Catalytic reduction of N_2O by NH_3 in presence of oxygen using Fe-exchanged zeolites

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The influence of ammonia on the reduction of N_2O in presence of oxygen over Fe-zeolite has been studied. It is found that BEA zeolite is the most efficient host structure for iron ions to catalyse the reduction of N_2O with NH_3.

Keywords: nitrous oxide, reduction, ammonia, iron, zeolite

1. Introduction

Nitrous oxide (N_2O) reduction is the next target of the nitrogen oxides elimination technology since it has been recognized as a greenhouse gas component and contributes to the catalytic depletion of the stratospheric ozone layer. The 0.2–0.3% increase of N_2O in the atmosphere is mainly caused by anthropogenic activities [1,2]. Man-made N_2O arises as a by-product from several processes as in adipic acid and nitric acid productions. The direct catalytic decomposition of N_2O to N_2 and O_2 would constitute the most convenient process, but the most efficient catalysts till now exhibit too low an activity in real conditions. An attractive alternative would be the addition of a reductant as ammonia in the process which is moreover available in the acid nitric production plants. NH_3 has been reported to enhance the reduction of N_2O over Co–MgO catalysts [3] and to reduce N_2O over Fe-MOR and Fe-FAU [4]. Aika et al. [3] suggested that N_2O and O_2 compete to supply active surface oxygen which can be eliminated with ammonia. N_2O is indeed a highly efficient oxidant of hydrocarbons, e.g., benzene to phenol [5], methane to methanol [6], in presence of iron-containing zeolites [7–11]. Moreover, Fe-Z (Z = zeolites) have been described as active catalysts for the reduction of N_2O and NO by hydrocarbons, CO and NH_3 [12–23]. The aim of the present paper is to demonstrate the effect of NH_3 on the reduction of N_2O in the presence of oxygen on Fe-Z as catalysts.

2. Experimental

2.1. Preparation of the catalysts

The Fe-Z were prepared from the different structure reported in table 1 by an ion-exchange technique. The zeolite (2 g) was stirred with 500 cm^3 of a 0.5–2×10^{-3} M iron(III) nitrate solution at room temperature for 24 h, with vigorous stirring. The solid was then separated from the liquid phase by centrifugation and washed with deionised water; this procedure was repeated four times. The samples were dried for 3 h in an oven at 353 K, and then calcined 8 h at 723 K (temperature ramp = 2 $K\,min^{-1}$) in air. The chemical analyses were performed using plasma atomic absorption spectroscopy at the Service Central d'Analyse du CNRS (Vernaison, France) and are reported in table 1. The catalysts were labelled as Fe(x)-Z, x being the Fe exchange level (300 Fe/Al (mol/mol)) and Z being the parent zeolite according to the nomenclature recommended by the IZA [24].

2.2. Temperature-programmed reduction

The nature and the amount of Fe species were determined by TPR. TPR of the calcined samples were carried out with a Micromeritics 2910 apparatus with H_2/Ar mixture (25/75, vol/vol) at 10 $K\,min^{-1}$ from 293 to 1373 K

2.3. Catalytic tests

The catalytic tests were performed in a flow reactor operating at atmospheric pressure. Catalyst aliquots ($\sim$100 mg) were activated *in situ* at 723 K in air (ramp = 10 $K\,min^{-1}$, flow = 50 $cm^3\,min^{-1}$), and cooled to room temperature. The reaction gas, a mixture of N_2O/O_2/He (0.2/3.0/96.8) or $N_2O/O_2/NH_3$/He 3% O_2 (0.2/3.0/0.2/96.6) was fed to the catalyst for the decomposition of N_2O and the SCR of N_2O with NH_3, respectively. The space velocity was 35,000 h^{-1}. The catalytic tests were carried out in temperature-programmed surface reaction (TPSR) from 298 to 823 K at 5 $K\,min^{-1}$. The effluent composition was monitored continuously by sampling on line

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Table 1
Chemical analyses of the samples.

