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The influence of holmium on catalytic properties of Fe or Cu-modified vermiculites

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Abstract: Natural layered clay, vermiculite, was modified and tested as catalyst for the selective catalytic reduction of NO_x with ammonia (NH₃-SCR). Its modification included the application of the blowing agent (azodicarbonamide), acid treatment and pillaring with Al₂O₃. Active phase (transition metals: Cu or Fe) was introduced via impregnation. The obtained materials were characterized by N₂ sorption (texture), XRD (structure), DR-UV-Vis (oxidation state and aggregation of the active phase), H₂-TPR (reducibility of the active phase), *in situ* DRIFTS (types of adsorbed species due to contact of the sample NH₃) and NH₃-TPD (type/strength of the acidic sites). The initial modification procedures (treatment with azodicarbonamide) resulted in the increase of specific surface area of vermiculite. The introduction of transition metal ions provided a significant amount of acidic sites. The promoting impact of holmium was confirmed by the increased strength of the sites. The highest catalytic activity was exhibited by the sample Fe-containing vermiculite and doped with Ho.

Keywords: selective catalytic reduction, deNO_x, holmium, vermiculite

1. Introduction

Nitrogen oxides (NO + NO₂ = NO_x) belong to major pollutants originating from the combustion of fossil fuels. NO_x are harmful to the environment, as they lead to the formation of acid rain and/or smog. For stationary sources, the limits of emission of NO_x is regulated by EU Directives: 2010/75/EU (The European Parliament and the Council of the European Union, 2010) and 2016/228/EU (The European Commission, 2015).

There are two major ways of NO_x reduction: (i) the modification of the combustion process, and (ii) conversion of NO_x present in flue gas. The most efficient technology of NO_x abatement especially in energy industry is selective catalytic reduction by ammonia (NH₃-SCR) (Chmielarz et al., 2010; Samojeden et al., 2019a). The method is based on the selective reaction of NO_x with ammonia (or urea) used as reducing agents, and mixed with gases passing through the installation. The reduction takes place in the catalyst chamber and the main products of the reaction are molecular nitrogen and water vapour (Stawiński et al., 2016). The most commonly applied commercial NH₃-SCR catalyst is V₂O₅-TiO₂ promoted with MoO₃ and/or WO₃. The system shows outstanding efficiency in the temperature range of 300-400°C. However, while the temperature increases, the side reaction of NH₃ oxidation takes place. As a result, both efficiency in NO conversion and selectivity to N₂ decrease (Hammershøi et al., 2018). Therefore, the search for a novel and well-performing NH₃-SCR catalyst is necessary.

In literature, there are many examples of catalysts used in selective catalytic reduction of NO by ammonia, based on activated carbons (Samojeden et al., 2008, 2017a; Wickramaratne et al., 2014; Rashidi et al., 2016; Wang et al., 2019; Yang et al., 2019), metal oxides (Li et al., 2011, 2018; Thirupathi et al., 2011, 2012; Worch et al., 2013; Hammershøi et al., 2018), zeolites (Carja et al., 2007; Dzwigaj et al., 2009; Wang et al., 2012; Loiland et al., 2014; Rutkowska et al., 2018), montmorillonites (Long et al., 1999; Chmielarz

et al., 2003, 2004; Barama et al., 2009; Sultana et al., 2012; Komadel, 2016), or MCM-41 (Goscianska et al., 2007, 2008; Kowalczyk et al., 2018).

So far, activated carbons and clay minerals (e.g., vermiculites) are very attractive for adsorption and catalytic processes (Grzybek, 2007; Motak, 2008; Chmielarz et al., 2010; Motak et al., 2015; Samojuden et al., 2017b; Ziemiański et al., 2017), including NH_3 -SCR. Vermiculites (one of the most abundant materials) is built of an octahedral sheet sandwiched between two tetrahedral sheets, and is classified as 2:1 phyllosilicate (Temuujin et al., 2003). Due to its remarkable features and relatively simple modification, the material has already been widely used in agriculture, industry and environmental applications, e.g. in waste water treatment (Suvorov et al., 2003; Drelich et al., 2011; Malandrino et al., 2011). Both inorganic and organic substances can be adsorbed in the interlayer space of vermiculite. Appropriate modification procedure can significantly enhance the required properties of such materials (Chmielarz et al., 2010). Exfoliation is one of methods that can be used to enhance the porosity of the material and increase its specific surface area (Bergaya et al., 2006; Hashem et al., 2015). According to Hashem et al. (Hashem et al., 2015), exfoliation of vermiculite can be carried out by thermal or chemical treatment. The thermal treatment procedure includes rapid heating of vermiculite at 400°C. It results in the transformation of interlayer water of the clay into steam and separation of the silicate layers. Subsequently, the layers form packets which are several times thicker than initial sheets of vermiculite. It was confirmed that the volume of the clay is expanded ca. 10-20 times due to exfoliation (Hashem et al., 2015). The alternative route of vermiculite exfoliation is sonication using ultrasonic or microwaves (Ali et al., 2014). On the other hand, chemical treatment of vermiculites is based on the intercalation with alkyl ammoniums and hydrogen peroxide. In this process H_2O_2 is introduced into the interlayer space of the clay and its decomposition into gaseous oxygen and water results in the generation of expansion rate much bigger than in case of thermal exfoliation (Hashem et al., 2015).

