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Selective catalytic reduction of nitric oxide over zeolite catalysts in the presence of hydrocarbons and the excess of oxygen

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Abstract

The selective catalytic reduction (SCR) process of NO in the presence of modified zeolite catalysts has been studied. Low molecular weight hydrocarbons (methane and ethene) were used as reducing agents. The catalytic performance of Cu-containing ZSM-5, mordenite and ferrierite was exemplified using ethene. The effect of Cu content was shown for ferrierite matrix and related to the performance of its pure hydrogen form. A comparison of the catalytic properties of Cu-MFI and Co-FER was carried out for methane and ethene. A series of doubly substituted In,Co-FER catalysts with different metal loading (0.25–0.75Co and 0.6–1.2In) were studied using methane. The cobalt and indium ions, when present simultaneously in ferrierite, exert a pronounced synergetic effect in the title reaction in the presence of methane. This effect was evidenced in the broad range of the In–Co loading. Finally, the question of how the zeolite matrix does affect the SCR process with methane, when using the In,Co-forms, was addressed for ferrierite and ZSM-5 type zeolites.

Keywords: Selective catalytic reduction; Nitric oxide; Ferrierite; Mordenite; ZSM-5; Methane; Ethene; Copper; Cobalt; Indium; Contact-induced ion exchange

1. Introduction

Catalytic removal of nitrogen, and to a lesser extent, sulfur oxides, has focused attention of many laboratories world-wide. It is evident that catalyst's activity, viable for commercial applications, should be high enough and also coupled with the highest achievable selectivity to the non-toxic products of the process. Thus nitrogen and sulfur oxides abatement from both stationary and mobile sources is a primary objective of such studies. Time-on-stream stability of the catalyst in the presence of steam and surplus of air/oxygen is another property of the catalysts, which cannot be neglected [1]. Different agents have been suggested as the reductants, including alkanes, alkenes, CO and H_2.

A large number of catalysts have been tested in the SCR of NO_x, including mixed oxides, supported metals and zeolites of different compositions [2,3]. Of these catalysts, copper-containing ZSM-5 zeolites were mostly studied [4–7]. Other structures, like mordenite, ferrierite were also suggested [8–10]. While the SCR of NO with olefins proceeds usually smoothly on zeolite catalysts [11], it is much more difficult to perform the title reaction using methane, which is a very stable molecule.

Li and Armor showed that methane can be successfully used as a reductant of NO on Co^{2+}, Mn^{2+} and Ni^{2+}-exchanged ferrierites [12,13]. Ga/ and In/H-ZSM-5 were active catalysts in the title reaction [14]. Doubly substituted cobalt–indium ferrierites were studied [15]. Indium oxide supported on TiO_2–ZrO_2 showed significant activity for reduction of NO with propene, but not with methane, ethene, propane or alcohols [16]. Most of the published works studied the NO reduction under dry conditions. However, behaviour of catalysts is changed if steam is present. We therefore apply in this study feed containing some water.

The objective of this work was to synthesize and characterize a number of zeolite catalysts for the selective catalytic reduction of nitric oxide NO (SCR NO), in the presence of hydrocarbons (first of all methane) and surplus of oxygen. Our aim was to compare catalytic properties of zeolite samples modified either with one (Cu^{2+}, Co^{2+} and In^{3+}) or two cations (Cu^{2+}–Co^{2+} and In^{3+}–Co^{2+}). The other

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goal was to explore further contact-induced ion exchange (c.i.i.e.) for the preparation of effective de-NO_x catalysts.

