



REDUCTION OF NO WITH METHANE OVER METAL ION-EXCHANGED MORDENITE

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ABSTRACT

This article presents the results of research studies on the possibilities of application of natural zeolite-mordenite for the reduction of nitrogen oxide. Various kinds of metal ions were added to the zeolite samples using the ion-exchange method. The effect of metal contents was shown for the mordenite and related to their catalytic properties. The catalytic properties of Cu-, Co-, Ni- were compared for NO reduction with methane. High nitric oxide conversions were observed for copper and cobalt-mordenite, especially in the temperature range between 400 and 500°C. Copper- and cobalt-mordenite catalysts showed higher activities and selectivities than catalysts composed of nickel-exchanged mordenite.

Keywords: selective catalytic reduction of NO, mordenite, catalysts, Co(II), Ni(II), Cu(II)

INTRODUCTION

Since the selective reduction of NO by hydrocarbons over a Cu-ZSM-5 catalyst in an oxidizing atmosphere was first reported, this reduction technology has become available. The main advantage of the corresponding reaction is the use of a gas mixture which is very similar to that found in exhaust gases. The process opens new possibilities for the catalytic elimination of NO from exhaust gases. [1-3] The selective catalytic reduction of nitrogen oxides by hydrocarbons has drawn much attention since it may offer an attractive alternative to the selective catalytic reduction by ammonia. The selective catalytic reduction of NO by methane is suitable for small stationary sources such as power plants because methane is easily available as natural gas, which is supplied through

pipelines in many countries, and many power plants use natural gas as a fuel. Removal of nitrogen oxides in the exhaust gases from industrial boilers and vehicle engines is necessary to protect our environment. Selective catalytic reduction of NO with hydrocarbon reductants is an attractive means for the purification of exhaust gases, especially for the purification of gases containing excess oxygen, emitted from lean-burn engines and diesel engines. [3-6] For off-gases from stationary sources of emission, both NO reduction by hydrocarbons and direct NO decomposition represent alternative methods of NO removal. Catalysts containing noble and non-noble transition metals supported on zeolites were investigated in SCR (Selective Catalytic Reduction) of NO_x by methane in the presence of excess oxygen. [4-8] A decade ago, Armor [5] showed that Co-zeolites catalyzed the selective reduction of NO with methane in the presence of excess water. The addition of a second metal, such as Pd or Pt, was shown to enhance the catalytic performance and decrease the deleterious effect of water. [9-12] Co- and Pd catalysts supported on zeolites were investigated by numerous scientists. [13-16] Co- and Pt, Co-mordenite catalysts were found to lose about 50% of their initial NO-reduction and CH₄-oxidation activity during a long catalytic NO_x-SCR test. [21-23] Pieterse et al. [24] studied the influence of the zeolite structure type (mordenite, ferrierite and ZSM-5) on the activity and durability of the Co, Pd-forms of zeolites. They concluded that the formation of metal oxides, loss of dispersion and dealumination are the three factors involved in the deactivation of catalysts having mordenite, ZSM-5 or ferrierite structures. This work aims to provide additional insight into the catalytic reduction process using natural zeolite catalysts enriched with copper, cobalt, nickel.

EXPERIMENTAL

Catalysts preparation

MOR (mordenite) zeolites in the protonic form were provided by Zeolysts. The MOR catalysts were prepared from the sodium form of mordenite with Si/Al = 6. The addition of metals into zeolites was performed by ion exchange with Cu, Co, Ni acetate solution, following the method described.

The mixture was kept under agitation at the desired temperature (30 and 50°C) for 12 hrs. Next, the suspension was filtered and thoroughly washed with deionized water in order to completely remove the occluded salt, and the solid was then air dried at 120°C for 12 hrs. The whole procedure was repeated twice for all of the catalysts. Finally, the samples were air-calcined at 550°C for 1 hr. Information about the prepared catalysts is summarized in Table 1. These catalysts were referred to as a function of temperature of ion exchange and number of ion exchange steps (1 or 2). The ion exchange level specified in Table 1 was determined taking as a reference the number of aluminum atoms contained in the structure.

