ELSEVIER

Catalysis Today 75 (2002) 373–378

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The catalytic activity of FeO_x/ZrO_2 for the abatement of NO with propene in the presence of O_2

Simonetta Tuti [a,1], Franco Pepe [a,1], Daniela Pietrogiacomi [b], Valerio Indovina [b,*]

[a] Dipartimento di Ingegneria Meccanica e Industriale, Università degli Studi Roma Tre, Via della Vasca Navale 79, 00159 Rome, Italy
[b] Dipartimento di Chimica, Università di Roma La Sapienza, P.le Aldo Moro 5, 00185 Rome, Italy

Abstract

FeO_x/ZrO_2 samples, prepared by impregnation with $Fe(NO_3)_3$, were characterised by means of DRS, XRD, FTIR, redox cycles and volumetric CO adsorption. Volumetric CO adsorption, combined with FTIR, showed that 45% of iron in the sample containing 2.8 Fe atoms nm^{-2} was capable of forming iron carbonyls. DRS evidenced Fe_2O_3 on samples with Fe-content $\geq$ 2.8 atoms nm^{-2}. The selective catalytic reduction of NO with C_3H_6 in the presence of O_2 was studied with a reactant mixture containing NO = 4000 ppm, C_3H_6 = 4000 ppm, O_2 = 2%. The dependence on iron-content suggests that only isolated iron, prevailing in dilute FeO_x/ZrO_2, is active for NO reduction, whereas iron on the surface of small oxide particles, prevailing in concentrated FeO_x/ZrO_2, is active for C_3H_6 combustion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO abatement; ZrO_2 support; Supported iron oxides

1. Introduction

For the abatement of NO with hydrocarbons in the presence of O_2, transition metal ion (TMI) exchanged zeolites are generally more active than the relevant supported catalysts [1,2]. A possible reason for their higher activity is that zeolites disperse the active TMI at atomic level, whereas on supported catalysts TMI dispersion strongly depend on the support, metal loading and calcination temperature.

Using propene as the reducing agent in the presence of O_2, we found that the activity of TMI supported on ZrO_2 depended on metal dispersion. On CuO_x/ZrO_2 catalysts containing up to 2.5 Cu atoms nm^{-2}, namely below the limit for high copper dispersion, the turnover frequency (NO molecules converted per second per Cu-atom) was nearly independent of Cu-content and almost equalled that of Cu-ZSM5 [3,4]. In a more recent study we found that the same result holds for CoO_x/ZrO_2 where isolated cobalt was as active as isolated Co^{2+} in ZSM5 [5].

Some papers have previously addressed preparation and characterisation of FeO_x/ZrO_2 [6–8]. In agreement with Boot et al. [7], Okamoto et al. [8] reported that on FeO_x/ZrO_2, three kinds of iron species were present, depending on concentration: isolated Fe^{3+}, most abundant below 2.8 Fe atoms nm^{-2}, small Fe^{3+} oxide clusters (diameter <8 nm), and α-Fe_2O_3 particles above 4 atoms nm^{-2}.

For the present investigation, using the same approach we used before in studying CuO_x/ZrO_2 and CoO_x/ZrO_2 [3–5], we prepared FeO_x/ZrO_2 catalysts with iron-content up to 5.7 atoms nm^{-2}. We characterised these samples by means of XRD, DRS, FTIR, redox cycles and volumetric adsorption of CO, and we

---

[*] Corresponding author. Tel.: +39-6-4991-3381; fax: +39-6-490-324.

E-mail addresses: tuti@uniroma3.it (S. Tuti), valerio.indovina@uniroma1.it (V. Indovina).

[1] Fax: +39-6-55173252.

PII: S0920-5861(02)00068-8

studied their catalytic activity and selectivity for NO abatement with propene in the presence of O_2.