2. Experimental

2.1. Catalysts preparation

Ferrierite samples were synthesized hydrothermally by using Ludox AS-40 as the silica source and pyrrolidine (pyr) or piperidine (pip) as the organic templates. The gels with the molar composition of $12.0SiO_2$:6.0pyr:$1.3Na_2O$:$1.0Al_2O_3$:$436.0H_2O$, and $22.7SiO_2$:9.0pip:$6.8Na_2O$:$1.0Al_2O_3$:$385H_2O$ have been homogenized for few hours and allowed to crystallize in the Teflon-lined stainless-steel autoclaves under autogenous pressure for 13 days at 200 °C and for 4 days at 200 °C, when using pyrrolidine and piperidine, respectively. Mordenite was prepared starting from the second gel containing piperidine, but crystallization was carried out at 200 °C for 1 day and the gel was stirred during the synthesis. After calcination at 550 °C ferrierite and mordenite were ion-exchanged with ammonium nitrate (four times at ambient temperature) and transformed into the corresponding hydrogen form (H-FER and H-MOR) by calcination at 550 °C. The 100% crystalline ZSM-5 sample was synthesized at the Institute of Industrial Chemistry, Warsaw, and had the Si/Al ratio 35 (batch no. T-1000). The Si/Al ratio of H-FER(I), synthesized from pyrrolidine, was 6.1 and its BET (Ar) = 335.7 m^2/g; for H-FER(II) prepared using piperidine, the Si/Al ratio was 8.8, and BET (Ar) = 320.4 m^2/g; for H-MOR the Si/Al ratio was 5.0 and BET (Ar) = 332.8 m^2/g. The analysis of diffractograms showed the samples consisted of either pure ferrierite or mordenite type zeolites. H-FER and H-MOR forms were modified further by Cu^{2+}, Co^{2+} and In^{3+} ions using contact-induced ion exchange (c.i.i.e.) procedure [17]. The Cu-forms of ferrierite, mordenite and ZSM-5 were obtained by mixing copper acetate with the hydrogen forms of zeolites followed by calcination in the air or helium flow at 550 °C for 2 h. The modification level with the metal cations is marked by a fraction inserted before the ion symbol. For example, 0.5Cu-FER refers to a sample of ferrierite with the 50% exchange level of copper. The Co-containing catalysts were obtained from cobalt acetate (Merck, p.a.) by c.i.i.e. (the samples were calcined at 550 °C for 2.5 h). The In-FER samples were prepared by careful grinding ferrierite and indium(III) oxide, heating in He to 400 °C and followed by reduction with hydrogen at this temperature for 2 h. The catalyst containing simultaneously the two types of ions (Cu^{2+}–Co^{2+}) was also prepared by c.i.i.e. method. The Co,In-forms of ferrierite were prepared from the Co-FER(I) or Co-FER(II) samples by applying the additional c.i.i.e. procedure to the cobalt form: thus Co-forms of ferrierite were ground with In_2O_3, heated in the helium flow to 400 °C, reduced with hydrogen for 2 h and cooled to ambient temperature in He [18,19].

2.2. Catalytic tests

The catalytic tests were performed in a continuous-flow laboratory unit consisting of a fixed bed reactor operating at atmospheric pressure. The standard reaction conditions were: NO = 1000 ppm, C_2H_4 (or CH_4) = 2000 ppm, O_2 = 4%, H_2O = 2500 ppm (feed composition); He (carrier gas); T = 250–550 °C; GHSV = 10,000 h^{-1}. All the samples were pelletized without the binder and the 0.2–0.5 mm fraction was used for the catalytic tests. The analysis of NO was performed by a Photovac 10S50 gas chromatograph equipped with a photoionization detector and KCl-Alumina column. The other products were analyzed by a *Chrom-5* gas chromatograph. Methane, O_2, N_2 and CO were analyzed using a column packed with zeolite 5A. Ethene, CO_2, N_2O and water were analyzed using a HayeSep R packed column. In both cases TCD was used as a detector. NO_2 content in the product mixture was analyzed by a colorimetric method. All the catalytic data are related to steady-state conditions, which were established usually after 2 h time-on-stream.

3. Results and discussion

A ferrierite type zeolite has been chosen as a basis for the catalyst preparation, due to its unique structure, high resistance against hydrothermal conditions and the ability to form strong acid centres. Mordenite and ZSM-5 based catalysts were prepared for comparison purposes.

The X-ray diffraction patterns of zeolites used for the preparation of catalysts are shown in Fig. 1. All the samples were checked for purity, and no contamination with the other phases was found. Using contact-induced ion exchange method Cu, Co and In ions were inserted into the zeolites.

