

Influence of the exchanged metal ions (Cu, Co, Ni and Mn) on the selective catalytic reduction of NO with hydrocarbons over modified ferrierite

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This article presents the research results concerning the possibilities of natural zeolite-ferrierite application for the reduction of nitrogen oxide. H-FER forms were modified by Cu^{+2} , Co^{+2} , Mn^{+2} , Ni^{+2} using an ion exchange procedure. The effect of metal contents was shown for the ferrierite matrices and related to their catalytic properties. The catalytic properties of Cu-, Co-Ni-, and Mn- were compared for NO reduction with methane. High NO conversion was observed for copper and cobalt-ferrierite catalysts, especially in the temperature range 400 and 500°C. It was found that copper- and cobalt-ferrierite catalysts have higher activity and N_2 selectivity than the catalysts composed of nickel and manganese doped on ferrierite. Moreover, the nickel and manganese containing catalysts produced more nitrous oxide than nitrogen. The presence of both copper and cobalt species seems to be an indispensable condition for a large activity and selectivity in the NO reduction.

Keywords: catalytic reduction, nitrogen oxides (NO_x), ferrierite, selective catalysts, ion exchanged.

INTRODUCTION

The selective catalytic reduction (SCR) process with NH_3 is now commercially used to remove nitrogen oxide, especially nitrogen monoxide (NO), from a large scale stationary sources such as industrial and utility boilers¹. The development of the low-temperature SCR catalysts working at 150–250°C can offer a great solution to avoid all problems associated with the existing commercial system^{2–4}. However, the use of NH_3 still includes several operational problems such as handling and storage difficulties, NH_3 slip causing secondary pollution. Recently, the selective reduction of nitrogen monoxide (NO) by hydrocarbons in an oxidizing atmosphere has been reported over various catalysts⁵. It is promising that these new types of NO reduction may overcome the disadvantages of the use of NH_3 described. It can also be applied to NO_x emission from diesel engines as well as from sanitary facilities. One may not need to supply the reductants, hydrocarbons, in this reaction system since the exhaust stream from a diesel engine already contains hydrocarbons which can be utilized for the removal of NO_x. Therefore, catalytic removal of NO from diesel engines without the supply of reductants is one of the most attractive features of this reaction system. Since the selective reduction of NO by hydrocarbons over a Cu-ZSM-5 catalyst in an oxidizing atmosphere has been 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. This process opens new possibilities for the catalytic elimination of NO from exhaust gases^{4,5}. 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 the gases containing excess oxygen emitted from lean-burn engines and diesel engines^{5–7}. For the off-gases of stationary sources of emission both, NO reduction by hydrocarbons and direct NO decomposition represent alternative methods of NO removal. SCR of NO_x with ammonia is widely used for cleaning flue gases emitted by the powder stations and chemical industrial plants. The substitution of ammonia by methane seems to be economically attractive and cheapest. Methane is also quite neutral for living organisms though it belongs to greenhouse gases. But it can be an internal reducing agent of NO in the effluent gases of boilers using natural gas as a fuel. Catalysts containing noble and non-noble transition metals supported on zeolites were investigated in SCR of NO_x by methane in the presence of excess oxygen^{6–9}. A decade ago, Armor⁸ showed that Co-zeolites catalyze 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^{10–13}. However, the durability of both mono- and bimetallic zeolite catalysts is still a key issue.

Co- and Pd catalysts supported on zeolites were investigated by numerous scientists^{14–17}. The Co-ferrierite catalyst with the addition of Pd showed higher activity in the temperature range 300–500°C than the Co-ferrierite catalysts with the addition of Pt, Ir, La, In^{18–21}. The PtIn-ferrierite catalysts show high activity for NO reduction and conversion of NO to N_2 was observed below 500°C²². Co- and Pt, Co-ferrierite catalysts were found to lose about 50% of their initial NO-reduction and CH_4 -oxidation activity during a long catalytic NO_x-SCR test^{23–26}. Pieterse et al.²⁷ studied the influence of the zeolite structure type (mordenite, ferrierite and ZSM-5) on the activity and durability of the Co, Pd-forms of zeolite. They concluded that formation of metal oxides, loss of dispersion and dealumination are the three factors involved in the deactivation of catalysts of ZSM-5 or ferrierite structures. This work aims to provide additional insight into the catalytic reduction

process using natural zeolite catalysts enriched in copper, cobalt, nickel, manganese.

