



Full paper/Mémoire

Modification of the physicochemical properties of the commercial CHA zeolite and examination of its activity in nitrogen oxide abatement



Modification de la zéolithe CHA commerciale pour les besoins de la réduction catalytique des oxydes d'azote

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ABSTRACT

In this manuscript, studies of catalytic activity in two environmental processes were performed: NO reduction with NH₃ (DeNO_x process) and N₂O decomposition over the commercial CHA zeolite. In the first part of the studies, the parent CHA zeolite was modified with different contents of copper (1, 5, 10 and 15%) by wet impregnation, and optimum Cu loading was chosen. In the second part of the studies, CHA was modified by the use of different bases and acids (NaOH, TPAOH (tetrapropylammonium hydroxide), HCl, and Na₂H₂EDTA (ethylenediaminetetraacetic acid)) in order to generate mesoporosity. The influence of demetallation agent concentration, temperature and duration of treatment was examined. The most efficient treatment, resulting in an almost four-fold increase in the mesopore volume, was found to be with a 0.2 M Na₂H₂EDTA solution (treatment for 4 h at 100 °C). Moreover, despite the modification of the textural properties, the phase composition, acidity and form of the introduced copper species were also influenced by the applied modification techniques (the samples were examined with the use of techniques such as N₂ sorption, XRD, NH₃-TPD and UV–vis-DRS). The Cu-CHA samples obtained with the use of commercial zeolite supplied by Clariant (Germany) exhibited high activity in the DeNO_x process under the applied conditions. The stability of the Cu-CHA sample (doped with 5% of Cu) in the DeNO_x process was examined by five subsequent catalytic runs, and only a small drop in catalytic activity was observed. Moreover, the treatment of CHA with Na₂H₂EDTA increased its activity in N₂O decomposition, which makes the applied modification techniques interesting for the potential application of this zeolite in catalysis.

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R É S U M É

Dans cet article, l'étude de l'activité catalytique a été réalisée dans deux processus environnementaux : la réduction de NO avec NH₃ (processus de DeNO_x) et la décomposition de N₂O sur la zéolithe CHA commerciale. Dans une première partie de l'étude, la zéolithe CHA mère a été modifiée selon des teneurs variables en cuivre (1, 5, 10 et 15%) par imprégnation

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NH₃-SCR
Décomposition du N₂O

humide et une charge optimale en Cu. Dans une seconde partie de l'étude, la CHA a été modifiée par l'utilisation de bases et d'acides différents (NaOH, TPAOH (hydroxyde de tétrapropylammonium), HCl, Na₂H₂EDTA (acide éthylènediaminetétracétique)) afin de générer la mésoporosité. Les influences respectives de la concentration de l'agent de démétallation, la température ainsi que la durée du traitement ont été examinées. Le traitement le plus efficace qui a été observé concerne une solution de Na₂H₂EDTA 0,2 M (traitement pendant 4 h à 100°C); il a entraîné une augmentation d'environ quatre fois le volume de mésopores initial. En outre, malgré la modification des propriétés texturales, la composition de phase, l'acidité et la forme des espèces de cuivre introduites ont aussi été influencées par les techniques de modification appliquées (les échantillons ont été examinés en utilisant des méthodes telles que la sorption de N₂, la XRD, la NH₃-TPD et l'UV-vis-DRS). Les échantillons Cu-CHA obtenus en utilisant la zéolithe commerciale fournie par Clariant (Allemagne) ont présenté une activité élevée et une stabilité dans le processus de DeNO_x. De plus, le traitement de la CHA avec Na₂H₂EDTA a augmenté son activité dans la décomposition du N₂O, ce qui rend les techniques de modification appliquées intéressantes pour l'application potentielle de cette zéolithe en catalyse.

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1. Introduction

Chabazite (CHA topology) is a small pore, 8-membered ring zeolite. During the last few years, Cu-modified zeolites with CHA topology in the form of silicoaluminates or silicoaluminophosphates (such as e.g., Cu-CHA, Cu-SSZ-13, Cu-SAPO-34) gained great scientific interest due to the high catalytic performance (in a large temperature range) and superior hydrothermal stability in NO_x reduction [1,2]. These exceptional properties of Cu-CHA led to its implementation as part of the emission control systems for diesel-powered passenger vehicles (reduction of NO_x under the highly oxidizing lean-burn conditions). Since that time, various aspects of SCR (Selective Catalytic Reduction) catalysts based on copper-modified chabazite were studied. Factors such as the form of active Cu sites [e.g., Refs. [3–5]], type of ammonia species formed on the catalyst surface and their interaction with the catalyst [e.g., Refs. [6–8]], poisoning effect of propene during SCR of NO_x [e.g., Refs. [9,10]] and impact of different hydrothermal treatment and aging conditions [e.g., Refs. [10–12]] were investigated. Moreover, various experimental and kinetic modelling studies were performed [e.g., Refs. [13–15]] concerning different Cu-CHA catalysts.

Recent trends in zeolite modifications are mainly focused on the generation of mesoporosity [16,17]. The presence of micropores (pore size <2 nm) is a very important feature of zeolites, which is responsible for their various catalytic properties, including shape selectivity. However, they are also responsible for the low rate of molecule access into the zeolite crystals, as well as the unwanted adsorption effect of reactants and/or products during the catalytic process. Thus, by steric limitations, the accessibility of micropores is restricted and the catalytic potential of zeolites is not being used effectively, especially in the case of bulky molecules. It is very important to mention that the modification of zeolite porosity, despite the textural properties, also affects their acidity as well as the content, form and reducibility of the introduced transition metal species. The modification of such properties is

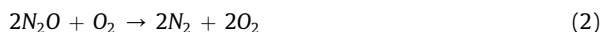
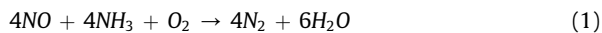
very important for catalytic reactions (with the participation of significantly smaller molecules, such as the DeNO_x process or N₂O decomposition), which proceed on acid or red-ox active sites.

