be the explanation of higher activity of the materials modified with HNO_3. The opposite results were obtained for bentonite functionalized with copper. However, it is believed that lower activity in NO conversion is caused rather by oxidizing character of copper, especially at the temperature above 300 °C then by the type of acid used for leaching. Therefore, partial oxidation of the reducing agent (NH_3) could result in lower activity of the catalysts, regardless of the modification route of the sample. It was observed that above 250–300 °C the activity of Cu-based catalysts was significantly limited (Jingli et al., 2015; Ma et al., 2013; Song and Jiang, 2012). Moreover, the specific surface area of the samples modified with HCl might have not increased enough to facilitate the access of reacting molecules to the active centers of the catalyst. Nevertheless, to examine the structure and texture of the materials, additional S_{BET} analysis before and after modification of the samples should be carried out.

The concentration of N_2O in the flue gas detected for all catalysts in the temperature range of 100–400 °C is presented in Fig. 5. In case of HCl treated samples, the amount of N_2O was significantly higher than that in the case of bentonites activated with HNO_3. The type of metal introduced as an active phase did

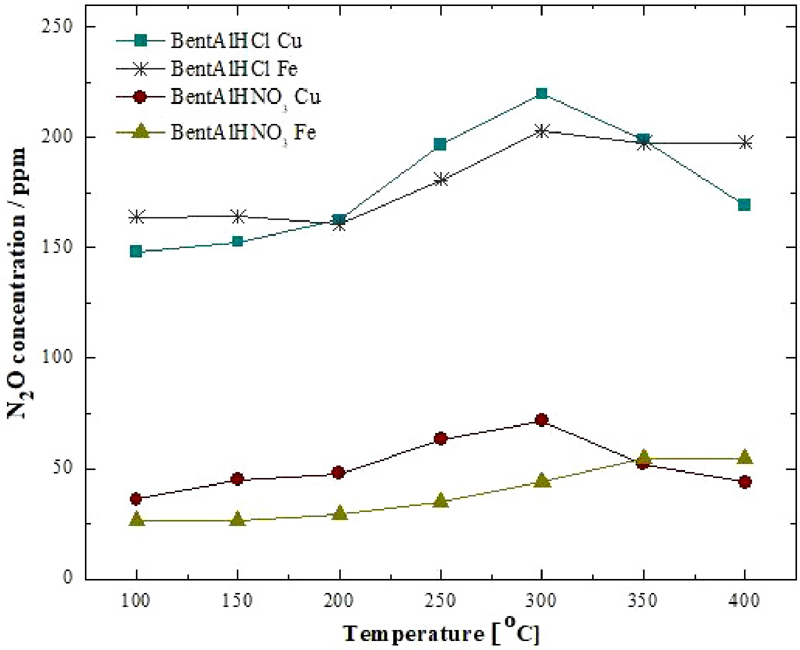

Fig. 5. N_2O concentration in the flue gas detected for BentAlHCl Cu, BentAlHCl Fe, BentAlHNO$_3$ Cu, BentAlHNO$_3$ Fe samples. Reaction conditions: NO – 800 ppm, NH_3 – 800 ppm, O_2 – 3.5 vol.%, balance He

not influence substantially nitrous oxide concentration. However, in the temperature range of 200–350 °C, for both Fe-containing samples, the amount of N_2O was substantially lower. It is possible that for the samples activated with HNO_3 better dispersion of the active phase, resulting in lower N_2O concentration was obtained. Nevertheless, to prove this expectation, additional H_2–TPR studies should be carried out. Generally, the results indicated that both catalytic activity and N_2O concentration were more satisfactory for the materials activated with HNO_3 and containing Fe as an active phase.

4. CONCLUSIONS

Bentonites treated with HCl or HNO_3, pillared with Al polycations and containing iron and copper species were tested as potential NH_3–SCR catalysts. The results of catalytic tests were compared to the NO conversion exhibited by commercial systems. It was observed that especially for the samples activated with HNO_3 and containing Fe as an active phase, the temperature of 50% NO conversion was similar to the vanadium catalyst. Moreover, it was observed that the type of activating acid strongly influenced the catalytic activity and the concentration of N_2O in the flue gas. It was probably caused by stronger interaction of HNO_3 with the clay structure, resulting in increased specific surface area and enhancement of the pore system. It is expected that the addition of promoters to the bentonite-based catalyst could improve its catalytic activity and decrease the concentration of N_2O.

XRD analysis carried out over prepared catalysts proved the presence of phase characteristic for montmorillonite, which is the main component of bentonite. It should be mentioned that the samples activated with acids showed poorer crystallinity. Introduction of Cu and Fe did not affect the basal spacing of montmorillonite present in the clays.

FT-IR measurement had a significant contribution into the understanding of the structure and Si–O and Al–O bonding present in the modified clays. Characteristic absorption bands assigned to the vibration modes of Si–O, Al–O–Si, Mg–O–Si or H_2O molecules were detected. Acid activation visibly affected the position of characteristic bands, shifting up some of them to the higher values of the wavelength. Additionally, it was confirmed that acid activation resulted in leaching of octahedral cations on to tetrahedral sheets.

The results of the following research proved that bentonite is characterized by complicated structure and phase composition. Modifications, such as acid treatment or pillaring, resulted in the formation of more complex materials with diversified surface and structure properties. In view of very strong impact of these modifications on the catalytic performance, more detailed studies focused on the influence of acid activation and pillaring on the activity of bentonites in NO conversion are indispensable.

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SYMBOLS

D_p	average crystal size, nm
NO_{inlet}	inlet NO concentration, ppm
NO_{outlet}	outlet NO concentration, ppm
T_{50}	temperature of 50% conversion, °C
θ	the scattering angle, °
β	line broadening, rad
λ	X-ray wavelength, nm

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