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Journal of Catalysis 218 (2003) 348–353

JOURNAL OF
CATALYSIS

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Structure-activity relations for Ni-containing zeolites during NO reduction
I. Influence of acid sites

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Received 14 November 2002; revised 21 February 2003; accepted 24 February 2003

Abstract

The influence of the zeolite structure on the catalytic properties for the reduction of NO with propane and propene was studied. A relation between concentration and strength of acid sites and the activity of Ni-exchanged ZSM-5, MOR, and MCM-22 was found. Ni/ZSM-5, which contains a high concentration of strong acid sites, is the most active catalyst for the NO reduction with propane. Using propene as reductant Ni/ZSM-5 and Ni/MCM-22 rapidly deactivate due to the acid site-catalyzed formation of carbonaceous deposits, while Ni/MOR is less affected by the deposits formed because of its larger pore size.

Keywords: Hydrocarbon-SCR; Propene; Propane; Ni-exchanged zeolites; Structure; Acid site concentration

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1. Introduction

Transition metal-containing zeolites exhibit high activity and selectivity in the catalytic reduction of NO_x with hydrocarbons in oxidizing atmosphere. For copper-containing zeolites it is known that water inhibits the reaction and causes deactivation of the catalyst [1], while zeolites exchanged with other transition metals such as CoZSM-5 [2–5] and FeZSM-5 [6–10] remain active catalysts for the reduction of NO to N_2 also in the presence of H_2O or SO_2. Ni, Co, Pt, and Pd supported on ZSM-5 [11], FER [3,11], MOR [12,13], BEA [14,15], and MCM-22 [14] are also known to be effective catalysts for the reduction of NO with hydrocarbons.

In general, the activity of transition metal-containing zeolites for NO reduction depends on the type of metal and on the nature of the zeolite with respect to the strength and concentration of acid sites, pore dimensions, and accessibility of acid sites. Several authors suggested that the pore geometry is the main reason for the different activity of zeolite-based catalysts in NO reduction [16]. Therefore, the difference in activity between the different zeolites should be more pronounced, when bulky hydrocarbons are used as reducing agents [11].

We have already described the reduction of NO with propane and propene on Ni-exchanged mordenite [17]. The formation of two Brønsted acid sites for each Ni atom incorporated was observed on the Ni/MOR samples. In the samples prepared from the sodium form of mordenite we observed an enhanced activity with increasing nickel content, which was directly coupled to the increase in the acid site concentration. As the concentration, strength, and accessibility of the acid sites is a function of the zeolite structure we describe in this contribution the activity of Ni supported on three zeolites (ZSM-5, MOR, and MCM-22) having different pore geometry and channel diameter, but exchanged with the same concentration of Ni, for the reduction of NO with propane and propene.

2. Experimental

2.1. Catalyst preparation

ZSM-5, mordenite, and MCM-22 were used. Mordenite in the sodium form was supplied by Tosoh, MCM-22 in the protonic form was supplied by Shell, and ZSM-5

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doi:10.1016/S0021-9517(03)00145-3

was synthesized in our laboratory according to Ref. [18]. MCM-22 and ZSM-5 were exchanged to the sodium form by liquid-phase ion exchange with $NaNO_3$ solution at 50 °C and loaded with Ni by ion exchange as described in Ref. [17].

2.2. *Physicochemical characterization and catalytic activity*

The chemical composition of the samples was obtained by atomic absorption spectroscopy (AAS UNICAM 939). Crystal size of the zeolite samples was examined using a JEOL 500 scanning electron microscope. The micro- and mesopore distributions were obtained on the basis of nitrogen adsorption measurements and the pore volume was calculated by using the t-plot method. The concentration, type, and strength of acid sites was measured by temperature-programmed desorption of NH_3 (NH_3-TPD) and by adsorption of pyridine and benzene followed by infrared spectroscopy as described in Ref. [17].

The catalytic activity of the samples was studied in a continuous flow system with a fixed-bed quartz reactor. Details of the kinetic experiments are described in Ref. [17]. The catalytic activity reported was measured 120 min after the stepwise change in the temperature.