As found in our previous studies, micro-mesoporous zeolites obtained by different techniques such as the mesotemplate-free method [18–20], desilication [21] or delamination as well as pillaring of layered zeolites [22] are characterised by enhanced catalytic activity, improved stability and increased resistance against the coke deposit formation.

In contrast to the other zeolite topologies, the modification of the CHA framework by mesopore generation is still an open field for scientists. The reports presenting studies in this area are connected with the following methods of CHA modification: (i) preparation of the hierarchical CHA structure using the supramolecular (double templating) method [23–25] e.g., for the CO₂ capture under moderate temperatures and high pressure conditions, (ii) desilication of SSZ-13 with NaOH solution for the application in the methanol-to-olefin (MTO) process [26], (iii) dealumination of CHA and SSZ-13 zeolites using ammonium hexafluorosilicate [27] and (iv) the generation of mesopores by solid templating using carbon nanoparticles or nanotubes [28].

In the presented studies, commercial CHA zeolite supplied by Clariant was modified with different amounts of copper and tested as a catalyst of two environmental processes, which is related to the reduction of nitrogen oxide emission into the atmosphere: (i) NO reduction with ammonia (DeNO_x process) and (ii) N₂O catalytic decomposition. The emission of NO_x into the atmosphere is one of the main factors contributing to acid rain, depletion of the ozone layer and the greenhouse effect. One of the major sources of NO emission is the transportation sector and its selective catalytic reduction (DeNO_x) with NH₃ (Eq. 1) is considered one of the most promising technologies [29]. While in the case of N₂O, the production of nitric acid is the most important anthropogenic emission source. Direct catalytic decomposition of N₂O (in the presence of oxygen, which is a typical

component of tail gases and is regarded as a reaction inhibitor), presented in Eq. 2, is a preferable way for its emission abatement [20].



In the second part of the studies, the parent CHA catalyst was modified by treatment with different basic and acidic solutions (under various treatment conditions) in order to modify its physicochemical properties. The sample chosen with the optimal textural parameters was modified with copper and tested in both of the above-mentioned catalytic processes.

2. Experimental methods

2.1. Catalyst preparation

Commercial CHA zeolite used in this work was delivered in H-form by Clariant Company (Germany) in the form of silicoaluminophosphate (3.5 wt. % Si, 20.2 wt. % Al, 55.8 wt. % O, 18.7 wt. % P, and 1.8 wt. % Ti).

In the first part of the studies, the parent CHA zeolite was modified with copper by the wet-impregnation method with water solution of copper acetate tetrahydrate: $Cu(CH_3COO)_2 \cdot 4H_2O$. The concentration of the copper acetate solution was adjusted to introduce 1, 5, 10 and 15 wt. % of copper to the samples. After impregnation, the samples were dried at 60 °C and calcined at 600 °C for 6 h. The obtained samples were denoted as x%Cu-CHA, where x is the assumed, calculated percentage content of Cu in the samples.

In the second part of the studies, the parent CHA sample was modified in order to generate mesoporosity. For this purpose, two techniques were applied: (i) base treatment (BT) (NaOH or TPAOH (tetrapropylammonium hydroxide)) and (ii) acid treatment (AT) (HCl or Na_2H_2EDTA (ethylenediaminetetraacetic acid)). The obtained samples were denoted as: CHA(BT/AT- C_{MA} - MA - T)/ t , where BT/AT is the type of modification, C_{MA} is the concentration of the modification agent, MA is the modification agent, T is the temperature of treatment, and t is the duration of treatment. Sample codes and conditions of the performed modifications are presented in Table 1.

In the case of each modification, a solution of acid or base was introduced into a round-bottomed flask and heated using an oil bath. When the proper temperature was achieved, CHA zeolite was added to the solution with 1 g of zeolite per 100 mL of solution and stirred. After the proper time, the sample was filtered and washed three times with double-distilled water. In the next step, the sample was dried at 60 °C and calcined at 600 °C for 6 h (synthesis details are presented in Table 1). When Na_2H_2EDTA or NaOH were used, an additional synthesis step was applied—triple ion-exchange with a solution of NH_4NO_3 (0.5 M, Sigma–Aldrich) at 80 °C for 1 h (ion-exchange $Na^+ \rightarrow NH_4^+$). Finally, the samples were washed, dried and calcined to convert NH_4^+ to H^+ under the same

conditions as in the case of the samples obtained directly in H^+ -form.

The chosen micro-mesoporous sample obtained in the second part of the studies (CHA(AT_0.2_EDTA_100)4) was modified with 5 wt. % of copper by using the wet-impregnation method using aqueous solution of copper acetate tetrahydrate: $Cu(CH_3COO)_2 \cdot 4H_2O$. After impregnation, the sample was dried at 60 °C and then calcined at 600 °C for 6 h.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D2 Phaser diffractometer (Cu $K\alpha$ radiation; $\lambda = 1.54056 \text{ \AA}$). The measurements were performed in the 2 theta range of 5–50° with a step of 0.02°.