Another example of methods applied to improve both chemical and physical properties of vermiculites is acid activation. It is based on ion-exchange of interlayer charge-balancing cations (K^+ , Mg^{2+}) for H^+ cations, and results in the increase of the specific surface area, porosity and acidity of the material (Santos et al., 2015; Stawiński et al., 2017). As the presence of acid sites in NH_3 -SCR catalysts facilitates adsorption of the reducing agent, acid activation can be used for the initial pre-treatment of vermiculite-based catalysts applied in the SCR process (Chmielarz et al., 2012).

In order to turn the vermiculite into an effective NH_3 -SCR catalyst, deposition of an active phase is indispensable. Transition metals, such as iron or copper were confirmed to have an outstanding impact on the catalytic properties of layered clays (Chmielarz et al., 2009; Samojuden et al., 2017b). On the other hand, holmium oxide has been found to possess a significant amount of Lewis acidic sites which according to reaction mechanism positively influence NO conversion. As an example Fe-Mn/TiO₂ doped with holmium and tested in NH_3 -SCR exhibited almost 95% conversion of NO at the temperature range of 140-200°C and 85% at 60-100°C (Zhu et al., 2017).

Holmium as a promoter has been rarely mentioned in literature concerning catalytic processes. There are only a few literature examples of the use of Ho as a catalysts, e.g. (Gaigneaux et al., 2002; Mekhemer, 2004; Cai et al., 2008; Pârvulescu et al., 2010; Zhou et al., 2012; Zhu et al., 2017; Huang et al., 2018). Ho-oxides containing catalysts exhibited relatively high catalytic activity for different processes, such as synthesis of methanol or CO₂ production (Gaigneaux et al., 2002).

Taking into account the above arguments, this work has been devoted to analyse the influence of Ho introduction on the catalytic performance of Fe- and Cu-containing modified vermiculites in NH_3 -SCR.

2. Materials and methods

2.1. Catalysts preparation

The procedure of the modification of natural vermiculite (Sigma-Aldrich) with the blowing agent (azodicarbonamide) was based on the Kudła's work (Kudła et al., 2007). First azodicarbonamide was mixed with vermiculite, pressed in a hydraulic press at 10 MPa and ground. The obtained mixture was introduced into the xylene solution and then the suspension was poured into a round bottom flask with a reflux condenser, constantly stirred and heated to 90°C, and subsequently distilled at 138°C until xylene was completely removed. Subsequently the obtained aluminosilicate was dried in an oven at 140°C for 24 h, in the next step, modified vermiculites was intercalated with Al-oligocations. The

pillaring aluminium hydroxy-oligomeric solution was prepared using the method described by Chmielarz et al. (Chmielarz et al., 2004). Vermiculite modified by the blowing agent was introduced into distilled water (1 g of vermiculite in 100 cm³ of distilled water). Then, the pillaring solution was added dropwise to vermiculite-containing mixture until the Al/clay ratio reached the value of 10 mmol Al/g clay. The obtained material was filtered, dried at 110°C and calcined at 500°C for 12 h.

Subsequently, Fe or Cu (with the loading of 3 wt.%), and Ho as a promoter (with the loading 0.5 wt.%), were deposited on calcined vermiculites using incipient wetness impregnation, using the following salts: iron(III) nitrate nonahydrate, Merck; copper(II) nitrate trihydrate: Merck, holmium(III) nitrate pentahydrate, Merck. The materials were dried at 120°C for 24 h and again calcined at 500°C for 1 h. The designation of the prepared catalysts is presented in Table 1.