3. Results

3.1. *Physicochemical characterization*

The composition and the acid site concentration of all samples studied are summarized in Table 1. The Na/Al ratio of approximately 1 for NaMOR and NaZSM-5 indicates that the samples were completely in the sodium form, while for NaMCM-22 with a Na/Al ratio of 0.7 a fraction of protons remained. All Ni-containing samples had a Ni content of approximately 2 wt%. Sodium was still present in Ni/MOR and Ni/ZSM-5 after the ion exchange with Ni. The scanning electron micrographs of the three samples are shown in Fig. 1. Ni/MOR consisted of crystals with a size within the range 2–8 µm, while Ni/ZSM-5 had homogeneous crystals of 3–4 µm size. Ni/MCM-22 consisted of thin platelets of 1 µm size that formed agglomerates of approximately 15 µm.

Table 1
Chemical composition of Ni-exchanged samples determined by AAS and acid site concentration determined by NH_3-TPD

Sample	Si/Al	Ni/Al	Na/Al	Ni loading (wt%)	Acid site concentration (mmol/g)
NaMOR	8.6	–	1.1	–	0.0
NaZSM-5	15.6	–	1.1	–	0.1
NaMCM-22	12.6	–	0.7	–	0.2
Ni/MOR	8.9	0.2	0.6	1.9	0.4
Ni/ZSM-5	16.4	0.4	0.3	2.0	0.7
Ni/MCM-22	12.3	0.2	0.0	1.8	0.8

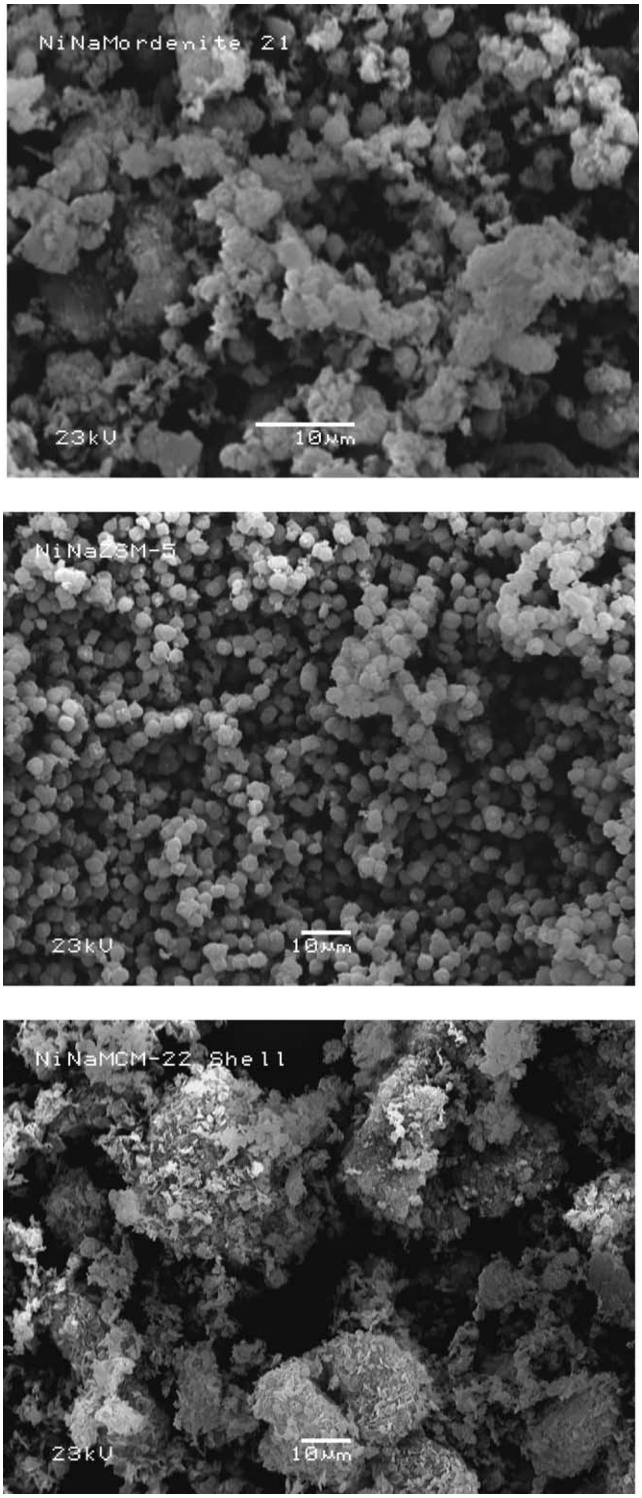

Fig. 1. Scanning electron micrographs of Ni-exchanged zeolites.