Textural properties of the samples were determined by N_2 sorption at –196 °C using a 3Flex v1.00 (Micromeritics) automated gas adsorption system. Prior to the analysis, the samples were degassed in a vacuum at 350 °C for 24 h. The specific surface area (S_{BET}) of the samples was determined using the BET (Braunauer–Emmett–Teller) model according to the recommendations of Rouquerol et al [30]. The micropore volume was calculated using the Harkins and Jura model (t-plot analysis, thickness range 0.55–0.85 nm). The mesopore volume was calculated from the desorption branch using the BJH model (Kruk–Jaroniec–Sayari empirical procedure) in the range of 1.7–30 nm.

Coordination and aggregation of Cu introduced into CHA zeolite were studied by using UV–vis–DR spectroscopy. The measurements were performed using an Evolution 600 (Thermo) spectrophotometer in the range of 200–900 nm with a resolution of 2 nm.

Surface acidity (concentration and strength of acid sites) was studied by temperature-programmed desorption of ammonia (NH_3 -TPD). The measurements were performed in a flow microreactor system equipped with QMS detector (Prevac). Prior to ammonia sorption, a sample was outgassed in a flow of pure helium at 600 °C for 30 min. Subsequently, the microreactor was cooled to 70 °C and the sample was saturated in a flow of gas mixture containing 1 vol. % of NH_3 diluted in helium for about 120 min. And then, the catalyst was purged in a helium flow until a constant base line level was attained. Desorption was carried out at a linear heating rate (10 °C/min) in a flow of He (20 mL/min).

2.3. Catalytic tests

Catalytic studies of NH_3 -SCR were performed in a fixed-bed quartz microreactor. The experiments were performed at atmospheric pressure and in the temperature range from 100 to 400 °C. The reactants concentration was continuously measured using a quadrupole mass spectrometer (Prevac) connected directly to the reactor outlet. For each experiment, 0.1 g of catalyst (particles sizes in the range of 0.160–0.315 mm) was placed on a quartz wool plug in the reactor and outgassed in a flow of pure helium at 600 °C for 1 h. The gas mixture containing 2500 ppm of NO, 2500 ppm of NH_3 and 25,000 ppm of O_2 diluted in pure helium (at a total flow rate of 40 mL/min) was used.

Table 1

Sample codes, modification conditions and textural parameters of the mesostructured CHA samples.

Sample code	MA ^a	C _{MA} /M	Time/h	Temp./°C	S _{BET} [m ² /g]	S _{EXT} [m ² /g]	V _{MIC} [cm ³ /g]	V _{MES} [cm ³ /g]
CHA	—	—	—	—	706	54	0.246	0.078
CHA(BT_0.1_NaOH_20)0.5	NaOH	0.1	0.5	20	18	14	0.003	0.016
CHA(BT_0.1_NaOH_20)1	NaOH	0.1	1	20	17	13	0.002	0.015
CHA(BT_0.1_NaOH_20)2	NaOH	0.1	2	20	19	15	0.003	0.017
CHA(BT_0.2_NaOH_65)0.5	NaOH	0.2	0.5	65	21	14	0.004	0.023
CHA(BT_0.2_NaOH_65)1	NaOH	0.2	1	65	14	11	0.002	0.016
CHA(BT_0.2_NaOH_65)2	NaOH	0.2	2	65	14	12	0.001	0.017
CHA(BT_0.1_TPAOH_65)0.5	TPAOH	0.1	0.5	65	38	27	0.006	0.036
CHA(BT_0.1_TPAOH_65)1	TPAOH	0.1	1	65	40	30	0.007	0.039
CHA(BT_0.1_TPAOH_65)2	TPAOH	0.1	2	65	38	28	0.006	0.039
CHA(BT_0.025_TPAOH_65)0.5	TPAOH	0.025	0.5	65	713	22	0.259	0.040
CHA(BT_0.05_TPAOH_65)0.5	TPAOH	0.05	0.5	65	631	27	0.231	0.053
CHA(BT_0.2_TPAOH_65)0.5	TPAOH	0.2	0.5	65	176	88	0.057	0.180
CHA(BT_0.3_TPAOH_65)0.5	TPAOH	0.3	0.5	65	205	181	0.016	0.260
CHA(AT_0.2_HCl_65)0.5	HCl	0.2	0.5	65	531	38	0.188	0.059
CHA(AT_0.2_HCl_65)1	HCl	0.2	1	65	538	37	0.191	0.056
CHA(AT_0.2_HCl_65)2	HCl	0.2	2	65	525	36	0.185	0.054
CHA(AT_0.2_EDTA_25)4	Na ₂ H ₂ EDTA	0.2	4	25	746	29	0.265	0.037
CHA(AT_0.2_EDTA_50)4	Na ₂ H ₂ EDTA	0.2	4	50	743	32	0.264	0.043
CHA(AT_0.2_EDTA_100)4	Na ₂ H ₂ EDTA	0.2	4	100	258	189	0.030	0.292
CHA(AT_0.04_EDTA_100)4	Na ₂ H ₂ EDTA	0.04	4	100	819	35	0.290	0.044
CHA(AT_0.1_EDTA_100)4	Na ₂ H ₂ EDTA	0.1	4	100	657	54	0.225	0.064
CHA(AT_0.15_EDTA_100)4	Na ₂ H ₂ EDTA	0.15	4	100	324	166	0.062	0.188
CHA(AT_0.3_EDTA_100)4	Na ₂ H ₂ EDTA	0.3	4	100	247	190	0.025	0.261

(*) Modification agent.