Catalyst	Zeolite[a]	Origin of the zeolite	Si (wt%)	Al (wt%)	Na (wt%)	Fe (wt%)	Si/Al (mol/mol)	Na/Al (mol/mol)	Fe /Al (mol/mol)	Exchange level[b] (%)
Fe(x)-MOR	Mordenite	Zéocat	35.05	3.55	0.65	0.30	9.5	0.21	0.04	12
Fe(x)-MFI	ZSM-5	Zeolyst	37.50	2.46	0.46	0.33	14.6	0.22	0.06	19
Fe(x)-BEA	Beta	Zeolyst	38.11	2.56	1.08	0.42	14.3	0.50	0.08	24
Fe(x)-FER	Ferrierite	TOSOH	35.60	3.98	0.15	0.65	8.6	0.04	0.08	24
Fe(x)-FAU	Faujasite Y	Süd Chemie	37.30	2.90	0.40	0.90	12.4	0.16	0.15	45
Fe(x)-BEA	Beta	Zeolyst	35.45	2.65	0.75	0.90	12.9	0.33	0.16	49
Fe(x)-MAZ	Mazzite	Home made	29.80	7.92	0.14	1.1	3.6	0.02	0.07	20
Fe(x)-OFF	Offretite	Home made	29.65	6.20	0.12	1.87	4.6	0.02	0.15	44

[a] The structures are described in [24].
[b] Defined as: 300 Fe/Al (mol/mol).

to a quadrupole mass spectrometer (Pfeiffer Omnistar) equipped with Channeltron and Faraday detectors (0–200 amu). Nine masses characteristic of NO ($\underline{30}$), NO_2 ($30,\underline{46}$), N_2O ($28,30,\underline{44}$), N_2 ($\underline{28}$), NH_3 ($\underline{17},18$), H_2O ($17,\underline{18}$), O_2 ($16,\underline{32}$) and He ($\underline{4}$) were followed. The intensities of NH_3 (17), H_2O (18), N_2 (28) and NO (30) were determined by solving a linear system of equations. The concentrations were derived from intensities by using prior standardization procedures before and after each experiment.

3. Results and discussion

In agreement with previous works on the TPR by H_2 of Fe-MFI [25] and of Fe-Y [26], the first peak of hydrogen consumption (figure 1) would correspond to the reduction of Fe^{3+} to Fe^{2+} and the high reduction peak to the reduction of Fe^{2+} to Fe^0 with collapse of the zeolite network. The absence of reduction between these two peaks of reduction and a H_2/Fe ratio (mol/mol) below 0.5 show that the presence of iron oxide aggregates is unlikely or as traces. Similar TPR profiles were obtained for the other Fe-Z samples which allow us to affirm that Fe species in the different zeolite host structures are exchanged cationic species only. The TPSR of both direct N_2O decomposition and N_2O reduction by NH_3 on the various Fe-Z are reported in figure 2.

As far as the N_2O decomposition is concerned, the catalysts have been ranked according to their activity identified by the light-off temperature (temperature for 50% N_2O conversion): Fe(24)-FER (718 K) > Fe(24)-BEA, Fe(49)-BEA (740 K) > Fe(44)-OFF (804 K) > Fe(19)-MFI, Fe(20)-MAZ (815 K) > Fe(45)-FAU, Fe(12)-MOR (>823 K). The exchange level in Fe ions does not seem to modify the N_2O conversion over BEA catalysts. It is generally accepted that the catalytic decomposition of N_2O on Fe-Z catalysts is regulated by the redox cycle $Fe^{3+} \rightleftharpoons Fe^{2+}$ (see Kapteijn for a review [27]. In dehydrated Fe-FAU, Fe^{2+} ions have a high affinity for site I and site I′ and Fe^{3+} ions for site I′ [28,29]. These sites are localised at the opening and within the hexagonal prisms.

Therefore, the hindered access to these sites, mainly to site I, may explain the low activity observed in the N_2O decomposition on Fe(45)-FAU. Fe ions in hindered sites may also explain the low activity of Fe(12)-MOR.