Table 1. The designation of the obtained catalysts

Sample	Sample code	Preparation procedure
Raw vermiculite	Ver	-
Vermiculite intercalated with Al ₂ O ₃	VerInt	Vermiculite intercalated with Al ₂ O ₃
Vermiculite impregnated with Fe	VerFe	Vermiculite intercalated and modified with Fe
Vermiculite impregnated with Cu	VerCu	Vermiculite intercalated and modified with Cu
Vermiculite impregnated with Fe and Ho	VerFeHo	Vermiculite intercalated and modified with Fe and Ho
Vermiculite impregnated with Cu and Ho	VerCuHo	Vermiculite intercalated and modified with Cu and Ho

The choice of 3 wt.% of Fe or Cu was based on the following arguments:

1. Our previous studies (Samojeden et al., 2017b) were carried out on vermiculites modified differently than this work and promoted with 3 wt.% or 5 wt.% Cu. It was shown that the increase in Cu content led to a considerable increase in N₂O formation. The latter should be avoided in the products because of its well-known greenhouse effect.
2. Additionally, Kowalczyk et al. (Kowalczyk et al., 2018) presented SCR catalytic results on MCM-41, promoted with 0.5 to 2.7 wt.% Cu. NO conversion was reported to increase with Cu content. However, simultaneously N₂O was also influenced. On the whole, 2.7 wt.% Cu-containing catalyst showed the best performance.
3. 3 wt.% Fe was taken to have a comparison with Cu-containing catalysts.

2.2. Catalysts characterization

Textural properties of the samples were determined by low-temperature nitrogen sorption at -196°C using ASAP 2010 (Micromeritics) automated gas adsorption system. Before the analysis, the samples were outgassed under vacuum at 350°C for 12 h. The specific surface area was determined using BET equation (from the N₂ adsorption isotherm measured in the range of $p/p_0=0.05-0.35$).

The mineralogical compositions and structure of the samples were determined by the XRD analysis. The X-ray diffraction patterns were collected using Panalytical Empyrean diffractometer, equipped with copper-based anode (Cu-K_α LFF HR, $\lambda = 0.154059$ nm). The instrument settings were 40 mA and 45 kV and the step of scans and a counting time were 0.02° and 1 s per step, respectively.

Temperature programmed reduction with H₂ (H₂-TPR) was carried out in order to determine the reducibility of the active phase. The analysis was performed with an AMI-100 apparatus (Altamira Instruments). After oxidizing pre-treatment in the synthetic air, the sample was reduced with a mixture of 5 vol.% H₂ in Ar at the temperature range of 40 and 650°C with the heating ramp of 5°C·min⁻¹. H₂ consumption was determined with thermal conductivity detector (TCD).

Thermal stability and surface acidity studies were carried out using temperature-programmed desorption of NH₃ (NH₃-TPD) at the temperature range of 100-500°C. The analysis was performed using a NETSCH STA409C apparatus equipped with a quadruple mass spectrometer. 50 mg of the catalyst was packed into a quartz down-flow reactor positioned inside a three-zone electrical furnace. The sample was evacuated isothermally at 300°C for 30 min in a flow of helium. Then it was cooled down

to 90°C and saturated with NH₃/He mixture (20 cm³·min⁻¹) for about 30 min. Subsequently the catalyst was purged in a He steam until a constant baseline was registered. Desorption was carried out with a linear heating rate of 10°C·min⁻¹ in the flow of He (20 cm³·min⁻¹).

In order to get more insight into ammonia interaction with the surface, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out for selected samples. The spectra were recorded using Vector 22-FTIR Bruker spectrometer equipped with MCT detector. First of all, 50 mg of the sample was mixed with 200 mg of KBr and introduced into spectratech DRIFTS high-temperature cell. Prior to the FT-IR study, the sample was pre-treated *in situ* with a flow of N₂ at 500°C for 30 min. Afterwards, the material was cooled down to 90°C and saturated with 3 vol.% NH₃/Ar for 30 min (50 cm³·min⁻¹). Then the sample was heated in a flow of N₂ at the temperature range of 150-500°C, kept at a selected temperature for 5 min and cooled down to 90°C. The spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. The background spectrum was collected prior to the experiments and subtracted from each sample spectrum.

