The synergetic effect of cobalt and indium in ferrierite catalysts for selective catalytic reduction of nitric oxide with methane

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A pronounced synergetic effect was found in the title reaction when indium and cobalt ions were present simultaneously in zeolite ferrierite.

A number of catalysts have been tested in the SCR of NO_x, including mixed oxides, supported metals and zeolites of different compositions.[1] While the SCR of NO with olefins proceeds usually smoothly on zeolite catalysts,[2] it is much more difficult to perform the title reaction using methane, a very stable molecule, and to achieve the reduction of NO while preventing total oxidation of the organic molecule by oxygen. 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.[3] Ga and In/H-ZSM-5 were active catalysts in the title reaction.[4] 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.[5] We wish to report on the characterization and performance of Co^{2+} and/or In^{3+} containing ferrierite in the SCR of NO with CH_4, in the presence of excess oxygen.

Ferrierite was synthesized hydrothermally by using pyrrolidine (pyr) or piperidine (pip) and Ludox AS-40. The gels having compositions of (10–12) SiO_2 : (4.8–7.0) pyr : (0.48–0.64) NaOH : 1.0 Al_2O_3 : (380–460) H_2O and (11–12) SiO_2 : (4.0–6.0) pip : (6.5–7.5) NaOH : 1.0 Al_2O_3 : (160–220) H_2O have been homogenized for few hours and allowed to crystallize in the Teflon-lined stainless-steel autoclaves under autogenous pressure for 2–13 days at 160–200 °C. After calcination at 550 °C ferrierite was ion-exchanged with ammonium acetate (twice) and transformed into the hydrogen form (H-FER) by calcination. The Si/Al ratio of H-FER (I) was 6.1 and BET (Ar) = 335.7 $m^2\ g^{-1}$; for H-FER (II) the Si/Al ratio was 7.8 and BET = 321.1 $m^2\ g^{-1}$, respectively. XRD showed both samples contained pure ferrierite phase (no mordenite or other phases were present).

^{29}Si MAS NMR spectra of both hydrogen forms were typical for pure ferrierite phase,[6] giving three signals at -108.2, -113.6 and -117.5 ppm. A fourth weak signal was found at -102.7 ppm. ^{27}Al MAS NMR revealed that aluminium in all the samples is present in tetrahedral positions. More detailed discussion of silicon and aluminium NMR spectra of ferrierites will be given elsewhere.

H-FER was modified further by Co(II) and In(III) ions using standard and solid-state ion exchange (s.s.i.e.) procedures.[7] Cobalt acetate (Merck, p.a.) was mixed with H-FER (I) in an agate mortar and calcined in air (heating rate 50 °C h^{-1}) at 550 °C for 2.5 h to yield Co-FER (I) with Co/Al molar ratio of 0.27. The sample In-FER (1) was obtained by ion exchange from indium nitrate solution at pH = 2.1, washed, dried and calcined in air at 550 °C for 2 h (In/Al = 0.12). Another catalyst was prepared by grounding zeolite and indium(III) oxide, heating in He to 400 °C and reducing with hydrogen at this temperature for 2 h. The sample was cooled down to ambient temperature in the He flow to give In-FER (2) with In/Al = 0.99. Finally, Co,In-FER was prepared from the Co-FER (I) sample by applying the additional s.s.i.e. procedure. Thus Co-FER (I) was ground with In_2O_3, heated in the helium flow to 400 °C, reduced with hydrogen for 2 h and cooled to room temperature in He. The catalyst labelled Co,In-FER had Co/Al = 0.27 and In/Al = 0.23.

The catalytic tests were performed in the continuous flow microreactor connected on-line with a gas chromatograph, at GHSV = 10 000 h^{-1}. All the data in Tables 1–3 are related to steady-state conditions. After these conditions were established (*ca.* 2 h) no measurable loss of catalysts activity was observed up to two days on stream (except H-FER).