Catalytic studies of N₂O decomposition were performed in a fixed-bed quartz microreactor. The experiments were performed under atmospheric pressure and in the temperature range from 300 to 600 °C in intervals of 50 °C. The composition of outlet gases was analysed using a gas chromatograph (SRI 8610C) equipped with TCD detector. For each experiment, 0.1 g of catalyst (particles sizes in the range of 0.160–0.315 mm) was placed on a quartz wool plug in a microreactor and outgassed in a flow of pure helium at 600 °C for 1 h. And then, the gas mixture containing 1000 ppm of N₂O and 40,000 ppm of O₂ diluted in pure helium (at a total flow rate of 50 ml/min) was passed over the catalyst and the reaction proceeded for about 1 h to stabilise the catalyst. The analysis of the outlet gases was performed 20 min after temperature stabilisation and a steady state regime was achieved.

3. Results and discussion

3.1. Conventional (microporous) CHA zeolite

The crystalline structure of the parent CHA zeolite and the samples modified with different amounts of Cu were investigated by using the XRD method (Fig. 1). The XRD pattern of the starting material corresponds to patterns of the CHA chabazite structure [31]. However, the analysis of the parent sample diffractogram with X'Pert HighScore (PDF-4+ database) revealed the presence of impurities in the form of silicoaluminophosphate SAPO-11 (AEL topology) and titanium-phosphorus oxide (TiP₂O₇). The modification of CHA with copper by using the incipient wetness impregnation method (with the assumed Cu wt. % of about 1, 5, 10 and 15) did not influence the crystalline structure of the samples; however, the intensity of the reflections

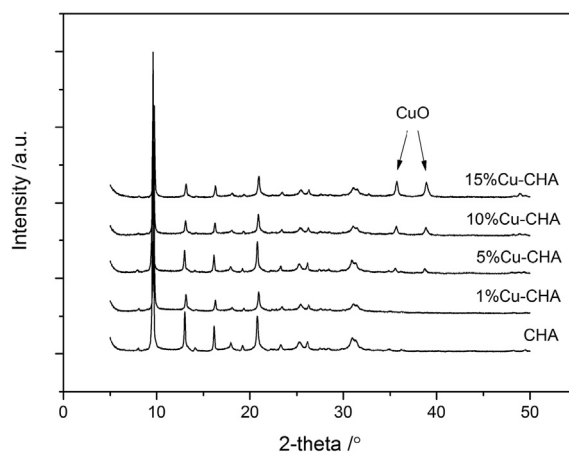


Fig. 1. XRD patterns of the parent CHA and the samples modified with Cu.

slightly decreased. Moreover, in the case of the samples with the copper content above 1%, new reflections at about 35.7° and 38.9° 2 θ appeared, which is connected to the formation of CuO aggregates on the catalyst surface. The average CuO crystal sizes calculated using Scherrer's equation ($k = 1$, $\lambda = 0.154$ nm) for (111) reflection are in the range of 30–40 nm.

The textural properties of the parent CHA zeolite and its modifications with different amounts of copper were characterised by using the low-temperature N₂ sorption (Table 2). CHA zeolite used in the presented studies is characterised by the relatively high BET surface area (about 700 m²/g) and micropore volume (about 0.240 cm³/g). After modification of the samples with copper, values of textural parameters (such as BET surface area, external

Table 2

Textural properties of the samples determined from the N₂-sorption measurements.

Sample code	S _{BET} [m ² /g]	S _{EXT} [m ² /g]	V _{MIC} [cm ³ /g]	V _{MES} [cm ³ /g]
CHA	706	54	0.246	0.078
1%Cu-CHA	679	14	0.243	0.030
5%Cu-CHA	631	33	0.222	0.053
10%Cu-CHA	570	19	0.202	0.026
15%Cu-CHA	550	23	0.193	0.031

surface area, and volume of micro- and mesopores) decreased. The observed changes can be connected to a partial blocking of the zeolite pores by CuO aggregates, which led to a decrease in BET and external surfaces of the samples. Not all changes in the textural properties had a similar trend, which can be connected to the random deposition of copper oxide aggregates; however, the BET surface area and the volume of micropores decreased together with an increase in the Cu content of the samples. Nitrogen adsorption–desorption isotherms obtained for all the samples (Fig. 2) are of type I(a) (according to the IUPAC classification [32]), which is characteristic of microporous materials. The slight increase in the adsorbed N₂ volume at higher partial pressures can be connected to the interparticle porosity. After modification with copper, the sorption isotherms shifted to lower values of adsorbed nitrogen, which corresponds to a decrease in the BET surface area and micropore volume of the samples.

The coordination, aggregation and oxidation state of copper species deposited on CHA zeolite was examined by using the UV–vis-DR spectroscopy (Fig. 3). The obtained spectra indicated the presence of four absorption bands, which can be assigned to (i) charge transition between the zeolite lattice oxygen and isolated Cu⁺/Cu²⁺ cations (about 220–230 nm), (ii) two charge transfer bands in Cu_xO_y complexes, which can be attributed to O–Cu–O and Cu–O–Cu respectively (about 250–450 nm) and (iii) d–d transitions in dispersed CuO particles, where Cu²⁺ is surrounded by oxygen in distorted octahedral coordination (about 600–800 nm) [33–35]. Moreover, the absorption at

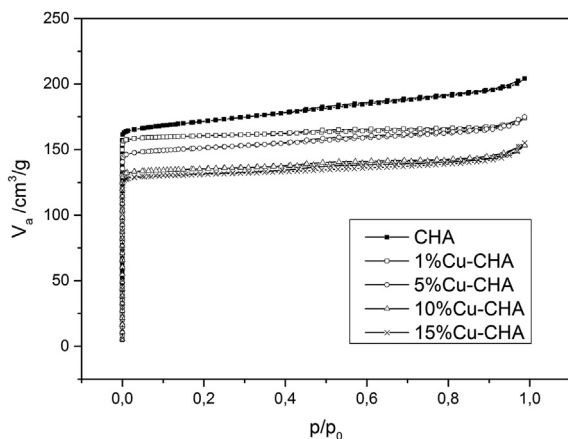


Fig. 2. Nitrogen adsorption–desorption isotherms of the parent CHA and the samples modified with Cu.