EXPERIMENTAL

Catalysts preparation

The FER (ferrierite) in the protonic form were provided by the Zeolysts Company. Doping the metals to the zeolite was performed by the ion exchange with Cu, Co, Ni and Mn acetate solution, according to the method described below. The mixture was kept under agitation at the desired temperature (30 or 50°C) for 12 h. The whole procedure was repeated twice for all catalysts. The obtained precursor was then washed with distilled water, dried and calcined for 1 hour at 500°C in air. The catalyst was tableted with the extruder, then it was pressed through a sieve with the holes of the 1–1.2 mm diameter. At the end of the procedure the prepared samples were put to the reactor and reduced in a hydrogen atmosphere at 500°C for one hour.

These catalysts were referred to as a function of temperature of ion exchange and number of the ion exchange phases (1 and 2). The ion exchange level presented in Tab. 1. was determined by the number of alumina atoms contained in the structure of the zeolite.

The chemical composition of the monolayer surface and phase composition were determined in order to characterize the catalysts. The content of individual metal cations added into the matrix ferrierite, for all the tested catalysts, were determined using the spectrophotometer AAS, Spektr AA 800, Varian, after previous mineralization of samples using a microwave digestion system, and was measured with the XRF method (X-ray fluorescence) in Department of Analytical Laboratory, Faculty of Chemistry of UMCS.

Catalytic activity measurement

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

The stream of gases (NO + CH₄) was monitored by supervising the flow and then was passed into the mixer. Before the measurements the studied catalyst was reduced by hydrogen, whose flow was adjusted with a manostat and a fleometre. The reactor temperature was controlled with a controller Trol-8120, 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. The consecutive measurements were performed step by step starting from 200 up to 500°C. All kinetic experiments were carried out in an atmosphere of helium, determining isothermally relationship between the reaction rate of NO reduction and the degree of

NO conversion. The total concentration of hydrocarbon (CH₄), nitrogen oxide (NO), N₂ and carbon dioxide (CO₂) over the tested catalysts was checked by Chrompak-GC equipped with the TCD detector. Conversion of NO was calculated from the yield of N₂, and the methane conversion was calculated by 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 catalytic activity of catalysts. Temperature dependences of the reaction rate as a function of NO conversion was measured (for the respective degree of conversion T = const). From the functions of the reaction rate obtained from the degree of NO conversion at the given temperatures, temperature dependences 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 by production of N₂ (yield N₂). The activity of the catalyst is defined as the percent 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 the outlet concentrations of the reactant (NO). The reaction selectivity to N₂ {S_{N₂}} is defined as follows:

$$S_{\text{N}_2}(\%) = \frac{[\text{N}_2]_{\text{out}}}{[\text{N}_2]_{\text{out}} + [\text{N}_2\text{O}]_{\text{out}}} \cdot 100 \quad (2)$$

The conversion to specific products (NO and N₂) was presented in the relevant figures below.

RESULTS

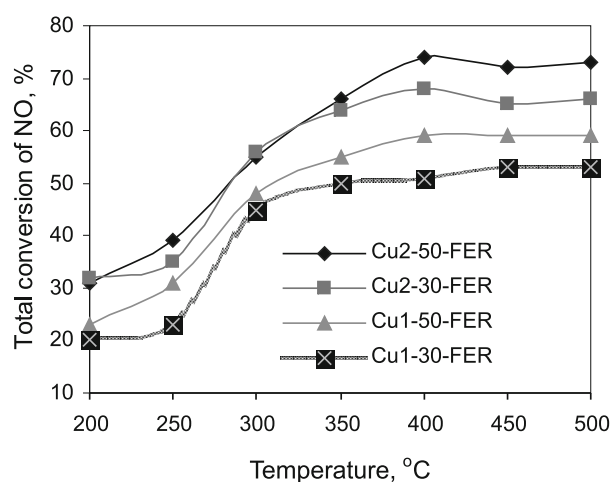
The contents of the active metal (Cu, Co, Ni, Mn) and characteristics of zeolite-based catalysts are summarized in Table 1.

According to Table 1 preparation of copper, cobalt, nickel and manganese catalysts from zeolite structure, and metal contents led to the catalysts have a great impact on the Me/Al ratios. As a consequence, metals of the weight range 1–4% were doped to the structure of each zeolite. The reaction of NO reduction in the inert atmosphere was followed by monitoring NO consumption, N₂ production and selectivity to N₂, as a function of time in the temperature range 200–500°C. NO consumption was always higher than N₂ production, especially at low temperature and low conversion. Fig. 1a compares the profiles obtained for the four exchanged catalysts Cu2-50-FER, Cu2-30-FER, Cu1-50-FER, Cu1-30-FER containing similar Si/Al ratios and copper contents in the range: 2.82–4.55%. The most favorable range of temperature for all the catalysts was 400–500°C. The total conversion of NO level achieved 74% for the Cu2-50-FER catalyst. The catalysts containing smaller quantities of copper let to obtain lower NO reduction-50–60%.