The selective catalytic reduction (SCR) of NO by a hydrocarbon molecule (here methane) in the presence of oxygen proceeds according to eqn. (1):

$$2\ NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2\ H_2O \qquad (1)$$

In addition to reaction (1), at least two other parallel processes can be envisaged. First, the hydrocarbon can be fully oxidized by the molecular oxygen [eqn. (2)]:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \qquad (2)$$

Second, NO can be oxidized to NO_2 instead of being reduced [eqn. (3)]:

$$NO + 1/2\ O_2 \rightarrow NO_2 \qquad (3)$$

Table 1 A comparison of the selective catalytic reduction (SCR) of NO on indium forms of ferrierite. The oxidation of NO to NO_2 without methane in the feed is also shown (*O*)[a]

	In-FER (1)			In-FER (2)		
T_R/°C	*X*	*Y*	*O*	*X*	*Y*	*O*
250	24.4	tr.	17.0	6.3	4.7	0
300	28.0	3.1	21.4	14.4	8.1	18.9
350	23.9	4.2	19.5	8.9	11.3	8.1
400	21.6	8.2	15.0	4.1	14.2	6.4
450	28.3	15.7	12.7	2.3	32.2	0
500	39.4	24.8	9.5	4.9	50.1	0
525	40.5	38.6	9.4			

[a] Reaction conditions: NO = 1000 ppm, CH_4 = 2000 ppm, O_2 = 4%, H_2O = 2500 ppm; GHSV = 10 000 h^{-1}; *X* = conversion of NO (mol%), *Y* = conversion of methane (mol%) in the presence of NO, *O* = oxidation of NO to NO_2 (mol%) in the absence of methane.

Table 2 Selective catalytic reduction of NO on the hydrogen and cobalt forms of ferrierite, in the presence of methane and oxygen; reaction conditions as in Table 1

	H-FER (II)			Co-FER (I)		
T_R/°C	*X*	*Y*	*O*	*X*	*Y*	*O*
250	21.3	tr.	23.1			
300	19.8	2.3	27.4	~2	7.5	10.2
350	10.7	3.8	17.2	10.8	11.7	42.1
400	1.0	5.0	8.1	37.2	10.7	50.1
450	0	6.1	1.3	40.9	20.7	28.2
500	2.6	9.3	0	45.1	42.6	13.0
525				44.7	66.6	3.6

Table 3 Selective catalytic conversion of NO on Co,In-ferrierite, in the presence of methane and oxygen. Reaction conditions as in Table 1

	Co,In-FER		
T_R/°C	*X*	*Y*	*O*
300	20.0	4.1	19.8
350	61.3	14.6	42.7
400	91.7	29.3	43.3
425	98.4	42.0	34.4
450	97.6	52.9	27.3
475	95.5	63.0	
500	91.5	87.0	15.5

Third, the partial reduction of NO to N_2O may proceed. However, in the presence of methane and ethene the yield of N_2O was low (up to 5%). Accordingly, the following three reactions have been studied on ferrierite-based catalysts: (i) the SCR of NO; (ii) the oxidation of NO to NO_2 in the absence of methane; and (iii) the combustion of CH_4 to CO_2 and H_2O (without NO in the feed).

On pure hydrogen form of ferrierite the conversion (*X*) of NO at 250–300 °C was *ca.* 20% (Table 2). However, the zeolite loses its activity relatively quickly (< 1 h on stream). Moreover, the conversion of NO decreases sharply with the temperature. Above 400 °C the solid becomes essentially inactive. In the absence of CH_4 the oxidation of NO to NO_2 proceeds at low temperatures and above 450 °C is negligible (Table 2, column *O*).

The activity of the catalysts containing indium shows much more pronounced conversion in the temperature range 250–350 °C (Table 1). Contrary to the H-FER sample, the oxidation of NO to NO_2 was observed on In-FER (1) in the whole temperature range studied, up to 525 °C. However, under the SCR conditions, the oxidation of NO prevails only at temperature 200–250 °C, while above 350 °C the SCR of NO was the main process. The conversion level of NO does not exceed *ca.* 40% at 500–525 °C. The sample In-FER (2) is much less active; the oxidation of NO to NO_2 above 350 °C becomes negligible, while the total conversion of NO is nearly the same as found for H-FER. Finally, the oxidation of methane on this catalyst rises quickly with the temperature. As is seen from Table 1, no simple parallelism exists between the ability of catalysts to oxidize CH_4 and its performance in the SCR of NO.