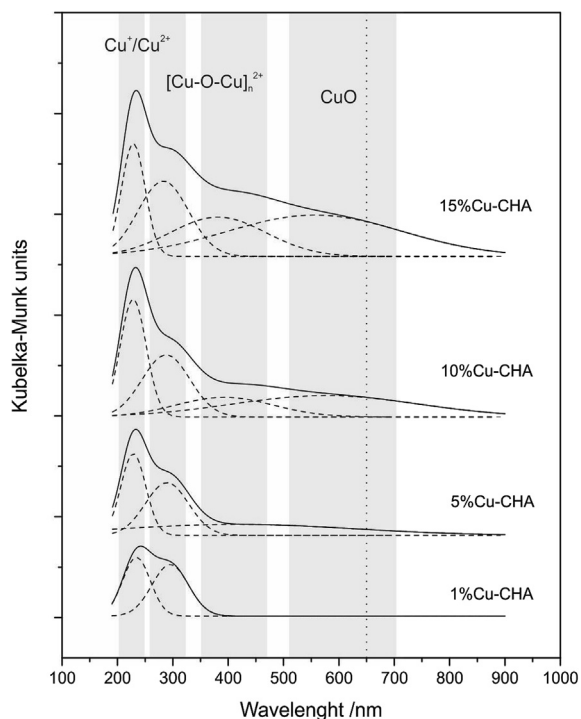


Fig. 3. UV–vis-DR spectra of the CHA samples modified with Cu.

about 650 nm is related to the presence of bulk CuO, the presence of which was also confirmed by XRD analysis [36,37]. Together with an increase of the copper content in the samples, the bands related to aggregated copper species appeared. The absorption in the range of 400–900 nm was observed for the sample with Cu loading above 5 wt. %, which is in agreement with the presence of CuO reflections in XRD patterns for this series of samples.

The obtained samples modified with copper were examined in two catalytic reactions: DeNO_x process (Fig. 4A) and N₂O decomposition (Fig. 5). In the case of both reactions, the unmodified CHA sample does not show any catalytic activity. After modification with copper, the catalytic activity of the samples significantly increased. In the case of the former reaction, the NO conversion increased together with an increase of the copper content up to 10%. The differences in NO conversions obtained for the samples modified with 5, 10 and 15 wt. % of Cu are very small and close to the experimental error. However, the conversion drop observed in the case of 15%Cu-CHA could be connected to the high Cu content resulting in the formation of CuO aggregates on the catalyst surface and partial blockage of micropores (decrease in the catalyst BET surface area). The reaction selectivity to N₂ is significantly high in the case of all samples (above 90%) and remains stable over a wide temperature range (only slight drop at high temperatures was observed). The lower reaction selectivity to nitrogen was connected with the increased Cu content, which is especially evident in the case of the 15%Cu-CHA sample. Yu et al. [38] identified surface CuO aggregates as a phase responsible for the consumption of ammonia and the formation of N₂O at high temperatures. Also, Yashnik et al.

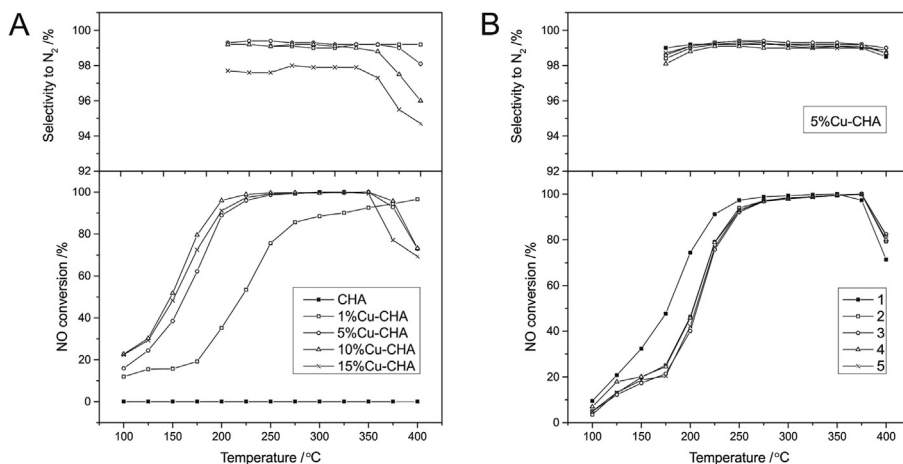


Fig. 4. Temperature dependence of NO conversion and N₂ selectivity in SCR of NO with NH₃ for the CHA samples modified with Cu (A) and for 5%Cu-CHA (stability test) (B). Conditions: the balancing gas is 2500 ppm NO, 2500 ppm NH₃, 25,000 ppm O₂; He; the total flow rate is 40 ml/min; and the weight of the catalyst is 0.1 g.