The analysis of the figure shows that the best temperature for the given process in the range of 400–500°C for all the catalysts. Cobalt catalysts are more favorable for the reduction of NO with methane than other metals, as they allow to obtain almost 80% reduction of NO. The content of cobalt added to all zeolites does not exceed

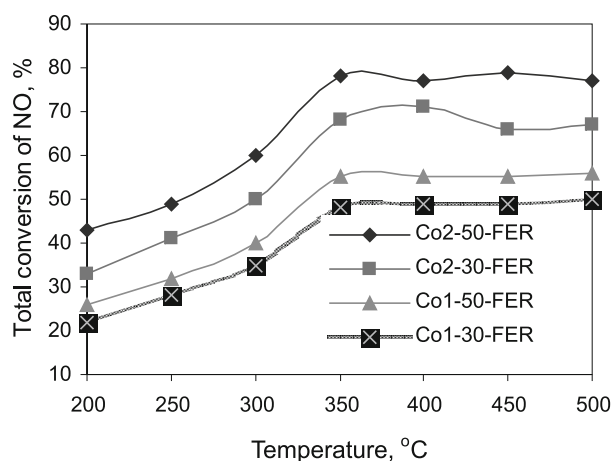
Table 1. Composition and characterization of the zeolite-based catalysts

Catalysts	Metal content (wt. %)	Number of the repetitions/T (°C)	Ion exchange level (%)	Me/Al ratio
Cu1-30-FER	2.82	1/30	47	0.235
Cu1-50-FER	3.02	1/50	50	0.250
Cu2-30-FER	4.22	2/30	69	0.345
Cu2-50-FER	4.55	2/50	75	0.375
Co1-30-FER	2.36	1/30	39	0.195
Co1-50-FER	2.56	1/50	42	0.210
Co2-30-FER	3.16	2/30	52	0.260
Co2-50-FER	3.46	2/50	57	0.285
Ni1-30-FER	2.04	1/30	34	0.170
Ni1-50-FER	2.15	1/50	36	0.180
Ni2-30-FER	2.34	2/30	39	0.200
Ni2-50-FER	2.65	2/50	44	0.220
Mn1-30-FER	1.99	1/30	33	0.165
Mn1-50-FER	2.34	1/50	39	0.195
Mn2-30-FER	3.10	2/30	51	0.255
Mn2-50-FER	3.41	2/50	56	0.280

**Figure 1.** Effect of temperature on the conversion of NO over Cu-FER

3.5% by weight. As in the case of copper, the cobalt catalysts have a positive impact on the effectiveness of the reduction process. Figure 2 shows the level of NO conversion for cobalt catalysts, which obtain the level of the 80% NO reduction.

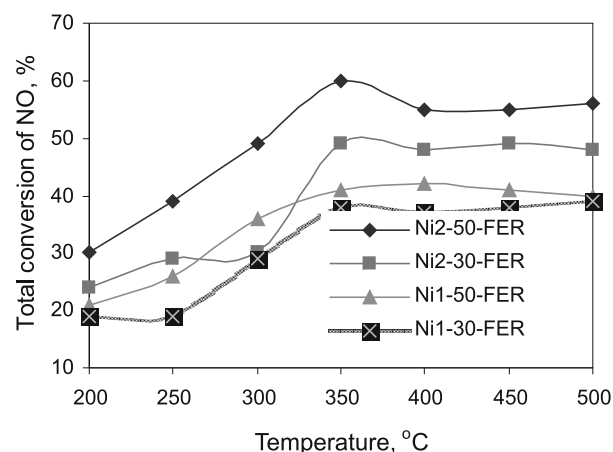
Nickel catalysts, as well as manganese NO, obtain the level of 60% reduction – Fig. 3. The reduction was best in the temperature range 350–500°C, and the process

**Figure 2.** Effect of temperature on the conversion of NO over Co-FER

was uniform. The Ni-FER catalysts including from 2.4 to 2.65% by weight of the metal allows to obtain a 60% reduction of NO at the temperature of 350°C. A smaller content of Ni results in a much lower degree of NO reduction, even in the higher temperature range 350–500°C.

Manganese is not a desirable metal. The amount of the metal added was 1.99–3.44 wt.% Mn for the FER catalyst obtaining 60% reduction of NO in the upper temperature range. The catalysts with a small amount of Mn obtain very poor properties towards the reduction of NO. Both Ni and Mn are very poor modifiers for the investigated zeolite catalysts.