The surface area and pore volume of the Ni exchanged zeolites are summarized in Table 2. The macro and mesopores surface volume is ascribed to the agglomeration of the primary zeolite particles.

Table 3 summarizes the distribution of cations on the exchange positions for the three Ni-exchanged zeolites. The

Table 2
Textural properties of Ni-exchanged samples

Sample	Micropore surface area (m^2/g)	Macro and mesopore surface area (m^2/g)	Micropore volume (cm^3/g)
Ni/MOR	267	106	0.104
Ni/ZSM-5	227	101	0.087
Ni/MCM-22	214	233	0.066

concentration of exchangeable sites and their occupation by Na^+ and the total Ni content were calculated from the elemental composition, while the concentration of ion-exchange sites occupied by SiOHAl groups and $[Ni(OH)]^+$ was calculated from the concentration of acid sites determined by NH_3-TPD. For NaZSM-5, Brønsted acid sites were observed in the NH_3-TPD, although elemental analysis indicated the absence of protons. The concentration of these sites was subtracted for the site balance for Ni/ZSM-5. The sites occupied by Ni^{2+} were calculated from the difference of the total exchangeable sites and the sites occupied by Na^+ and acid sites. Note that the calculated fraction of sites occupied by Ni^{2+} and the total concentration of Ni was identical for Ni/MOR and Ni/MCM-22, indicating that most of the $[Ni(OH)]^+$ groups were not detected by NH_3-TPD at 150 °C due to their weakly acidic character [17].

The strength of the Brønsted acid sites on the three zeolites was determined form the shift of the OH-stretching vibration of the Brønsted acid sites after adsorption of benzene. The highest shift was observed for ZSM-5 ($\Delta\nu_{OH} = 342\ cm^{-1}$) followed closely by MOR ($\Delta\nu_{OH} = 335\ cm^{-1}$), while MCM-22 had the lowest shift ($\Delta\nu_{OH} = 295\ cm^{-1}$), indicating the following order with respect to the acid strength: ZSM-5 $\approx$ MOR $>$ MCM-22.

The formation of oligomeric species was studied by temperature-programmed desorption of propane and propene (data not shown). In addition to propane, oligomeric species with fragments in the range 49–52, 77, 78, and 79, among others, were observed. Compounds associated to these masses are cyclic and partially aromatic intermediates, such as benzene and cyclohexadiene, which suggests that oligomerization and dehydrocyclization reactions of propane occurred.

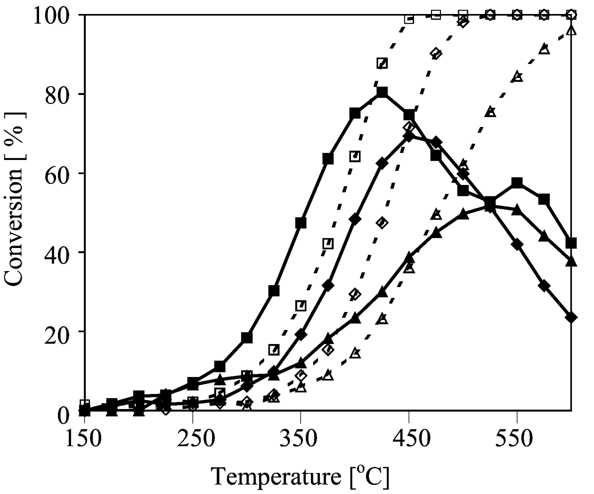

Fig. 2. NO conversion to N_2 (solid lines) and propane conversion (dashed lines) on (♦) Ni/MOR, (■) Ni/ZSM-5, and (▲) Ni/MCM-22.