2.3. Catalytic experiments

The catalytic experiments were performed in a fixed-bed microreactor system operated in continuous flow at atmospheric pressure. 0.2 g (0.5 - 1.0 mm particle size) of the catalyst was pre-treated in a flow of pure helium (100 cm³·min⁻¹, 250°C, 30 min). The reaction mixture contained 800 ppm of NO, 800 ppm of NH₃, 3.5 vol.% of O₂ and He as balance. The total flow of the gas mixture was 100 cm³·min⁻¹. The concentration of NO and N₂O (a possible side product of the reduction) were analysed by FT-IR detector (ABB 2000 AO series). The reactor was heated to appropriate temperature (140-180-220-260-300°C, with the heating rate of 10°C·min⁻¹), which was controlled by an electronic thermocouple (Lumel RE19) placed in the catalyst bed. The catalyst was kept at each temperature for 60 min.

He pretreatment was used in order to remove possible contamination of the surface with water. It is important to eliminate such influence at the preliminary stage of the SCR studies because H₂O influences NO_x conversion (Klinik et al., 2011).

Downstream of the reactor and upstream of NDIR there is a catalytic unit decomposing possible NO₂ to NO. Thus, in case NO₂ was formed during the reaction, we would register it together with unconverted NO. Thus, the possible formation of NO₂ is registered as unconverted NO. NO conversion thus illustrates only NO reduced to either N₂ or N₂O.

NO conversion was calculated according to the equation (1):

$$NO_{conversion} = \frac{NO_{inlet} - NO_{outlet}}{NO_{inlet}} \cdot 100\% \quad (1)$$

3. Results and discussion

3.1. BET surface area and textural properties

The specific surface area (S_{BET}) and texture of the parent vermiculite and the modified samples are presented in Table 2. After the series of pre-treatment with azodicarbonamide, pillaring and deposition of Fe or Cu, the specific surface area of the samples increased from 5 m²·g⁻¹ to 117-190 m²·g⁻¹.

Table 2. Specific surface area, total pore volume and average pore width of the selected modified vermiculites

Sample code	BET surface area (m ² ·g ⁻¹)	Total pore volume (cm ³ ·g ⁻¹)	Average pore width (nm)
Ver	5	0.002	5.7
VerFe	190	0.004	5.6
VerCu	117	0.004	5.7
VerFeHo	185	0.005	5.6
VerCuHo	125	0.005	5.5

The lowest specific surface area of 117 m²·g⁻¹, obtained for VerCu, may be correlated to the formation of bigger clusters of copper oxide which may have partially blocked the pores of the clay, as it was earlier

reported (Chmielarz et al., 2004). The promotion with Ho had a negligible influence on both S_{BET} and the average pore width of the samples. However, total pore volume increased for the samples doped with Ho as compared to non-promoted samples.

3.2. X-ray diffraction studies

The X-ray diffraction (XRD) patterns of the analysed samples are shown in Fig. 1. The analysis was carried out for parent vermiculite, vermiculite intercalated with Al_2O_3 , vermiculite with the deposited transition metals (Cu or Fe) and that additionally doped with Ho. The parent sample exhibited characteristic diffraction lines at 2θ of ca. 8.9° correlated with the presence of interlayer cations, such as Mg^{2+} or Ca^{2+} . The characteristic line at 28.9° is associated with the presence of quartz impurities, usually present in this natural material (Chmielarz et al., 2009). On the other hand, it was observed that the modifications performed over vermiculite resulted in the disappearance of this line. Low-intensity reflections at 2θ of ca. 35.8° , 41.2° , 49.4° , 64.8° indicate the presence of iron in vermiculite structure (Santos et al., 2015).

The introduction of active materials (Fe or Cu) resulted in the appearance of new diffraction lines with low intensity. Thus, it may be assumed that the active phase is either well dispersed or amorphous or partly amorphous material was formed. The presence of Fe_3O_4 , FeO and Fe_2O_3 is confirmed by the reflections at 2θ of about 34.1° , 35.8° and 54.2° , respectively. However, they could also arise from Fe in the parent sample. New diffraction lines at 2θ of 38.9° and 44.8° in VerCu are assigned to the presence of CuO and Cu_2O , respectively. The introduction of Ho did not result in any new reflections. Thus, Ho was well-dispersed or formed an amorphous phase, possibly under the detection level of XRD.