The catalysts Cu-FER and Co-FER are more active in the reduction reaction of NO with methane than Mn-FER and Ni-FER- Figs. 1–4. The total NO reduction by methane on the Ni-FER catalysts was 60% at the level of reduction of NO (Fig. 3). The research results of catalysts of NO reduction with the use of Mn-FER are higher and obtain the level of 62% – Fig. 4. The obtained results allow to conclude that the new catalytic materials obtained by the addition of Mn and Ni cations into ferrierite networks are not suitable for the testing process.

**Figure 3.** Effect of temperature on the conversion of NO over Ni-FER catalysts

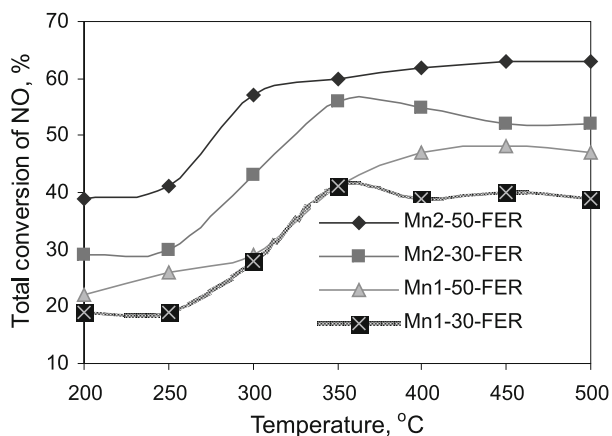


Figure 4. Effect of temperature on the conversion of NO over Mn-FER

The selectivity of catalysts for N_2 of Cu-FER is compared in Fig. 5. The maximum NO conversion for N_2 and the most favourable temperature (T_{max}) clearly depends on the type of zeolite and the type of metal.

The Cu2-50-FER catalyst presents the highest NO conversion into N_2 , which is about 62% at 500°C – Fig. 5. The Cu1-30-FER catalyst presents a very low level of NO conversion, which is 45% in the temperature range 400–500°C. Comparing the total nitrogen oxide conversion, one can see the same trends in all temperature ranges.

Figures 5–8 compare the selectivity to N_2 over zeolite with different metals, approximate metal exchange level, but differing metal contents. This set of figures clearly illustrates that the catalytic activity profiles for NO SCR with methane depend on the zeolite structure, either for the exchanged catalysts, Cu catalysts always being distinguished by their highest activity.

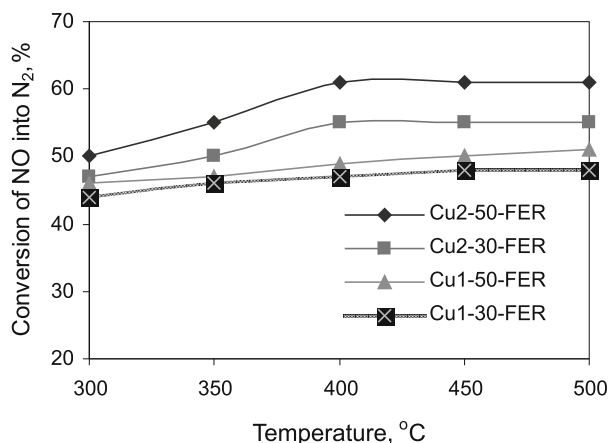


Figure 5. Effect of temperature on the conversion of NO to N_2 over Cu-FER

Doped cobalt catalysts have slightly different profile curves of NO reduction to N_2 , which in the range 350–500°C varies within 63–65% – Fig. 6. Figure 7 presents the curves of the reduction of NO to N_2 for the modified Ni-zeolites. The process is stable in the 350–500°C range and reaches the level of 53%. A similar process is observed with the Mn catalysts. In the range of 350–500°C the curves are almost a straight course, reaching 50% of reduction of NO to N_2 – Fig. 8.

The selectivity to nitrogen for different catalysts at the function of the temperature reaches the level of 65%.