To characterize the catalysts, the chemical composition of the surface monolayer and the phase composition were determined. The content of individual metal

cations added into the ferrierite matrix of each test catalyst were determined using the AAS spectrophotometer, Spekr AA 800, from Varian, after previous mineralization of samples using the microwave digestion system Mars 5, CEM Analytical Laboratory, at the Maria Curie-Skłodowska University in Lublin.

Catalytic activity measurement

The catalytic tests were carried out under atmospheric pressure in a gradientless reactor, using 1 g of catalysts pretreated in situ at 550°C for 1 hr under helium flow (60 cm³/min). The reaction mixture, comprising NO (1500 ppm), CH₄ (4000 ppm) and He as balancing gas, was passed over the catalysts at a total flow rate (10 cm³/min) in the temperature range between 200°C and 500°C. The reactants and products were analyzed by means of an on-line gas chromatograph with a 5A Molecular Sieve-packed column, used for separating nitrogen, nitrogen oxide methane and carbon monoxide.

The stream of gases (NO + CH₄) was monitored using the flow and fed into the mixer. Before the measurements the studied catalyst was reduced by hydrogen, of which the flow was adjusted with a manostat and a fleometre. The reactor temperature was controlled using a Trol-8120 controller, combined with a thermocouple located in the reaction space reactor.

The catalysts were pretreated in helium at 500°C for 1 hour, where they were annealed before the steady-state experiment in the reaction mixture and consecutive measurements were performed stepwise starting from 200 up to 500°C. All kinetic experiments were carried out under helium, determining isothermally the relationship between the reaction rate of NO reduction and the degree of NO conversion. The total concentration of hydrocarbon (CH₄), nitrogen oxide (NO), N₂ formation and carbon dioxide (CO₂) over the tested catalysts was checked by Chrompak-GC equipped with a TCD detector. The NO conversion was calculated from the yield of N₂, and the methane conversion was calculated from its consumption, which included the methane consumed in the reaction with nitric oxide. The extent of NO conversion to N₂ was used to evaluate the catalyst's activity. Temperature dependences of the reaction rate vs. NO conversion were measured (for the respective degree of conversion T = const). From the reaction rate functions obtained from the degree of NO conversion at the given temperatures, the temperature dependence of the reaction rate at the constant degree of NO conversion for various catalysts was plotted. The extent of NO reduction was evaluated in different ways: for NO, by determining the consumption of NO (X_{NO} – conversion of NO) as well as the production of N₂ (yield N₂). A catalyst's activity is defined as the percentage of conversion [X(%)] of the reactant (NO) to all products:

$$X_{\text{NO}}(\%) = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \cdot 100 \quad (1)$$

The subscripts *in* and *out* indicate the inlet and outlet concentrations of the reactant (NO). The reaction selectivity to N₂ {S_{N₂}} is defined as follows:

$$S_{N_2} (\%) = \frac{[N_2]_{out}}{[N_2]_{out} + [N_2O]_{out}} \cdot 100 \quad (2)$$

However, conversion to specific products (NO and N₂) is also indicated in the relevant figures.

RESULTS

The contents of the active metals (Cu, Co, Ni) and characterization of zeolite-based catalysts are summarized in Table 1.

Table 1. Composition and characterization of zeolite-based catalysts.

Catalysts	Metal content (wt. %)	Ion exchange steps and temperature (°C)	Ion exchange level (%)	Me/Al ratio
Cu1-30- MOR	1.92	1-30	32	0.160
Cu1-50- MOR	2.14	1-50	35	0.175
Cu2-30- MOR	3.40	2-30	56	0.280
Cu2-50- MOR	3.62	2-50	60	0.300
Co1-30- MOR	1.80	1-30	30	0.150
Co1-50- MOR	1.94	1-50	32	0.160
Co2-30- MOR	2.60	2-30	43	0.210
Co2-50- MOR	2.81	2-50	46	0.230
Ni1-30- MOR	1.44	1-30	24	0.120
Ni1-50- MOR	1.61	1-50	27	0.140
Ni2-30- MOR	2.04	2-30	34	0.170
Ni2-50- MOR	2.24	2-50	37	0.185

It follows from Table 1 that the preparation of copper, cobalt, nickel catalysts from zeolite structures with different metal contents led to obtaining catalysts having a broad range of Me/Al ratios. Consequently, metals in the amount of 1-4% by weight were added to the zeolite structures.