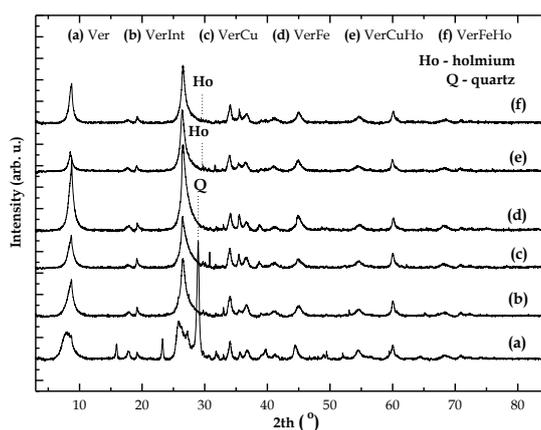


Fig. 1. X-ray diffraction patterns of the prepared catalysts

3.3. UV-Vis spectroscopy studies

In Fig. 2., the UV-Vis spectra recorded for the samples are presented. As iron is the main natural component of vermiculite, the UV-Vis spectra of the raw vermiculite can be characterized by the bands assigned to $\text{Fe}^{3+} \leftarrow \text{O}$ charge transfer (Chmielarz et al., 2010). Tetrahedrally and octahedrally coordinated isolated Fe^{3+} cations give rise to bands below 250 nm and between 250 and 300 nm, respectively. The spectra obtained for the raw vermiculite suggest that only negligible amount of Fe^{3+} ions is located in the tetrahedral coordination and most of them is present in the octahedral sheets (Del Rey-Perez-Caballero et al., 2000). The characteristic bands at 340 nm and above 400 nm are assigned to the presence of small oligonuclear clusters of Fe_xO_y and bulky particles of Fe_2O_3 , respectively (Mihaylov, 2011). After intercalation, the band characteristic for Fe^{3+} in the tetrahedral sheets disappeared completely and most of iron was present in a form of Fe_xO_y clusters and bulky Fe_2O_3 . Therefore, it can be assumed that intercalation influences the distribution of iron species, which occur naturally in the clay. Additionally, it was observed that after deposition of Ho into the raw vermiculite, intensity of the bands characteristic for octahedral Fe^{3+} ions and bulky Fe_2O_3 significantly decreased.

The introduction of iron or copper as active components changed the shape of the spectra, as compared to the raw vermiculite. Upon doping the material with Fe, the bands assigned to the small

oligonuclear Fe_xO_y species became more intense. Indicating the deposition of active phase in a form of small clusters of Fe_xO_y located in the interlayer space or on the external surface of the clay (Chmielarz et al., 2010). In case of the material treated with copper, four distinct regions can be distinguished. The absorption band centred at 250 nm is assigned to the charge transfer from oxygen to metal, related to monomeric Cu^{2+} cations (Rutkowska et al., 2017). The intense bands centred at 340 nm and 490 nm suggest the presence of oligomeric O-Cu-O and Cu-O-Cu species, while the broad band in the range of 600 nm to 900 nm is attributed to electron d-d transitions in Cu^{2+} in dispersed CuO particles (Bin et al., 2014; Zhang et al., 2014). The results are in agreement with XRD analysis and confirm that the active phase is well-dispersed on the catalysts surface.