2. Experimental

2.1. Catalysts preparation

The zirconia support was prepared by hydrolysis of zirconium oxychloride with ammonia. Before its use as a support, the material was calcined at 823 K (BET surface area 53 $m^2\,g^{-1}$). XRD spectra showed that ZrO_2 was in monoclinic phase. The FeO_x/ZrO_2 catalysts were prepared by impregnation with $Fe(NO_3)_3{\cdot}9H_2O$ aqueous solutions. All specimens were dried at 383 K in air for 24 h, ground into fine powder and thereafter heated in air at 823 K for 5 h. FeO_x/ZrO_2 catalysts are designated as ZFe*x*, where *x* gives the analytical iron-content (atomic absorption, $x = 0.5, 1.9, 2.8, 3.8, 5.7$ Fe atoms nm^{-2}). Two samples were also prepared as mechanical mixtures by grinding ZrO_2 and Fe_2O_3 in an agate mortar and are designated as ZFe*x*(m), where $x = 2.8$, 5.7 Fe atoms nm^{-2}.

2.2. Spectroscopic characterisations

The XRD patterns were obtained with a Philips PW 1729 diffractometer using Ni-filtered Cu Kα radiation. The DRS spectra were recorded in the wavelength range 200–2500 nm using a Cary 2300 spectrometer. FTIR spectra were recorded at RT on a Perkin Elmer 2000 spectrometer, collecting 4–20 scans at a resolution of 4 cm^{-1}. Powdered materials were pelleted (1.5×10^4 kg cm^{-2}) in self-supporting disks of about 20 mg cm^{-2} and 0.1–0.2 mm thickness. Disks were placed in an IR quartz cell allowing thermal treatments in vacuo (10^{-5} Torr) or in a controlled atmosphere. Before experiments, samples were heated in dry O_2 at 793 K for 1 h, and evacuated at the same temperature for 1 h (standard oxidation, s.o.).

2.3. Volumetric measurements

CO adsorption measurements and redox cycles with H_2 or O_2 were performed in a silica reactor connected to an all-glass circulation apparatus. From the pressure decrease we calculated the total amount of adsorbed CO, consumed H_2 or consumed O_2. ZFe s.o. were reduced with H_2 (50 Torr) at 653 K, evacuated at 773 K, and heated in O_2 at 773 K. The amount of H_2 consumed gave the reduction-extent, electron per iron atom, $(e/Fe)_{H_2}$, and the O_2 consumed gave the oxidation-extent, $(e/Fe)_{O_2}$.

2.4. Catalytic tests

The catalytic activity was measured in a flow apparatus at atmospheric pressure with GC analysis of reactants and products. Unless otherwise specified, the reactant gas contained $NO = 4000$ ppm, $C_3H_6 = 4000$ ppm, and $O_2 = 2\%$, with He as balance. The total flow rate was 50 cm^3 STP/min and space velocity (GHSV) was 24,000 h^{-1}. Before catalytic experiments, a portion of catalyst (0.25 g) was pretreated in a flow of 2% O_2/He mixture (100 cm^3 STP/min) at 793 K for 30 min. NO conversion was determined from the N_2 and N_2O produced. Reaction rates were calculated from the following reactions:

$$C_3H_6 + 2NO + \tfrac{7}{2}O_2 \rightarrow N_2 + 3H_2O + 3CO_2 \quad (1)$$

$$C_3H_6 + 2NO + 4O_2 \rightarrow N_2O + 3H_2O + 3CO_2 \quad (2)$$

$$C_3H_6 + \tfrac{9}{2}O_2 \rightarrow 3H_2O + 3CO_2 \quad (3)$$

$$C_3H_6 + 3O_2 \rightarrow 3H_2O + 3CO \quad (4)$$

The rate of NO abatement, r_{NO}, was calculated from $N_2 + N_2O$ molecules produced in reactions (1) and (2). The rate of the total consumed C_3H_6, $r_{C_3H_6}$, was calculated from total $CO_2 + CO$ molecules produced. The rate of C_3H_6 combustion, r_{comb}, was calculated as $r_{C_3H_6} - r_{NO}$. All rates were expressed as r (molecules $s^{-1}\,g^{-1}$). The percent selectivities, S_{SCR} (NO reduction rather than C_3H_6 combustion), S_{N_2} (N_2 rather than N_2O), and S_{CO_2} (CO_2 rather than CO) were calculated as follows: $S_{SCR} = 100(N_2 + N_2O/C_3H_6\text{ converted})$, $S_{N_2} = 100(N_2/N_2 + N_2O)$, $S_{CO_2} = 100(CO_2/CO_2 + CO)$.