The NO reduction reaction in the inert atmosphere was followed by monitoring NO consumption, N₂ production and selectivity to N₂ vs. time in the temperature range from 200 to 500°C. NO consumption was always higher than N₂ production, especially for low temperatures and low conversions.

Compared in Fig. 1 are the profiles obtained for the four exchanged catalysts Cu2-50-MOR, Cu2-30-MOR, Cu1-50-MOR, Cu-1-30-MOR. One favorable range of temperature, 400–500°C, was detected for all catalysts.

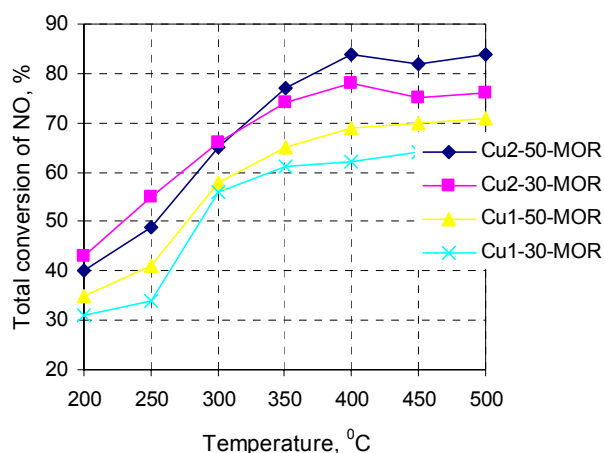


Fig. 1. The effect of temperature on the conversion of NO for Cu-MOR catalysts.

The Cu2-50-MOR catalyst (Fig. 1) has a higher conversion (86%) compared with other catalysts (in the range: 1.92-3.62%). The lowest conversion of NO reaches 64% in the most favorable temperature range. The curves representing the course of NO reduction for the Cu2-MOR catalysts have their maximums for two temperatures: 400 and 500°C. However, from an analysis of the figure it follows that the optimum temperature for a given process is in the range of 400-500°C for all the catalysts.

Cobalt catalysts are more favorable for the reduction of NO with methane, as they allow an almost 90% reduction of pollution. The content of cobalt added to the zeolite does not exceed 2.8% by weight. As in the case of copper, the metal added to the zeolite in the cobalt catalysts had a positive impact on the effectiveness of the reduction process. Figure 2 shows the level of NO conversion for the cobalt catalysts at a similar level of 90% for mordenite.

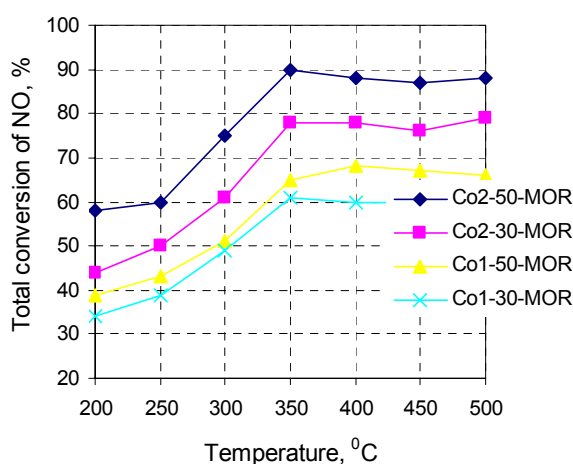


Fig. 2. The effect of temperature on the conversion of NO Co-MOR catalysts.

Nickel catalysts reduced the level of NO by about 70% (Fig. 3). Reductions were best in the range 350-500°C and the process was uniform. The Ni-MOR catalysts contain from 1.44 to 2.42% by weight of metal placed on the mor-denite and reduce NO by 68% in the entire temperature range 350-500°C. Lower contents of Ni result in much lower degrees of NO reduction, even in a higher temperature range 350-500°C.