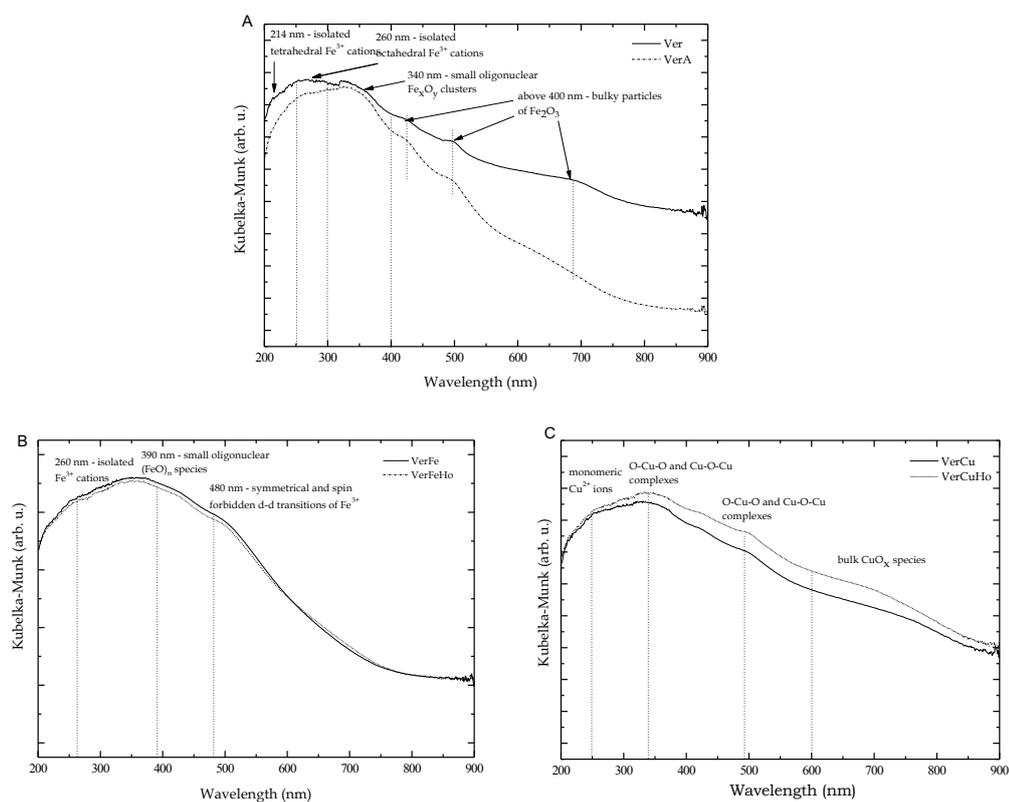


Fig. 2. UV-Vis spectra of raw and modified vermiculite (A), vermiculite with Fe and Ho (B) and Cu and Ho (C)

3.4. H_2 -TPR studies

H_2 -TPR profiles are presented in Fig. 3. Within the temperature range of 200-800°C the analysed materials exhibit several reduction peaks. Raw vermiculite shows only very low reducibility at higher temperature region, possibly resulting from iron present in this material. The deposition of active material - iron or copper resulted in the appearance of new reduction peaks.

The H_2 -TPR profile of VerFe consists of a broad peak at 390°C, an intense one at 530°C and shoulders at ca. 445-635°C. The low temperature peak is assigned to the reduction of aggregated oligomeric iron oxide species, while that at 530°C and the shoulders possibly originate from the reduction of monomeric Fe^{3+} species (Macina et al., 2016). This confirms high dispersion of iron on the catalyst surface. The addition of Ho changed the shape of TPR profile shifting the reduction peak from 445°C to higher temperature, suggesting the decrease in reducibility of iron species.

The H_2 -TPR curve for VerCu contains one sharp peak centred at 288°C. According to literature (Jabłońska et al., 2015), it is attributed to the reduction of well dispersed Cu^{2+} cations to metallic copper. As opposed to the results obtained for VerFe, the addition of Ho to VerCu shifted the reduction peak to lower temperature and increased copper species reducibility.

The results of H_2 -TPR analysis are in full agreement with the results from XRD and UV-Vis, which suggested that the active phase consists of monomeric Fe- and Cu-ions and small oligomeric FeO_x and CuO_x species.

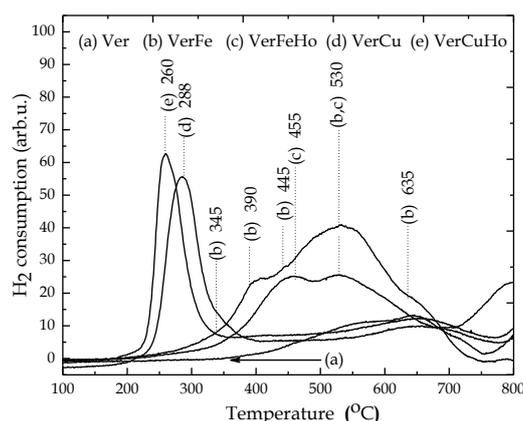


Fig. 3. H₂-TPR patterns obtained for the studied catalysts

3.5. NH₃-TPD studies

Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out for the selected samples in order to determine the type and the strength of acidic sites present on the surface of selected samples. The results are presented in Fig. 4.