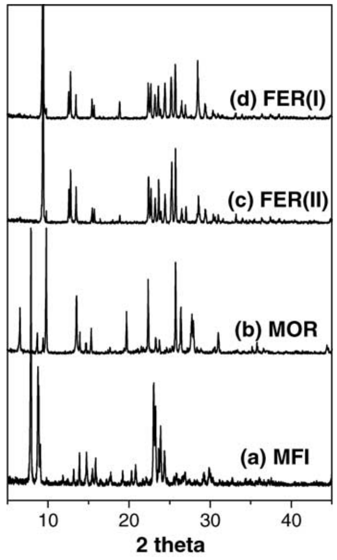

Fig. 1. XRD patterns of the synthesized zeolite matrices: ZSM-5 (a), mordenite (b) and ferrierite prepared using piperidine (c) and pyrrolidine (d) as a template.

Table 1
The composition of the ferrierite, mordenite and ZSM-5 catalysts used in the selective catalytic reduction of NO with methane and ethane

Catalyst	Modification degree (%)	Metal to framework Al ratio			Reducing agent
		Cu/Al	Co/Al	In/Al	
H-FER(I)					Ethene
0.5Cu-FER(I)	50% Cu	0.25			Ethene
1.0Cu-FER(I)	100% Cu	0.50			Ethene
1.0Cu-MOR	100% Cu	0.50			Ethene
1.0Cu-MFI	100% Cu	0.50			Ethene, methane
0.5Co-FER(I)	50%		0.25		Ethene, methane
0.25Co-FER(II)	50% Co		0.125		Methane
0.5Cu-FER(II)	50% Cu	0.25			Methane
0.5Cu/0.25Co-FER(II)	50% Cu + 25% Co	0.25	0.125		Methane
0.25Co-FER(II)	25% Co		0.125		Methane
0.5Co-FER(II)	50% Co		0.25		Methane
0.75Co-FER(II)	75% Co		0.375		Methane
0.6In-FER(II)	60% In			0.2	Methane
1.2In-FER(II)	120% In			0.4	Methane
0.6In/0.25Co-FER(II)	60% In + 25% Co		0.125	0.2	Methane
0.6In/0.5Co-FER(II)	60% In + 50% Co		0.25	0.2	Methane
1.2In/0.5Co-FER(II)	120% In + 50% Co		0.25	0.4	Methane
1.2In/0.75Co-FER(II)	120% In + 75% Co		0.375	0.4	Methane
0.6In/0.5Co-MFI	60% In + 50% Co		0.25	0.2	Methane

The samples obtained and listed in Table 1, were tested in the SCR NO process in the presence of ethane or methane as the reducing agents.

The catalysts were synthesized using the contact-induced ion exchange technique. This method has numerous advantages in comparison with the standard ion-exchange using water solutions. If the metal does not form volatile compounds (as a case of Co, Cu and In), all the metal introduced during the careful preparation is found in the solid obtained [17,20]. A stoichiometric of the preparation plays here a major role. The amounts of Cu, Co and In were calculated in proportion to aluminium content in a zeolite. Thus the Cu/Al = 0.5, Co/Al = 0.5 and In/Al = 0.33 ratios were labeled as 100% modification of a zeolite. We note the composition calculated from stoichiometry, due to very small amount of Al, and hence the low amount of the metal inserted, gives more accurate results rather than performing the chemical analysis. This was checked earlier for representative samples.

Since the balance framework aluminium and introduced metal ions is of major concern, we also checked the stability of ferrierite against possible thermal dealumination. Under the conditions of catalysts preparation no extraframework Al was observed in the samples, hence no thermal dealumination was found (^{27}Al MAS NMR spectra, not shown). Ferrierite is therefore a very stable structure against thermal dealumination. Additional XPS, IR and Raman studies of the catalysts (not discussed here) also confirm that the majority of cobalt introduced into the zeolite is in the ferrierite cationic positions, and a minor part forms an oxide phase.

Various combinations of the ions were also introduced into the zeolitic matrices (e.g., Cu–Co and Co–In). Different ion exchange levels were obtained, which allowed testing the activity of catalysts as a function of the ion(s) content (Table 1).

The influence of a zeolitic matrix on the NO conversion is illustrated in Fig. 2a. The SCR process of NO was performed in the presence of ethene as a reducing agent on the copper forms of ferrierite, mordenite and zeolite ZSM-5, modified to the same exchange level. As seen, the total conversion of NO on ferrierite- and mordenite-type catalysts is much higher than on ZSM-5, especially at temperatures 300–400 °C. At higher temperatures the conversion tends to level up. The maximum conversions of NO obtained over 1.0Cu-FER and 1.0Cu-MOR at 375 °C, were 78.1 and 70.9%, respectively. Ferrierite-type zeolite, yielding the highest conversion at relatively broad temperature ‘window’, has been therefore chosen as a principal matrix for further studies.