3.2. Kinetic measurements

3.2.1. Reduction of NO with propane

The reduction of NO to N_2 with propane obtained for the nickel-exchanged zeolites are shown in Fig. 2. Typically a rapid change of the activity was observed during the first 30 min time on stream after the change of the temperature. A detailed discussion of the time on stream behavior is included in Ref. [19]. The maximum NO conversion followed the order Ni/ZSM-5 $>$ Ni/MOR $>$ Ni/MCM-22. In general the NO conversion started at lower temperatures compared to the propane conversion. The ratio of N_2 molecules formed to propane molecules converted, used to assess the efficiency of the reducing agent, is shown in Fig. 3. A ratio of approximately 1 was observed at temperatures below 375 °C. It decreased to 0.2 at higher temperatures, indicating that at low temperatures one molecule of propane reduced selectively two NO molecules, while at higher temperatures the direct oxidation of the hydrocarbon dominated. The slope of the curves is the same for the three samples at higher temperatures, indicating a similar efficiency of C_3H_8 for the three catalysts.

The distribution of products was similar for the three catalysts. N_2 was the main product of the NO reduction. At temperatures above 400 °C, selectivities to N_2 were higher than 95%. At temperatures below 350 °C, small amounts of NO_2 were formed over the three catalysts. Selectivity to N_2 increased with increasing temperature, while selectivity to NO_2 decreased. Only at low temperatures the formation of small amounts of N_2O was observed.

3.2.2. Reduction of NO with propene

Fig. 4 compares the NO and propene conversions during the reduction of NO with propene. The activities of

Table 3
Distribution of exchangeable sites of Ni-exchanged zeolites

Sample	Exchangeable sites (mmol/g)	Sites occupied by Na^+ (mmol/g)	Sites occupied by H^+ or $[Ni(OH)]^+$ (mmol/g)	Sites occupied by Ni^{2+} (mmol/g)	Total Ni (mmol/g)
Ni/MOR	1.7	1.0	0.4	0.3	0.3
Ni/ZSM-5	1.0	0.2	0.6	0.2	0.3
Ni/MCM-22	1.1	0.0	0.8	0.3	0.3

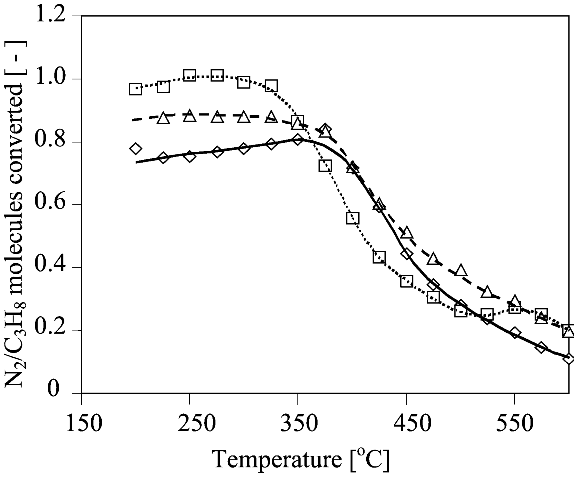

Fig. 3. Ratio between N_2 formed and C_3H_8 on (◊) Ni/MOR, (□) Ni/ZSM-5, and (△) Ni/MCM-22 during the reduction of NO with propane.

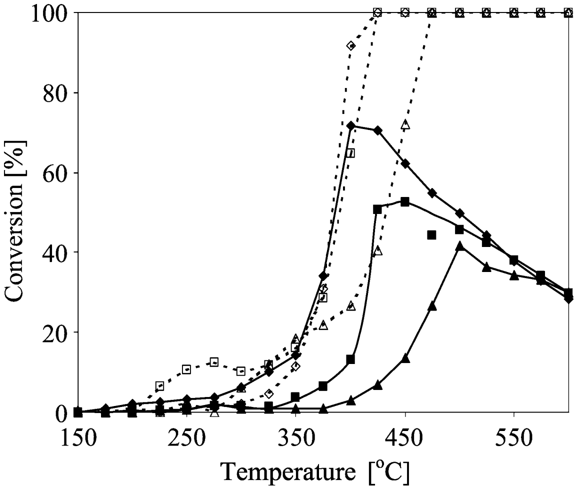

Fig. 4. NO conversion to N_2 (solid lines) and propene conversion (dashed lines) on (♦) Ni/MOR, (■) Ni/ZSM-5, and (▲) Ni/MCM-22.