The raw vermiculite did not exhibit any desorption peaks. Ammonia desorption profile for VerCu is spread in the range of 120-450°C and consists of an intense maximum centred at 197°C and a broader one at 418°C. The low temperature peak (LTP) corresponds to so-called α -acidic sites and is usually associated with NH₄⁺ ions adsorbed on Brønsted acidic sites. On the other hand, the high temperature peak (HTP) indicates the presence of strong acidic sites (so-called γ -acidic sites) and confirms the presence of NH₃ molecules coordinated to Lewis acidic sites (Rutkowska et al., 2017). The introduction of holmium resulted in the shift of both peaks forwards higher temperature. Thus, the strength of α acidic sites was enhanced. Zhu et al. (Zhu et al., 2017) reported promotional effect of Ho on Lewis acidity.

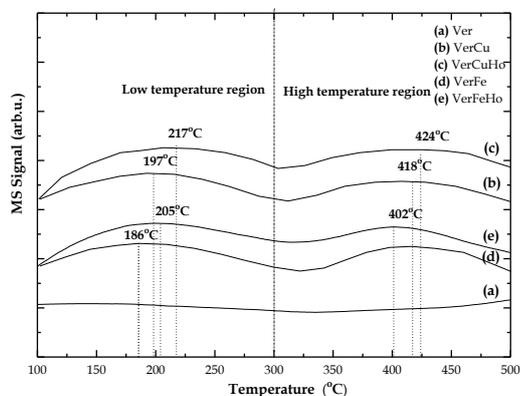


Fig. 4. NH₃-TPD profiles obtained for the selected catalysts and maximum temperature T_{max} of low-temperature (LTP) and high-temperature (HTP) peaks

Ammonia desorption spectrum recorded for VerFe was registered in the range of 120-480°C. LTP and HTP are situated at 186°C and 418°C, respectively. Brønsted acidity sites had higher strength for holmium promoted samples while Lewis acidic sites became slightly weaker.

The total acidity increased after Ho promotion, as evidenced by Fig. 4, where the intensity of both LTP and HTP peaks were higher for Ho-samples than unpromoted ones.

3.6. FT-IR of NH₃ adsorption studies (*in situ* DRIFTS)

DRIFT spectroscopy was applied in order to examine the interaction of the reducing agent with the surface of the selected catalysts. VerFe and VerFeHo were chosen as they exhibited the best catalytic performance in the NH₃-SCR catalytic tests. The obtained results are presented in Fig. 5.

Figures 5A and 5B depict the spectra obtained for ammonia adsorbed on VerFe and VerFeHo, respectively. The intensity of the characteristic bands decreases with the increasing temperature. The most intense band can be observed at 1400 cm^{-1} . It may be attributed to the formation of nitrate species of the catalyst surface below 250°C . The weak bands at 1512 cm^{-1} observed at the whole studied temperature range of $90\text{--}500^\circ\text{C}$ are assigned to the formation of nitrosyl ($-\text{HNO}$) species. The intensity of the bands decreased after increasing the temperature to $400\text{--}500^\circ\text{C}$. Another weak bands at 1656 cm^{-1} and 1604 cm^{-1} originate from asymmetric deformation modes of NH_3 molecules coordinated on Lewis acidic sites (Góra-Marek et al., 2015). In the N-H stretching vibration region, at $3550\text{--}3100\text{ cm}^{-1}$, two bands at 3133 cm^{-1} and 3308 cm^{-1} are observed. The peaks are ascribed to NH_4^+ species on Brönsted acid sites and NH_3 molecules coordinated on Lewis acid sites, respectively. A small peak at 3740 cm^{-1} , in the region of O-H stretching vibrations corresponds to the presence of Si-OH silanol groups (Rutkowska et al., 2017). After the introduction of Ho the intensity of the characteristic bands corresponding to Lewis species are much higher. The peaks at 1400 cm^{-1} and 1512 cm^{-1} become broader and the intensity is decreased.