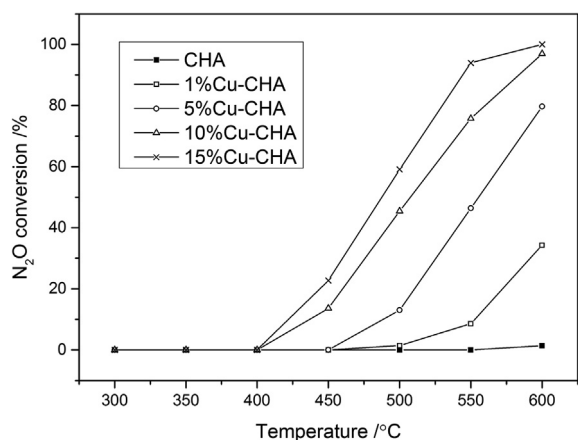
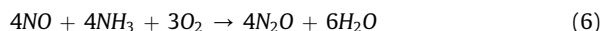
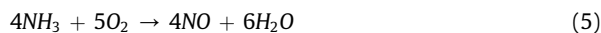
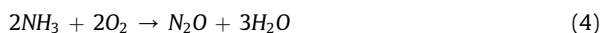


Fig. 5. Temperature dependence of N₂O conversion for the CHA samples modified with Cu. Conditions: the balancing gas is 1000 ppm N₂O, 40,000 ppm O₂; He; the total flow rate is 50 ml/min; and the weight of the catalyst is 0.1 g.

[39] recognised CuO-like species as copper sites with the relatively low activity in NO-SCR, which corresponds to the presented results.

This phenomenon can be connected to the competition to the DeNO_x process side-reaction of direct ammonia oxidation by oxygen at high temperatures. Ammonia can be oxidised to different nitrogen oxides (Eq. 3–5), which was also observed in the present studies; together with an increase in the copper content, the reaction proceeded toward N₂O (Eq. 4). N₂O could also be produced by the non-selective reduction of NO with ammonia (Eq. 6). However, a decrease in NO conversion highlights ammonia consumption in a side-reaction.



In the case of the second studied reaction (N₂O decomposition, Fig. 5), the catalytic activity increases continuously with an increase in the copper content (the best results were obtained for the 15%Cu-CHA sample). The only nitrogen product detected in this reaction was N₂. Taking into account the mechanism of N₂O decomposition, in which the rate-determining step is the recombining of desorbing oxygen atoms adsorbed on Cu sites, the overall reaction rate is higher for samples with higher Cu loading (shorter Cu–Cu distance) [40]. Groothaert et al. [41,42] attributed the high catalytic activity of Cu-modified zeolites in N₂O decomposition to the presence of Cu-dimers, bridged by two adsorbed oxygen atoms (from which O₂ can be easily desorbed), which are the so-called bis(μ-oxo) dicopper species. Thus, the increased catalytic activity in the Cu-CHA series can be related to the increase in the Cu content (decreased distance between the active sites) which facilitated oxygen desorption. It is worth noting that together with an increase in the copper content, the contribution of the Cu_xO_y oligomeric species, which are expected as the most active in this reaction, also increased (Fig. 3).

Taking into account the very high activity of the Cu-modified CHA samples in the DeNO_x process, the stability of such a system in this reaction was examined. Among the catalysts with different Cu contents, the 5%Cu-CHA sample was chosen (due to its high NO conversion and selectivity to N₂ with simultaneous low copper content (economical issue)) to perform the stability test. Over the chosen sample, five cycles of the catalytic test were conducted without any catalyst regeneration (Fig. 4B). After the first catalytic test, a small drop in NO conversion was observed in the low temperature range (100–275 °C). At higher temperatures

(275–350 °C), when the conversion reaches about 100%, the results do not practically differ from each other. During subsequent cycles, NO conversion remained practically unchanged. Also, in the case of reaction selectivity to N₂, no significant changes were observed. It seems that after the first catalytic run, the steady-state was obtained and the 5% Cu-CHA sample showed high stability during further cycles.

3.2. Mesopore-structured CHA zeolite

In the second part of the studies, CHA zeolite was modified by the use of base and acid solutions of various agents (with different concentrations), temperatures and durations of treatment (all modification parameters are presented in Table 1). The efficiency of the base and acid treatments was evaluated based on the changes in textural properties of the samples (S_{BET} , S_{EXT} , V_{MIC} , and V_{MES} ; Table 1). Upon base treatment with NaOH (the most frequently used desilication agent), a significant dissolution of CHA was observed. All of the textural parameters decreased significantly, even under relatively mild conditions (0.1 M NaOH, 0.5 h, 20 °C), which can be related to the low stability of aluminophosphate domains in alkaline media [43] (the content of phosphorus in the sample is significantly high). The application of weaker base solutions, such as quaternary amines (TPAOH), is known as a way for the generation of mesoporosity in zeolites with better preservation of their microporosity [44,45]. The best results were obtained with the use of TPAOH, when 0.2 and 0.3 M solutions were used, at 65 °C and for 0.5 h (the CHA(BT_0.2_TPAOH_65)0.5 and CHA(BT_0.3_TPAOH_65)0.5 samples). In the case of these samples, base treatment resulted in a significant development of the external surface area and mesopore volume, accompanied by a decrease in the BET surface area and micropore volume. In the case of the CHA(BT_0.3_TPAOH_65)0.5 sample, such modification of treatment conditions enabled the mesopore volume of CHA to increase by about 3 times. The use of strong acidic conditions (0.2 M HCl, 65 °C, 2 h) did not significantly influence the CHA porosity (all the textural parameter values were slightly decreased), in contrast to the use of NaOH solution, showing the higher sensitivity of the parent sample for the alkaline conditions. Acid treatment with Na₂H₂EDTA under mild conditions (low concentration—0.04 M or low temperature—25–50 °C; the CHA(AT_0.2_EDTA_25)4, CHA(AT_0.2_EDTA_50)4 and CHA(AT_0.04_EDTA_100)4 samples) enhanced the crystallinity of the CHA material. Both the BET surface area and volume of micropores increased, which could be connected to the dissolution of extra-framework aluminium or other impurities and resulted in enhanced microporosity [43]. More severe conditions resulted in a significant enhancement of mesoporosity and external surface area of the samples. The best results were obtained in the case of the CHA(AT_0.2_EDTA_100)4 sample, which was characterised by a mesopore volume that was almost 4 times greater than that of the parent CHA. Thus, the best results for mesopore formation were obtained with the use of TPAOH and Na₂H₂EDTA; however, taking into account the greatest volume of generated mesoporosity and the smallest decrease in S_{BET} and V_{MIC} , the CHA(AT_0.2_EDTA_100)4 sample was chosen as the

most promising for further modification with copper and expanded physicochemical characterisation.