Ni/ZSM-5 and Ni/MCM-22 were significantly lower for the reduction of NO with propene compared to propane. Ni/MOR was found to be the most active catalyst, with a NO conversion to N_2 of 72% at 400 °C. The conversion of propene started increasing almost in parallel to the conversion of NO for Ni/MOR, while for Ni/ZSM-5 and Ni/MCM-22, 100% conversion of propene was reached at temperatures below the maximum NO conversion. In general, propene was less efficient for the reduction of NO than propane. The ratio between N_2 molecules formed and propene molecules converted (not shown) indicated that for Ni/MOR two molecules of propene are required to reduce one molecule of NO at temperatures below the maximum NO conversion (400 °C) and even lower ratios were obtained for Ni/ZSM-5 and Ni/MCM-22.

At temperatures above 250 °C, N_2 was the main product. At lower temperatures, more N_2O was formed over Ni/ZSM-5 and Ni/MOR than in the case of propane. For propene, NO_2 was formed only at high temperatures when propene was directly oxidized, in contrast to the reduction of NO with propane, where NO_2 is formed at low temperatures. Higher amounts of N_2O were observed in the case of Ni/MCM-22, in comparison with Ni/ZSM-5 and Ni/MOR.

4. Discussion

4.1. Acid sites

From the three materials studied the highest NO conversion with propane was obtained with Ni/ZSM-5, followed by Ni/MOR and Ni/MCM-22. For the reduction of NO with propene, Ni/MOR was the most active catalysts followed by Ni/ZSM-5 and Ni/MCM-22. The NO conversion with propene was significantly lower compared to propane for Ni/ZSM-5 and Ni/MCM-22. Note that the activity for the reduction of NO with propane and propene of Ni/MOR catalysts has been found to depend on the acid site concentration [17]. For the same type of material a balanced concentration of acid sites is necessary to obtain high NO conversion with propane, while a low acid site concentration enhances the activity for the reduction of NO with propene [17].

Brønsted acid sites were formed during the calcination of the ion-exchanged samples and the concentration of acid sites was found to be primarily determined by the Ni content [17]. Since the Ni-exchanged zeolites studied here had the same Ni content a similar acid site concentration was expected. However, acid site concentration of Ni/MCM-22 and Ni/ZSM-5 was higher than that of Ni/MOR, because Ni/MCM-22 contained an additional fraction of acid sites already present in the parent material, while the slightly higher concentration of acid sites in Ni/ZSM-5 is tentatively attributed to the stronger acidic character of the $[Ni(OH)]^+$ groups (see Table 3).

All Brønsted acid sites on Ni/ZSM-5 and Ni/MCM-22 were accessible for pyridine, while on Ni/MOR 12% of the Brønsted acid sites were located in the 8-member ring channels (side pockets) and, therefore, not accessed by pyridine [20,21]. Brønsted acid sites were formed by hydrolysis during calcination and, therefore Ni^{2+} and SiOHAl groups should be in close proximity. Therefore, we would like to speculate that a fraction of Ni^{2+} should also be located in the side pockets of the zeolite.

4.2. Catalytic activity

The activity of the samples for the reduction of NO with propane followed the same order as the strength of the Brønsted acid sites. This indicates that the rate-limiting step during the reduction of NO with propane is primarily related to the strength of the acid sites, and apparently determines the activity of the catalyst.

The concentration of acid sites in Ni/MOR is, however, lower than in Ni/ZSM-5, while the strength of the acid sites is similar for both samples. Therefore, the maximum NO conversion for the reduction of NO with propane for Ni/MOR is slightly lower than that of Ni/ZSM-5.