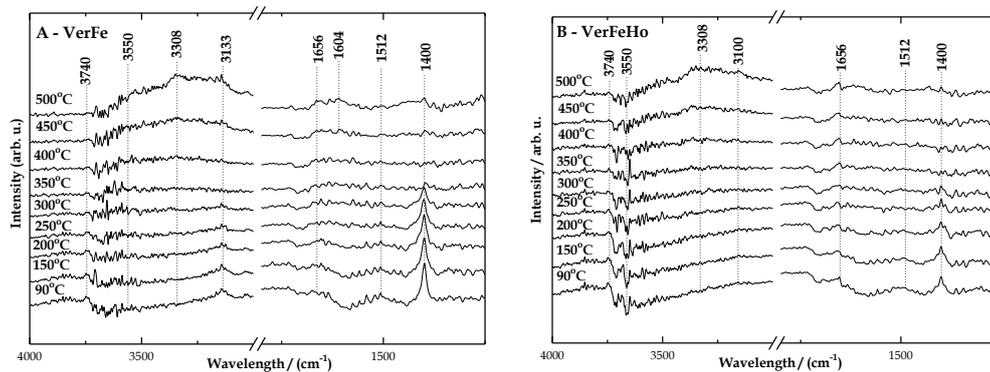


Fig. 5. DRIFT spectra of VerFe (A) and VerFeHo (B) treated in a flow of ammonia in the temperature range of $90\text{--}500^\circ\text{C}$ for 5 min and purged by N_2 at 90°C

4. Catalytic studies

The modified vermiculite samples containing transition metals as the active phase and doped with holmium were studied as catalysts for NO reduction with ammonia. NO conversion and N_2O formation are presented in Fig. 6. The catalytic performance of the clay was significantly enhanced by the modification procedures used in this study, with NO conversion reaching over 80% at 140°C . The introduction of Ho increased the NO conversion by 5-10% in comparison to the undoped sample. The highest conversion within the temperature range of $180\text{--}300^\circ\text{C}$ was obtained for VerFeHo, confirming that Ho can be an effective promoter of $\text{NH}_3\text{-SCR}$ catalysts.

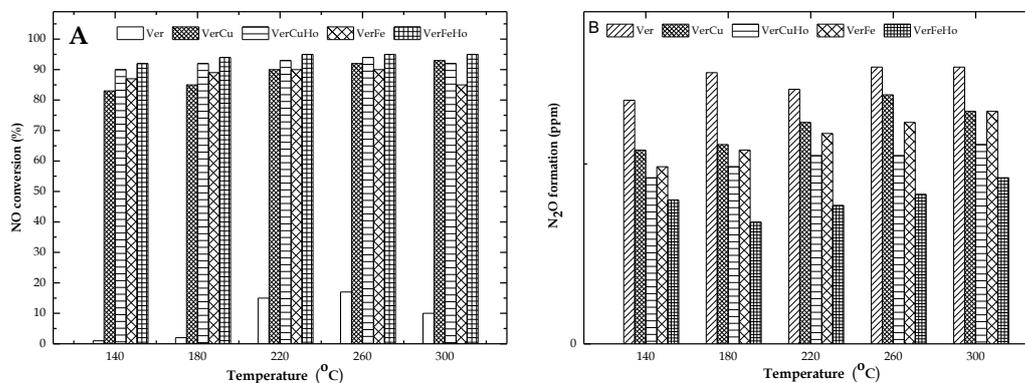


Fig. 6. $\text{NH}_3\text{-SCR}$ catalytic tests for the studied samples: NO conversion (A), N_2O concentration (B) (experimental conditions: $[\text{NO}] = 800\text{ ppm}$, $[\text{NH}_3] = 800\text{ ppm}$, $[\text{O}_2] = 3.5\text{ vol. \%}$, balance He, flow: $100\text{ cm}^3\cdot\text{min}^{-1}$, mass of the catalyst: 200 mg)

5. Conclusions

Modified vermiculites containing copper or iron as the active phase and promoted with holmium were characterized and tested as the catalysts for the selective catalytic reduction of NO with ammonia. Fe-containing vermiculite samples and doped with Ho (VerFeHo) exhibited the highest catalytic activity, reaching about 87% conversion of NO at 140°C. The introduction of Ho as promoter also had a positive effect on the NO conversion over VerCu. The prepared catalysts lead to relatively low production of N₂O. The addition of Ho further suppressed N₂O formation.

The analysis of physico-chemical properties of the samples indicated that the enhancement in catalytic properties may be the result of several factors. The initial modification, including blowing agent and intercalation resulted in the increased specific surface area and porosity, as confirmed by low-temperature N₂ sorption. Both XRD and UV-Vis analyses indicated that the active phase was well dispersed on the catalyst surface. H₂-TPR results showed that the addition of Ho influenced the temperature of the active phase reduction dependent on the active material. *In situ* FTIR of NH₃ sorption studies showed the increase in the number of Lewis acidic sites after Ho promotion. Ho also modified the strength of Brønsted acid sites to lower values. Thus, the studies indicate that Ho can promote activity of the NH₃-SCR catalysts.

Acknowledgments

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