A comparison of N₂ sorption isotherms of the parent CHA and the mesopore-modified CHA(AT_0.2_EDTA_100)4 sample is presented in Fig. 6A. A decrease in the adsorbed N₂ volume at low partial pressures is connected with the loss in microporosity. At higher partial pressures after porosity modification, a hysteresis loop, which is the result of capillary condensation, appeared in mesopores. The shape of the loop can be classified as H4 (according to the IUPAC classification [32]), which is characteristic of mesoporous zeolites with a wide distribution of pore sizes.

The modification of the porous structure also resulted in the changes of phase composition of the parent sample. Fig. 6B shows XRD patterns of the unmodified CHA material and the sample after treatment with Na₂H₂EDTA. The analysis of the obtained diffractogram with X'Pert High-Score (PDF-4+ database) revealed the presence of silicoaluminates of the MFI structure, silicon oxide and TiO₂ in the form of rutile and anatase. This result suggests the dissolution of the parent material and the formation (besides Si and Ti oxides) at high temperatures (100 °C) of a new phase with MFI topology or selective dissolution of the zeolite framework (dissolution and reverse incorporation), which resulted in a different zeolite structure. It is worth noting that, despite the partial transformation of the zeolitic matrix into MFI zeolite, the properties of the resulting material are significantly different in comparison to conventional ZSM-5 zeolite. The volume of micropores in the modified material is very low for the zeolite material, which means that the content of the MFI phase is relatively low and the majority of the sample consists of mesoporous TiO₂ and SiO₂.

The changes in the porous structure and phase composition observed after acid treatment of CHA were accompanied by changes in the strength and concentration of acid sites. Fig. 7A shows the NH₃-TPD profiles of CHA and the modified CHA(AT_0.2_EDTA_100)4 sample. In the case of both samples, two desorption maxima attributed to weak (about 200 °C) and strong acid sites (about 400 °C) were obtained [1,46]. After the modification of CHA with Na₂H₂EDTA, the concentration of acid sites significantly decreased (about 4.5 times), which can be connected to both a decrease in the external surface area and the extraction of framework aluminium. Moreover, the high-temperature peak was shifted to lower temperatures in comparison to the parent sample (overlapped with the low-temperature peak). This proves that the applied modification method disturbed the structure of CHA and resulted in a smaller quantity of acid sites of lower strength.

The changes in the porous structure and acidity caused by dealumination of zeolite with Na₂H₂EDTA also influenced the form and content of the introduced copper species. Fig. 7B shows the UV–vis-DR spectra of CHA and CHA(AT_0.2_EDTA_100)4 modified with 5 wt. % of copper by using wet impregnation. The generation of mesoporosity resulted in the introduction of copper, mainly in the form of monomeric cations and small Cu_xO_y aggregates (absorption at about 200–400 nm). Moreover, the contribution of the oligomeric Cu_xO_y species increased in relation to monomeric copper cations. It can be concluded that the

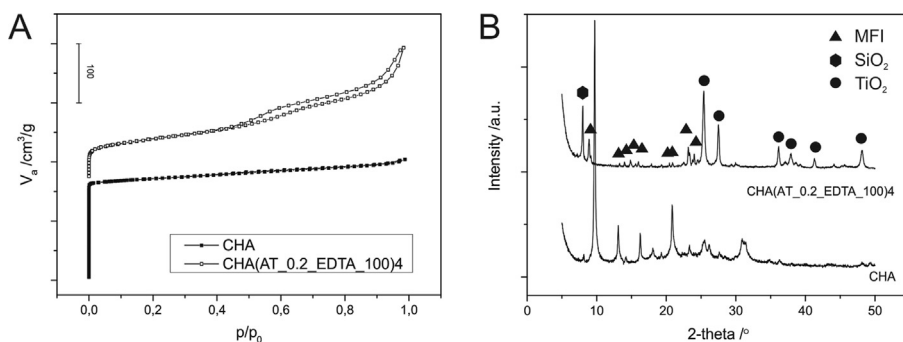


Fig. 6. Nitrogen adsorption–desorption isotherms (A) and XRD patterns (B) of the parent CHA and the micro-mesoporous sample CHA(AT_0.2_EDTA_100)4.

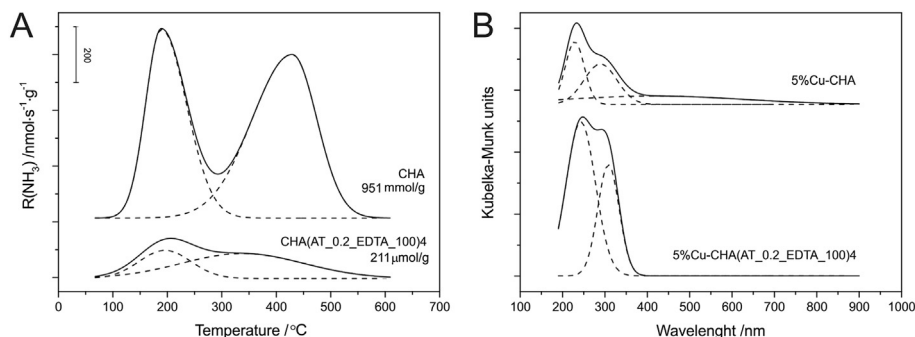


Fig. 7. NH_3 -TPD profiles (A) and UV–vis-DR spectra (of the samples modified with Cu) (B) of parent CHA and the micro-mesoporous sample CHA(AT_0.2_EDTA_100)4.

modified porous structure increased accessibility to the ion-exchange positions in the sample. Thus, the formation of Cu sites with high dispersion was favoured and the formation of bulk CuO on the catalyst surface was not observed.