The loading of ferrierite with copper was addressed next. Thus the SCR process of NO with ethene on the hydrogen and Cu-forms of ferrierite with a different copper content is compared in Fig. 2b and related to H-ferrierite. On the pure hydrogen form H-FER the conversion of NO at 350–450 °C is ca. 35%. However, the time-on-stream stability of H-FER is poor, and the zeolite deactivates very rapidly (below 1 h TOS).

As seen in Fig. 2b, the insertion of Cu^{2+} by c.i.i.e. exerts a positive effect on the NO conversion level for both catalysts containing copper, in comparison with H-FER. Moreover, the catalytic activity is stable with time. Although the catalyst 0.5Cu-FER(I) exhibits low activity at 300 °C, it gives much higher conversion than 1.0Cu-FER(I) in the 350–450 °C temperature range (82–86% versus 69–78%, respectively).

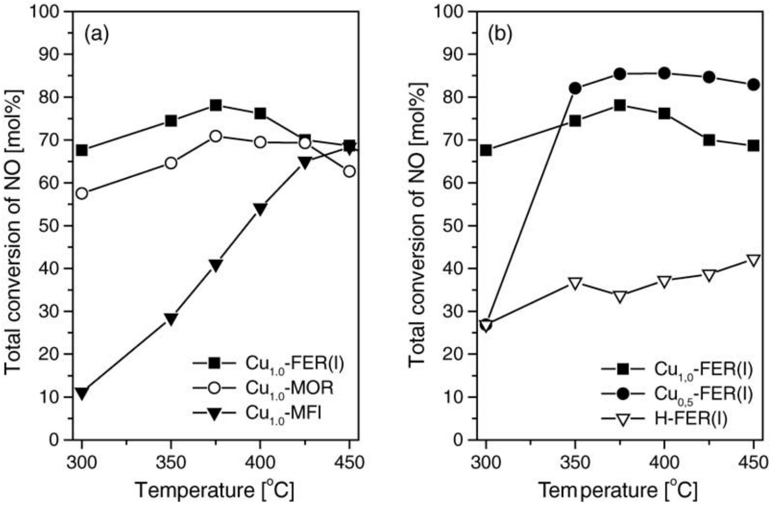

Fig. 2. Selective catalytic reduction of NO with ethene on different zeolite catalysts: copper forms of ferrierite, mordenite and ZSM-5; hydrogen and copper forms of ferrierite with different ion exchange level.

Influence of a hydrocarbon type on the reaction course was studied and Fig. 3 illustrates a comparison of SCR NO in the presence of either ethene or methane as a reducing agent, proceeding on the catalysts 1.0Cu-MFI (Fig. 3a) and 0.5Co-FER(I) (Fig. 3b). As was presumed, the two catalysts are much less active in the title reaction when methane is used. Methane is a very stable molecule, with C–H energy of 435 kJ/mol. It is evident from this study and earlier observations that it is more difficult to functionalize methane than ethene. The copper form of ZSM-5 type zeolite exhibits relatively low conversion of NO in the presence of methane, moreover K_{NO} decreases at higher temperatures (Fig. 3a). Similarly to the Cu-form of MFI, a cobalt form of ferrierite is also less active when using methane rather than ethene (Fig. 3b). At the temperature 300 °C no conversion of nitric oxide is observed on the catalyst 0.5Co-FER(I), while by using ethene the conversion of NO at the same temperature is already significant (40%). It increases to about 65% in the temperature "window" 325–375 °C. The advantage of applying cobalt-modified zeolite as a catalyst in the SCR NO process in the presence of methane stems from the fact that the 0.5Co-FER(I) catalyst does not loose its activity with the temperature and reveals higher activity. Further modifications in the catalyst preparation routes were however required, in order to obtain even more active catalysts for the CH_4-SCR NO process.

These set of experiments show clearly that ethene can be successfully applied for the NO removal using the same zeolitic catalysts. However, taking into account economical considerations (availability and the cost of ethene supply), it has been decided to focus predominantly on using as a reducing agent methane.