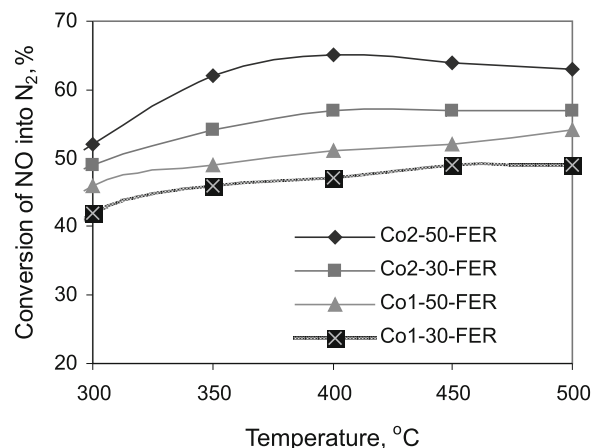


Figure 6. Effect of temperature on the conversion of NO to N_2 over Co-FER

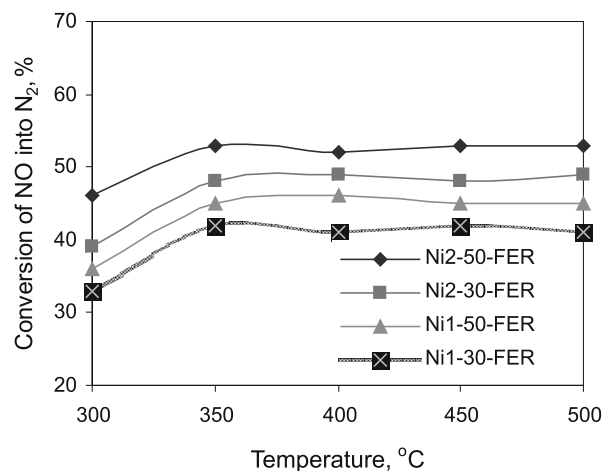


Figure 7. Effect of temperature on the conversion of NO to N_2 over Ni-FER

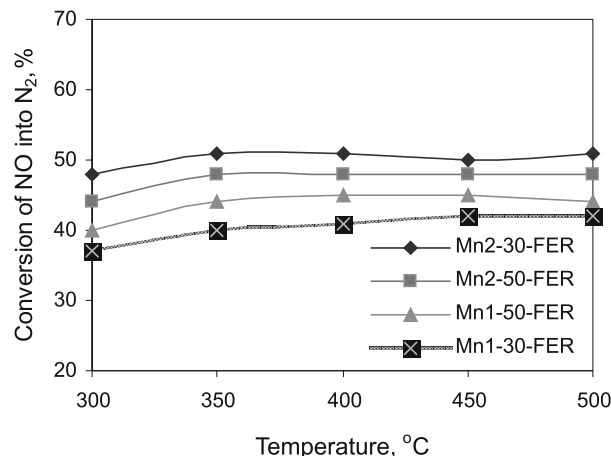


Figure 8. Effect of temperature on the conversion of NO to N_2 over Mn-FER

The analyzed data indicate that the Co-FER catalysts are ones of the most active and selective in the tested series.

DISCUSSION

The investigation results show that the structure of zeolite affects the nature and reducibility of metal ions, NO adsorption and the catalytic behavior for NO SCR with methane^{28–30}. For the Co catalysts our results are quite evident that this type of catalysts presents a high catalytic activity (the maximum NO conversion to N_2

observed for the catalyst was about 65%) for SCR of NO with methane. The maximum of conversion observed in the curves corresponding to the FER catalysts also indicate that there is a clear dependence between the catalytic activity of the studied catalysts and their composition, in terms of copper and Al contents. The highest value of maximum NO conversion to N₂ was observed for the Co-FER catalysts with Cu/Al = 0.28 and 57% of copper exchange level. The first approach to explain the differences in the catalytic activity observed between the four series of catalysts with a different metal could come from considering the corresponding differences in NO absorption capacity which indicates that the most active catalysts are those possessing a higher tendency to absorb NO. Li et al.²⁸ suggested that the catalytic activity of a catalyst to NO conversion is proportional to its NO absorption capacity at room temperature. They considered that the properties of the zeolites e.g. shape selectivity, did not influence the reaction of NO reduction with hydrocarbons^{25, 29, 30}.

The differences in activity found for these catalysts³¹ only concern an extension for lower temperatures of the active-temperature window, for the catalysts with higher Me/Al ratio. Taking into account all the results reported up to now for the four kinds of zeolites, confirmed the observed differences opportunity to clarify for all samples. The zeolite structure effects the nature of the metal that is incorporated in the catalysts with similar chemical compositions. Summarizing, the main effect of the zeolite structure is to create the conditions to ledge the metal in a peculiar environment.

CONCLUSIONS

This research 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-FER catalysts are most active, regardless of the ratio of Co-, Cu/Al and metal content in the zeolite. The obtained catalysts Co- and Cu-FER can prove to be the ones of the most active, regardless of metal content in the zeolite structure. The tests also confirmed the dependence of catalytic activity of different catalysts in the process of CH₄-NO SCR on the type and quantity of the cation introduced into the structure of the zeolite.

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