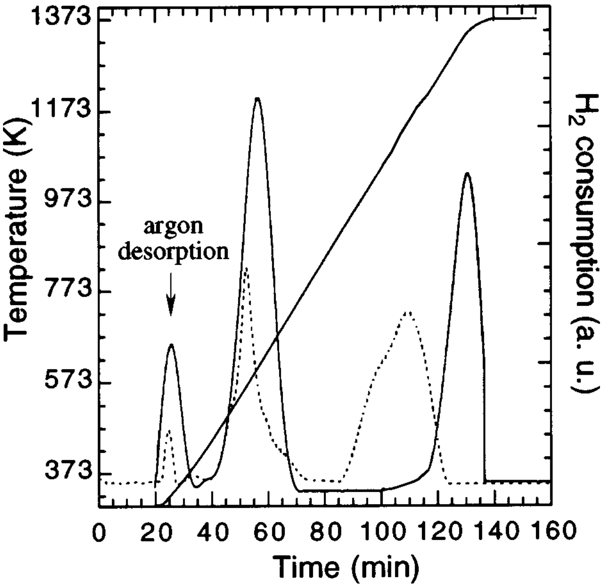

Figure 1. TPR by H_2/Ar (25/75) of Fe(49)-BEA (—) and Fe(12)-MOR (···) after activation in air at 823 K. Conditions: see section 2.

Fe(19)-MFI and Fe(20)-MAZ exhibit medium activities for N_2O decomposition. When expressed as TOF, number of N_2O molecules transformed per Fe atom and per second, the activity of Fe(19)-MFI, i.e., 9×10^{-4} s^{-1} at 743 K, is very similar with that reported by Chang et al. [30] for a Fe(59)-MFI (0.5 wt% Fe) catalyst, i.e., 6–10 $\times$ 10^{-4} s^{-1}. The higher activity of Fe-MFI compared to Fe-MOR and Fe-FAU was ascribed to the presence of stronger acid sites within the MFI structure [31]. Interaction with these acid sites would result in more effective activation of N_2O. Kustov et al. [32] have studied the interaction of nitrous oxide with strong Lewis acid sites in dehydroxylated zeolites and found that strong adsorption of N_2O occurred and that these acid sites are able to catalyse the reaction of N_2O decomposition via the formation of a chemisorbed atomic oxygen species. Fe^{n+} ions are Lewis acid sites but the role of the zeolite host would be to enhance this acidity. The behaviour of Fe(24)-FER and Fe(24)-BEA, which exhibit the high-