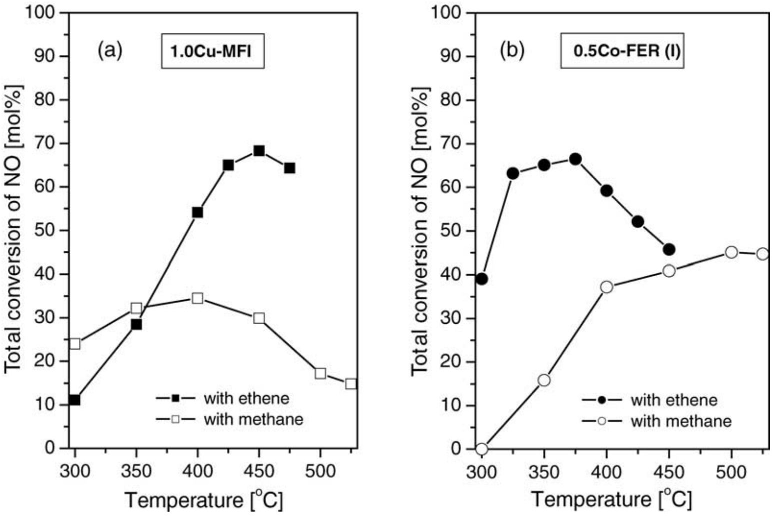

Fig. 3. A comparison of the selective catalytic reduction of NO with ethene and methane on the copper form of zeolite ZSM-5 (a), and cobalt form of ferrierite (b).

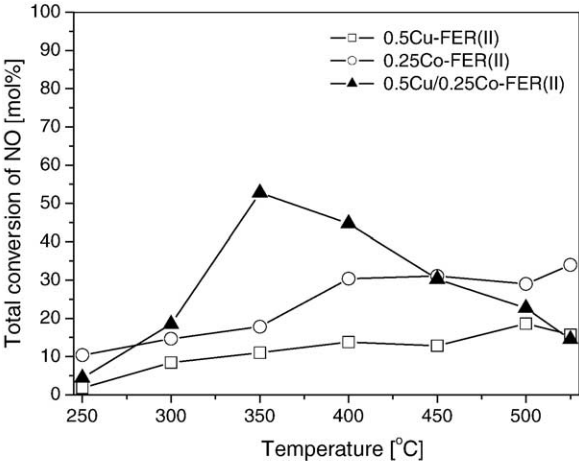

Fig. 4. The conversion of NO (mol%) in the presence of methane on pure Cu-, Co- and Cu,Co-ferrierite.

In the next paragraphs we will outline the SCR process using methane as a reducing agent. As seen in Fig. 4, a copper form of ferrierite exhibits low activity in the reaction. The conversion of NO does not exceed 20% at 500 °C. Higher activity was observed on the cobalt form, despite the lower metal loading. Upon insertion of both cobalt and copper ions into the ferrierite matrix, the catalysts exhibiting higher activity are obtained (0.25Co/0.5Cu-FER). We note that NO conversion on this catalyst can reach 53% at 350 °C (Fig. 4).

As the results presented above were also very encouraging in terms of the NO selectivity removal, it was thought that the conversion levels observed up to now might be still improved. We have explored earlier catalytic properties of the ferrierite matrix containing simultaneously cobalt and indium cations, with the metal loading 0.6In/0.5Co-FER(I) [15]. These preliminary tests have shown unambiguously that the indium–cobalt forms of ferrierite catalyze selectively NO at the temperature range 325–400 °C, with the selectivity approaching 80–85% using ethene, and even 90–100% at 350–450 °C when using methane as a reducing agent [15]. The ferrierite-based samples proved therefore to be extremely efficient and selective catalysts, especially in the CH_4-SCR NO process. Here we present data obtained for Co–In containing ferrierite using a broad variety of metal loading. However, before we will dwell on zeolite ferrierite modified with these ions, the influence of the single cations on the title process will be discussed first.

Thus the representative results obtained for Co- and In-zeolites are visualized in Fig. 5. As seen, the selective conversion of NO into N_2 on pure Co-forms of ferrierite(II) at the temperatures 300–400 °C is very low, moreover all the catalysts containing cobalt loose their activity at 350 °C ($K_{\mathrm{NO\,to\,N_2}} < 5\%$, Fig. 5a and b). Then the conversion of NO into nitrogen increases with temperature and with Co content to 23.3% for 0.25Co-FER(II); 31.3% for 0.5Co-FER(II) and 41.7% for 0.75Co-FER(II).