The activity of pure Co-FER (I) under the same conditions is similar to the In-FER (1) sample. The catalyst shows an ability to oxidize NO (Table 2, column *O*). Thus summarizing, moderate conversions of NO have been obtained on the catalysts containing either cobalt or indium cations in the zeolite matrix [In-FER (1), Co-FER (I)].

We have found, however, that when cobalt and indium ions were present simultaneously in ferrierite, a very significant synergetic effect was observed. The conversion of NO increases sharply from 20 to 98% in the temperature range 300–425 °C (Table 3, column *X*). It is also remarkable that on Co,In-FER no NO_2 was found in the effluents above 300 °C. As the conversion of methane reveals, at 300–425 °C the SCR of NO proceeds predominantly. This is confirmed further by a very low combustion of methane in the absence of NO (for example, combustion of CH_4 without NO was < 1% at 300 °C and 6% at 400 °C). Above 400 °C the competition between reactions (1) and (2) becomes more important. As a result the combustion of methane by molecular oxygen increases with temperature. We note, however, that even at 500 °C methane is still able to reduce NO. Another interesting feature of the Co,In ferrierite is low yield of N_2O, decreasing continuously from 5.6% at 350 °C to 0% at 500 °C.

The activity of Co,In-FER catalyst was measured for comparison purposes using ethene in the stream instead of methane. The results are summarized in Fig. 1. Surprisingly, the conversion of NO is lower at high temperatures when using ethene as the reductant. Moreover, high (> 90%) conversion of NO on the Co,In-FER catalyst in the presence of methane was observed in a broader range (400–500 °C). Two remarkable features of our catalyst formulation are seen: (i) higher activity at high temperatures when using methane as the reductant; and (ii) still high activity in the de-NOx process with ethene. Typical behaviour of other zeolite catalysts investigated by us (mordenite and ZSM-5) was different: high activity in the presence of ethene and *lower* when using methane.[8]

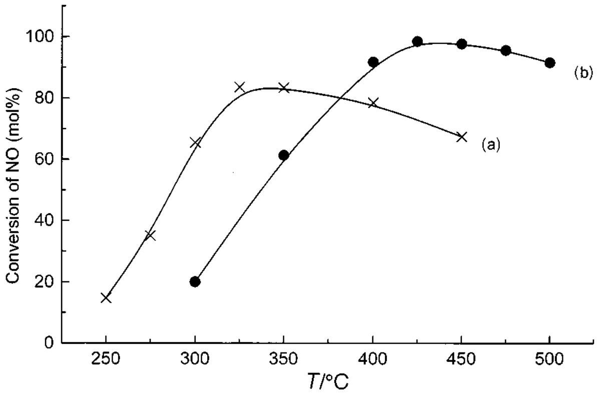

Fig. 1 Conversion of NO (mol%) on the Co,In-FER in the presence of ethene (a) and methane (b).

Finally, it is interesting to speculate on the surface species, as revealed in Co,In-FER by ESCA. We found the following concentrations of the catalyst components—Si : Al : O : In : Co = 0.261 : 0.045 : 0.647 : 0.031 : 0.016. The Si/Al ratio was 5.8 (in bulk, 6.1 was found by atomic absorption). Analysis of cobalt species gave Co(II) : Co(III) = 0.99. Upon heating to 400 °C, concentration of In and Co on the surface decreases to 0.023 and 0.013, respectively. This is in a very good agreement with higher initial activity of the catalyst (75.2% at 300 °C) in comparison with 65.5% steady-state value reached after 2 h on stream. Distribution of Co ions in crystals is very homogeneous, as seen by comparing Co/(Si+Al) = 0.038 (bulk) and 0.036 (surface). Contrary to this, even after heating at 400 °C the surface of ferrierite is enriched with indium oxide species [In/(Si+Al) = 0.064 (surface) and 0.033 (bulk)], at variance with the case demonstrated for large crystals of H-ZSM-5.[9]

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