The catalysts Cu-MOR and Co-MOR are more active in the reaction of NO reduction with methane, compared with Ni-MOR (Figs. 1-3). The total NO reduction by methane on the Cu-MOR catalysts is more than 80%, and for Co-MOR it reaches 90%. On the other hand, a 68% reduction of NO was obtained for the Ni-MOR catalysts (Fig. 3). The obtained results allow the conclusion that the new catalytic materials obtained by the addition of Ni cations into mor-denite networks are not suitable for the testing process.

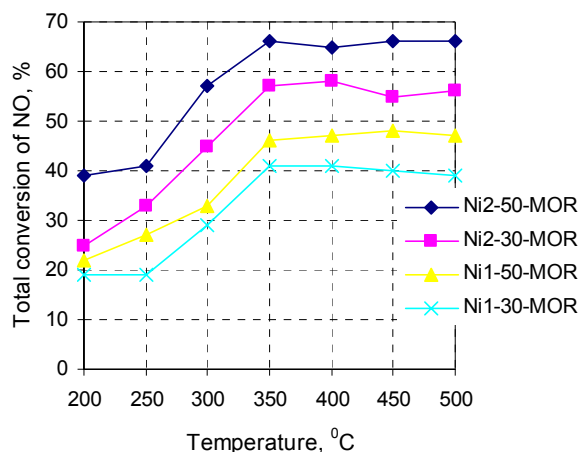


Fig. 3. The effect of temperature on the conversion of NO for Ni-MOR catalysts.

The catalysts selectivity to N_2 for Cu-MOR are compared in Fig. 4. The maximum NO conversion into N_2 and the most active temperature (T_{max}) clearly depend on the zeolite type.

The Cu2-50-MOR catalyst presents the highest maximum NO conversion into N_2 of about 70% at 500°C – Fig. 4. Cu2-30-MOR presents an intermediate value (60%) compared with the maximum conversion observed for Cu2-50-MOR, which is nearly constant in the temperature range 400-500°C. The Cu1-30-MOR catalyst showed a very low maximum NO conversion (50%) in the temperature range 400-500°C. As regards the total nitrogen oxide reduction, the same trends are observed in all the temperature ranges.

Compared in Figures 4-6 are the selectivity to N_2 for zeolite catalysts with different structures, approximate Me/Al ratios (or metal exchange level) but different metal contents. This set of figures clearly illustrates that the catalytic activity profiles for NO SCR with methane depend on the zeolite structure, and

the type of metal ion introduced into the zeolite and its contents. Cu catalysts always being distinguished by their highest activity.

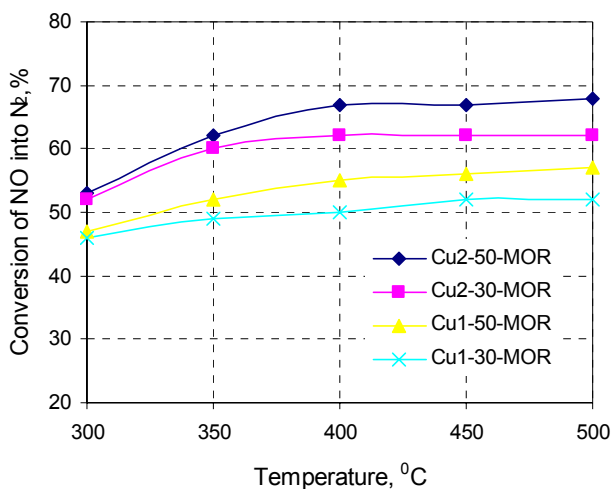


Fig. 4. The influence of copper loading of mordenite on the SCR with methane.

The cobalt exchanged mordenite catalysts have slightly different profile curves of NO reduction to N₂, which varies in the range 350-500°C within 71-73% (Fig. 5). Conversion of NO is stable in the 350-500°C range, reaching a level above 70%. A similar process is observed for the Ni catalysts. In the range of 350-500°C the curves have an almost straight course, reaching a 53% reduction of NO to N₂ (Fig. 6).