The activity of the catalysts containing indium introduced by c.i.i.e. with In_2O_3 decreases sharply with the temperature (Fig. 5a and b), despite of the In loading. For indium forms of ferrierite (with 60 and 120% exchange level) the observed conversion of NO into N_2 clearly depends on the ion exchange degree. Interestingly, more active is the catalyst 0.6In-FER(II) containing less amount of indium. In this case, the final selective conversion of NO observed at the temperature 500 °C was ca. 1/3 of the conversion shown at the temperature 300 °C, while for 1.2In-FER(II) was ca. 1/7 of the initial conversion only ($K_{\mathrm{NO\,to\,N_2}}$ decreases from 44.2% at 300 °C to 6.5% at 500 °C). Thus summarizing these experiments, moderate conversions of NO have been obtained on the catalysts containing either cobalt or indium cations introduced into the ferrierite matrix.

Finally, we have explored the influence of both cobalt and indium on the catalysts performance. Indeed, when cobalt and indium ions are present simultaneously in ferrierite, a very significant synergetic effect is observed. In the

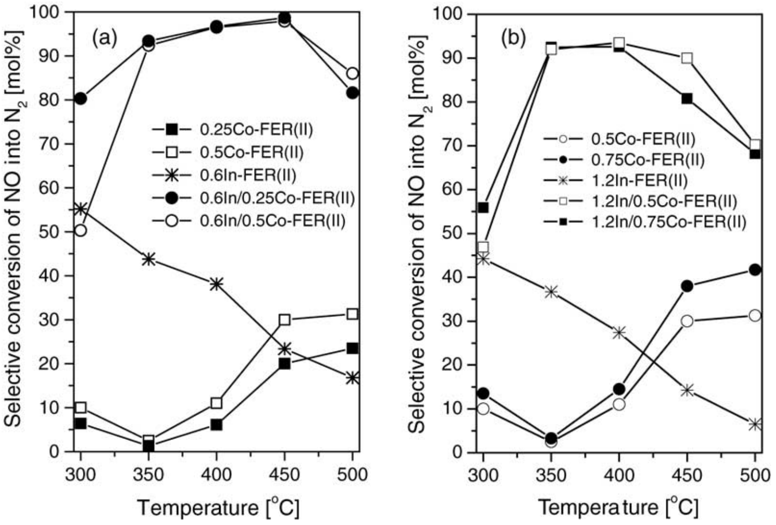

Fig. 5. Influence of cobalt, indium and indium–cobalt loading of ferrierite on the SCR NO with methane.

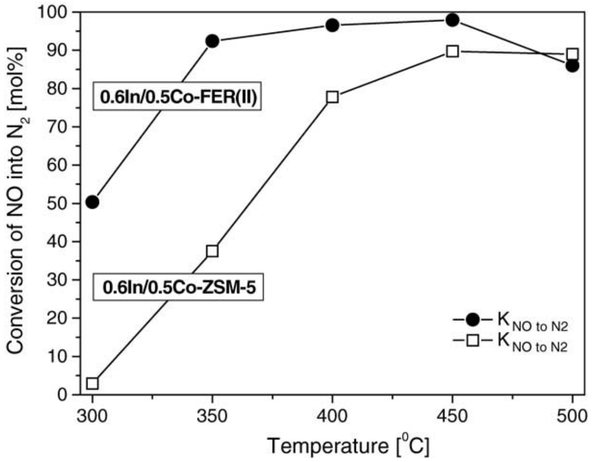

Fig. 6. A comparison of the overall conversion of NO and selective conversion of NO to nitrogen on In,Co-forms of ferrierite and ZSM-5.

temperature range 300–450 °C, the selective conversion of NO into N_2 increases sharply from 80 to 99% for 0.6In/0.25Co-FER(II) and from 50 to 98% for 0.6In/0.5Co-FER(II) (Fig. 5a). The two-component catalysts containing higher amount of indium (120%) reveal lower activity in the SCR NO reaction using methane (Fig. 5b). In the temperature range (300–400 °C), the selective conversion of NO into N_2 was 47–94% for 1.2In/0.5Co-FER(II) and 56–93% for 1.2In/0.75Co-FER(II) (Fig. 5b).