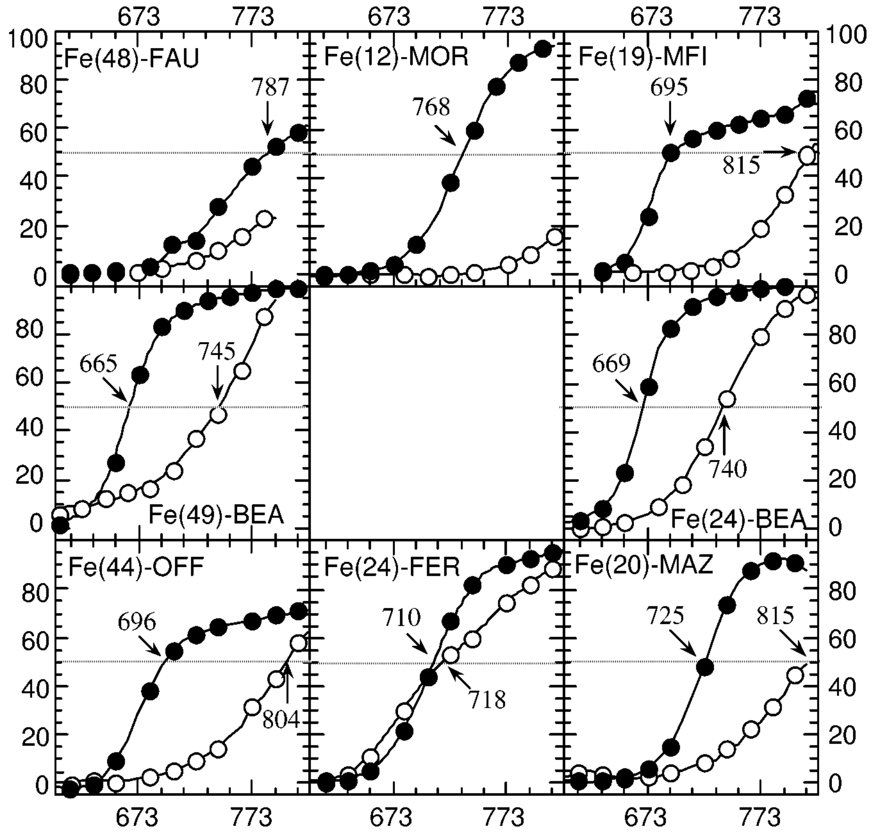

Figure 2. N_2O conversion in TPSR of (○) N_2O decomposition and of (●) N_2O reduction by NH_3. Conditions: see section 2.

est activity, may also be interpreted in this frame since it is known that FER and BEA are zeolites of very high acidity [33,34]. It is worthy to note that the most efficient host structure for N_2O decomposition are pentasil zeolites, e.g., FER, BEA and MFI. Fe-FER has been recently claimed as a very efficient catalyst for N_2O decomposition [35].

In presence of NH_3 the TPSR profile of N_2O conversion is generally shifted toward the low temperatures with the remarkable exception of Fe(24)-FER. This shift of the light-off temperature ranges from 70 to 120 K. The catalysts have been ranked according to their activity identified by the light-off temperature: Fe(24)-BEA, Fe(49)-BEA (665 K) $>$ Fe(44)-OFF (695 K) $\approx$ Fe(19)-MFI $\geqslant$ Fe(24)-FER (710 K) $>$ Fe(20)-MAZ (725 K) $>$ Fe(12)-MOR (768 K) $>$ Fe(45)-FAU (787 K).

The involvement of NH_3 in the process of N_2O reduction is proved by the consumption ration near 1 at 693 K on Fe(49)-BEA. At this temperature the oxidation of NH_3 by O_2 does not compete with N_2O free feed, as shown by separated experiments. Moreover, the catalytic decomposition of N_2O, in the absence of NH_3, only represents 15% of N_2O conversion. More insights into the role of NH_3 in the reduction of N_2O to N_2 can be found from the SCR of $^{14}N_2O$ with $^{15}NH_3$ on a Fe(97)-BEA at 623 K and steady-state conditions [33]. The presence of $^{14}N_2$, $^{15}N_2$ and $^{14}N^{15}N$ shows that different reaction mechanisms intervene in the N_2O reduction:

(1) $^{14}N_2O$ would decompose on the active iron sites to $^{14}N_2$ and adsorbed O. The sites are in turn regenerated by $^{15}NH_3$ with release of $^{15}N_2$ and H_2O.

(2) $^{14}N_2O$ and $^{15}NH_3$ would react together on a same site, after ^{14}N–^{14}N splitting of N_2O, leading to $^{14}N^{15}N$. There is some evidence that O_2 could be involved in this mechanism [36]. Moreover, at temperature above 673 K, the direct decomposition of N_2O, without the help of NH_3, can compete on Fe(49)-BEA, as well as the direct oxidation of NH_3 by O_2 but to a lesser extent. The different boosting effect of NH_3 for the reduction of N_2O depending on the catalyst can be accounted for by various distributions among the possible mechanisms and pathways described above. On that account, we could tentatively postulate that on Fe(24)-FER (i) NH_3 does not accelerate the desorption of O from the active site, and/or (ii) the coupling reaction between N_2O and NH_3 intervenes to a low extent. Works are in progress to elucidate this complex reaction of N_2O reduction by NH_3.

In conclusion, ammonia clearly improves the decomposition of N_2O to N_2 in presence of oxygen over Fe-Z. A gain of 70 K at least is obtained in comparison with the direct decomposition and a 50% conversion is reached at 670 K with a space velocity of 30,000 h^{-1} over Fe-BEA, the most active catalyst. Among the zeolite structures tested BEA seems the most efficient host for iron ions in the reduction of N_2O by NH_3 [37].

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