The influence of the applied modifications of the parent zeolite on its catalytic activity in both considered processes (NO reduction with NH_3 and N_2O decomposition) is presented in Fig. 8. In the case of the De NO_x process (Fig. 8A), the NO conversion over the modified CHA sample slightly decreased in comparison to conventional zeolite. The difference in the catalysts' activities was observed, especially at higher temperatures (300

–400 $^\circ\text{C}$). The drop in NO conversion at this temperature range can be connected to the competitive side-reaction of direct ammonia oxidation (Eq. 3–5), which suggests that the CHA(AT_0.2_EDTA_100)4 sample could be considered a better catalyst of the ammonia oxidation reaction. Especially, the selectivity of this process to nitrogen did not change significantly (results are not shown), which means that the main product of ammonia oxidation was nitrogen (Eq. 3).

The lower activity of the modified sample in comparison to the parent CHA material can be connected to the decreased BET surface area and acidity, which are important factors in the De NO_x process.

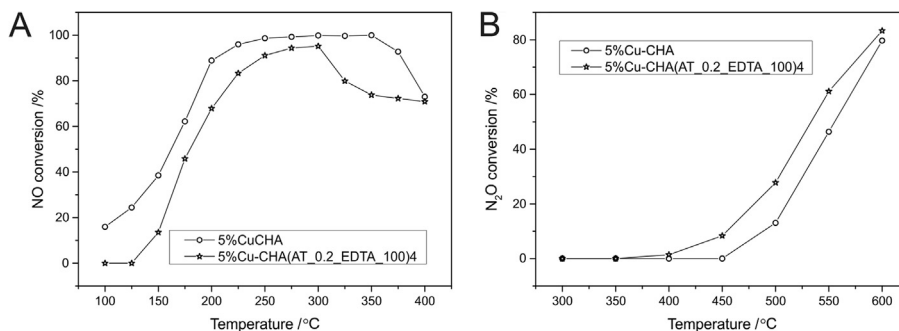


Fig. 8. Temperature dependence of NO (A) and N_2O (B) conversion over 5%Cu-CHA and 5%Cu-CHA(AT_0.2_EDTA_100)4. Conditions: the balancing gas is 2500 ppm NO, 2500 ppm NH_3 , 25,000 ppm O_2 and the total flow rate is 40 ml/min (A) and the balancing gas is 1000 ppm N_2O , 40,000 ppm O_2 and total flow rate 50 ml/min (B); He is the balancing gas and the weight of the catalyst is 0.1 g.

The comparison of catalytic activity of the 5%Cu-CHA and 5%Cu-CHA(AT_0.2_EDTA_100)4 samples in N₂O decomposition is presented in Fig. 8B. The treatment of CHA with Na₂H₂EDTA resulted in an increase in the catalytic efficiency. N₂O decomposition proceeds with the contribution of red-ox active sites, so that the higher catalytic activity of the modified sample can be related to the higher contribution of oligomeric Cu_xO_y species; these were found as active Cu forms in this reaction. However, the high contribution of TiO₂ in the modified sample can also play a significant role in N₂O decomposition. TiO₂ is known as an active component in this reaction, used both as the catalyst promoter [47] and the support [48]. The role of TiO₂ in this process could be related to the facilitation of oxygen species migration (through the oxygen vacancies sites) and its easier recombination [49] (oxygen desorption from the catalyst surface is regarded as a rate-determining step of this reaction).

4. Conclusions

Commercial CHA zeolite supplied by Clariant Company, modified with copper by wet impregnation method, was examined as a catalyst in two catalytic reactions: NO reduction with NH₃ and N₂O decomposition; this showed high catalytic activity, especially in a former reaction. Among the studied catalysts with various Cu contents (1, 5, 10 and 15%), the sample modified with 5 wt. % was chosen as the optimal sample; for this sample, the high catalytic stability in five subsequent reaction cycles was observed.

Modification of CHA by base and acid treatment with NaOH/TPAOH and HCl/Na₂H₂EDTA under various conditions enabled the selection of optimal modification parameters, resulting in the highest generated mesopore volume. Based on the results of nitrogen sorption measurements, the sample modified with 0.2 M Na₂H₂EDTA at 100 °C for 4 h was chosen as the most promising for the more detailed catalytic studies. The physicochemical characterisation of the mesopore-modified sample by using X-ray diffraction, NH₃-TPD and UV–vis-DR spectroscopy (the sample modified with Cu) revealed the changes in the phase composition, decrease in surface acidity and differences in the form of introduced copper species. The applied modification methods increased the catalytic efficiency of the Cu-CHA zeolite in N₂O decomposition, which can be related to the higher contribution of Cu species in a less-aggregated form (mainly in the form of monomeric cations and Cu_xO_y aggregates, which are known to be active in this reaction) and the higher contribution of TiO₂.

In conclusion, modification of the CHA zeolite by the applied methods enabled the adjustment of its porous and crystalline structure, acidity and form of introduced transition metal species, which increased its catalytic activity in the process of N₂O decomposition. Thus, based on the presented results, modification of the commercial CHA zeolite (Clariant) can influence its activity in catalysis.

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