Modified ZSM-5 zeolites are the most studied catalysts for the selective catalytic reduction of NO, and extensive literature exists for this structure [1–3]. It was therefore of interest to compare the activity/selectivity of ZSM-5 zeolite modified with the same Co and In ions. Thus by applying the c.i.i.e. procedure the catalyst 0.5In/0.5Co-ZSM-5 was prepared, tested under standard conditions and the catalytic results were compared with the catalyst 0.6In/0.5Co-FER(II). The results are shown in Fig. 6, and the In–Co modified ZSM-5 catalyst proved to be less active in the CH_4-SCR NO process. At lower range temperatures ferrierite matrix gives rise to a much higher activity. The performance of ZSM-5 is slightly better if temperature is higher than 450 °C. The conversion of NO to nitrogen on ZSM-5 is insignificant at 300 °C, while ferrierite gives much higher conversion (over 50%). This trend is observed until 400 °C, and the activities levels up at 450 °C (Fig. 6). It is therefore clear that ferrierite performance under the same conditions is superior to ZSM-5. In other words the structure of zeolitic matrix (and not the metals loading) plays the dominant role in the process under consideration.

Ferrierite catalysts described in this paper have also been examined using several methods: MAS NMR, UV–vis, XPS, IR and Raman spectroscopies. The complementary studies allowed us to describe both the status of the introduced ions and the type of active centres present in the zeolitic structures [21]. In particular, by using in situ IR spectroscopy it was possible to examine the interactions between the chosen zeolitic samples and probing molecules like NO and CO. It was thus possible to reveal the nature of the sorption complexes formed during the interaction of NO or CO with the active centres [22]. In particular, IR studies [23] showed that 0.6In-FER does not bind NO on cationic sites, but forms intensive bands characteristic of nitrates(III) and (V) and ONO^- species. In the Co-FER catalyst NO binds in a form of mono- and dinitrosyls on Co^{2+} cations. The sorption of NO on the binary In,Co-FER samples is not a simple superposition of the single-cation-exchanged ferrierites performance. For the binary systems, the most stable forms of adsorbed NO are ONO^- and –O–NO_2 anionic species. The origin of the synergetic effect observed for doubly-substituted In,Co-FER might be therefore rationalized by the concurrent action. Thus NO, at the beginning adsorbed weakly on the Co^{2+} cations, could be easily transformed into nitro-oxygen species exhibiting higher ionic character. This transformation takes place on indium–oxygen containing species, introduced during the solid-state ion exchange of ferrierite with In_2O_3 oxide. Hence the presence of both cobalt and indium species seems to be an indispensable condition for the high activity and selectivity in the NO reduction.

4. Conclusions

Taking into account the catalytic results discussed above the following conclusions can be made:

- in terms of the NO conversion Cu-FER is superior to mordenite and ZSM-5 type zeolites;
- the low-metal-content zeolites give better catalytic performance in the process investigated. The effect was illustrated for Cu-FER and In,Co-FER catalysts;
- Cu-MFI and Co-FER show higher NO conversion when ethene is used;
- Cu,Co-FER exhibits a medium synergetic effect in the presence of methane;
- for all the catalysts containing cobalt and indium simultaneously, the strong synergetic effect was observed in the CH_4-SCR NO process, in comparison with the one-component systems. The effect was demonstrated for the broad range of indium and cobalt loading. Thus doubly substituted In,Co-ferrierites yield maximum and selective NO conversion to N_2 (up to 98%) in a relatively broad temperature range;
- the effect of zeolite matrix on the SCR process of NO is also significant. This was shown for the same metal ions (In,Co) embedded in ferrierite and ZSM-5 type zeolites, leading to different catalytic performance in 300–450 °C.

To summarize, it was demonstrated that the effective de-NO_x catalysts can be prepared using contact-induced ion exchange technique and ferrierite type zeolite. It is also evident that the CH_4-SCR NO process catalyzed by the In,Co-containing ferrierite catalysts, due to the extremely high activity and selectivity observed, can be a subject of further fundamental studies coupled with the scaling-up procedures and aimed at implementing them on industrial scale.

Acknowledgements

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