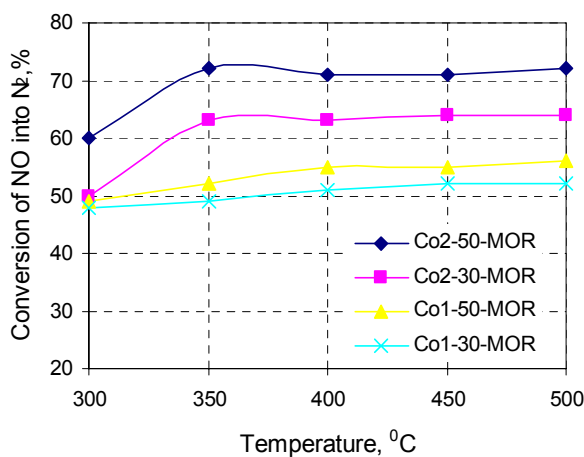


Fig. 5. The influence of cobalt loading of mordenite on the SCR with methane.

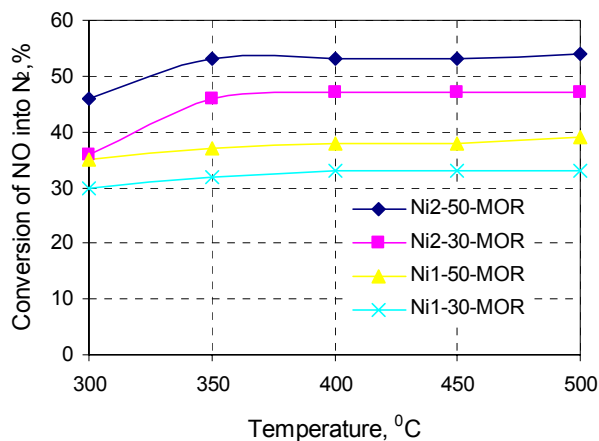


Fig. 6. The influence of nickel loading of mordenite on the SCR with methane.

Selectivity to nitrogen for different catalysts as a function of test temperature reaches the level of 70%. Data analysis indicates that the Co, Cu-Mor catalysts are among those with the highest activities and selectivities in the test series introduced by metals.

DISCUSSION

The investigation results show that the zeolite structure affects the nature and reducibility of metal ions, NO adsorption, and the catalytic behavior for SCR of NO with methane [22, 28, 33]. For the Co catalysts, our results are quite evident that this type of catalysts are characterized by a high catalytic activity (the maximum NO conversion to N₂ observed for the catalyst was about 70%) for SCR of NO with methane. The Co-MOR catalysts have the highest activity regardless of the Me/Al ratio. The maximum conversion observed in the curves corresponding to the MOR catalysts also indicates that there is a clear dependence between the catalytic activity of the studied catalysts and their composition, in terms of metal and Al contents. The maximum NO conversion to N₂ was observed for the Co2-50-MOR catalysts with Co/Al = 0.23 and 46% of the cobalt exchange level. The first approach to explain the different catalytic activities observed between the series of catalysts with different structures could be to consider the corresponding differences in the NO absorption capacity which indicates that the highest-activity catalysts are those characterized by a higher tendency to absorb NO. Li et al. [25] suggested that the catalytic activity of a catalyst to NO conversion is proportional to its NO absorption capacity at a room temperature. They considered that the properties of the zeolites, e.g., shape selectivity did not influence the reaction of NO reduction with hydrocarbons [22, 26, 27].

The differences in activity found for these catalysts [28] only concern extension for lower temperatures of the active-temperature window for the catalysts with higher Me/Al ratios. Taking into account all the results reported up to now for the two types of zeolites, we verified that, in all the cases, it was possible to explain the differences detected for each sample. The zeolite structure affects the nature of the metal that is incorporated in catalysts having similar chemical compositions. Summing up, we think that the main effect of the zeolite structure is to create conditions for the exchange of the metal in a peculiar environment.

CONCLUSION

This work showed that the zeolite structure affects the nature of the metal, its reducibility, NO absorption capacity and catalytic performances for SCR of NO with methane. Cu- and Co-MOR catalysts are characterized by the highest activities, regardless of the ratio of Me/Al and the metal content in the zeolite. The obtained catalysts Co- and Cu-MOR can prove to be those with the highest activities, regardless of metal ion content in the zeolite structure. The tests also confirmed the dependence of the catalytic activities of different catalysts in the process of CH₄-NO SCR on the type and quantity of the cations introduced into the zeolite structure.

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