It has been proposed frequently that the NO reduction involves first NO oxidation [16]. Nitrites and nitrates formed from the oxidation of NO [22,23] react with hydrocarbons forming a nitrogen-containing carbonaceous deposit on the catalyst, which further reacts in an unidentified pathway to N_2 [9,16,24]. The presence of NO_2 in the gas phase at the outlet of the reactor indicates that the activation of propane is the rate-limiting step at low temperatures [10]. In contrast, for propene NO_2 was present only at high temperatures, when the reducing agent was directly oxidized. This suggests that the alkenes are easier added to the NO_2 surface species, but—present in large concentrations—may react on competing reaction channels such as oligomerization and subsequent oxidation. Alkanes have to be activated (dehydrogenated) on the catalyst in a controlled way and this is obviously best met with the relatively slow protolytic dehydrogenation being catalyzed by the strongest Brønsted acid sites and the zeolite with the smallest pore size [25]. The activation (dehydrogenation) of propane might also occur on the Ni^{2+} ions shown to act as Lewis acid sites [26,27]. The same extent of propane dehydrogenation, however, is then expected to occur on the three catalysts since the loading of Ni is similar.

In contrast to the reduction of NO with propene, the amount of olefin available on the catalysts surface is limited during NO reduction with propane and, therefore, it reacts more efficiently with the adsorbed nitrites and nitrates to form N_2. From the catalytic results obtained during the NO reduction with propene we concluded that the reaction was not limited by the concentration of acid sites. Consequently, the strength of the acid sites has an important role for the activation of propene formed by propane dehydrogenation during the reduction of NO with propane. Oligomerization reactions took place during desorption of propane and propene from the Ni-exchanged samples, occurring to a higher extent for propene than for propane due to higher concentration of olefin ions in the channels. The extent of oligomerization follows the order Ni/MCM-22 $>$ Ni/ZSM-5 $\gg$ Ni/MOR (data not shown), which is identical to the order observed for the concentration of acid sites, indicating that a higher concentration of acid sites favors the oligomerization of the hydrocarbons leading to the formation of carbonaceous deposits blocking the active sites [10,28–30].

For the NO reduction with propene the activity followed the order Ni/MOR $>$ Ni/ZSM-5 $>$ Ni/MCM-22. In contrast to the reduction of NO with propane a strong inverse correlation of the activity for the NO reduction with propene with the concentration of acid sites is deducted from the characterizations and the catalytic results. Ni/MOR, which contains the lowest concentration of acid sites, was the most active for the reduction of NO with propene, while Ni/MCM-22 having the highest concentration of acid sites of the three materials, was the least active. The difference in activity of the three catalysts for the reduction of NO with propene is attributed to the formation of carbonaceous species that deposit on the materials. Ni/ZSM-5 and Ni/MCM-22 with higher concentrations of acid sites and smaller pore size are more affected than Ni/MOR.

The Brønsted acid sites are only located in the micropores of the zeolite. The macro and mesopore surface corresponds to the intraparticle void space formed by the agglomeration of particles in the material. A relation between the N_2 yield for the reduction of NO with propane and the micropore volume was not found, while a linear correlation was found between the maximum N_2 yield obtained from the reduction of NO with propene and the micropore volume. This indicates that for propene the limitation in the activity of the catalysts is related to the blocking of pores.

5. Conclusions

Ni/ZSM-5 was found to be the most active catalyst for the reduction of NO with propane compared to Ni/MOR and Ni/MCM-22. The higher activity of Ni/ZSM-5 is related to the high concentration and strength of the acid sites present in the material. At low temperatures, the rate-limiting step appears to be related to the activation of the alkane associated to the formation of olefins by dehydrogenation on SiOHAl groups and on the Ni^{2+} ions. The lower concentration of olefins during the NO reduction with propane leads to a more effective reaction with the adsorbed oxygenated nitrogen species, which is reflected in the higher activity and the lower formation of carbonaceous deposits compared to the reaction with propene.

Oligomerization of hydrocarbons related to the formation of carbonaceous deposits occurs on the three materials, being more severe in the case of propene. A high concentration of acid sites promotes the formation of carbonaceous deposits, which led to a partial blocking of the pores. Ni/MOR, the material with the largest pore diameter and the largest micropore volume, experiences the least severe deactivation resulting from the largest pore volume and the lowest concentration of acid sites, and it is, therefore, the most active among the three catalysts for the reduction of NO with propene.

Acknowledgments

This work was supported by STW/NWO, The Netherlands, under Project Number 326-710 and has been performed under the auspices of NIOK and PIT.

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