3. Results

3.1. DRS and XRD characterisation

DRS spectra of ZFe samples consisted of a strong band in the region 40,000–30,000 cm^{-1}, that increased in intensity with Fe^{3+}-content up to 3.8 atoms nm^{-2}. Higher metal contents induced no further increase.

Very weak bands were also detected at about 21,000, 18,800, 12,000 cm^{-1}, the latter two only on samples with Fe^{3+}-content ≥ 2.8 atoms nm^{-2}. All these bands are typical of Fe^{3+} complexes [9]. Bands in the region 40,000–30,000 cm^{-1} have been previously observed in zeolites and assigned to Fe^{3+}, both isolated and in small iron oxide clusters [10,11]. DRS spectra of mechanical mixtures, ZFe(m), markedly differed from those of ZFe. In particular, the strong band in the region 40,000–30,000 cm^{-1} was absent. ZFe(m) spectra consisted of a continuous absorption starting at about 18,000 cm^{-1}, and bands at about 15,500, 12,000 cm^{-1}, the intensity of all these bands increasing with Fe_2O_3-content. The comparison with ZFe indicated the presence of Fe_2O_3 particles only in ZFe with Fe-content ≥ 2.8 atoms nm^{-2}. XRD spectra of all ZFe samples showed ZrO_2 monoclinic reflections only, indicating that Fe_2O_3 particles, when present, were smaller than 5 nm.

3.2. FTIR characterisation

On s.o. ZrO_2, CO adsorption at RT yielded two bands at 2190 and 2185 cm^{-1}, assigned to σ-coordinated CO on two Zr^{4+} Lewis acid sites, in agreement with early reports [4,5]. On all s.o. ZFe samples, in addition to Zr^{4+}–CO species, CO adsorption at RT yielded: (i) bands of iron carbonyls in the region 2200–1950 cm^{-1}, assigned to various Fe^{2+}–CO and (ii) intense bands in the region 1800–1000 cm^{-1}, assigned to monodentate and bidentate carbonates [12] (Fig. 1, spectrum 1). On ZFe samples, heated in dry oxygen at 773 K, cooled at RT in the presence of dry O_2 and evacuated at RT, CO adsorption at RT yielded the same bands as observed on s.o. ZFe, showing that iron underwent no reduction during the treatment in vacuo at 773 K. On s.o. ZFe reduced with H_2 at 653 K and evacuated at 773 K, CO adsorption at RT yielded more intense Fe^{2+}–CO bands than those observed on the relevant s.o. samples, two bands at 2036 and 1994 cm^{-1}, tentatively assigned to a small fraction of Fe^0–CO, and extremely weak (or absent) carbonate bands (Fig. 1, spectrum 2).

On both s.o and reduced samples, the integrated intensity of iron carbonyls markedly increased with iron-content up to 2.8 atoms nm^{-2}, continued to increase, but less markedly, up to 3.8 atoms nm^{-2}, and decreased on the sample with 5.7 Fe atoms nm^{-2}.

On all s.o. ZFe samples, NO adsorption at RT yielded: (i) a very intense band at about 1820 cm^{-1}, consisting of unresolved components assigned to various Fe^{2+}–NO, (ii) bands in the region 1250–1000 cm^{-1}, assigned to nitrites species, and (iii) a weak band at 2245 cm^{-1}, reversible at RT, assigned to N_2O adsorbed on the ZrO_2 surface. On s.o. ZFe samples reduced with H_2 at 653 K and evacuated at 773 K, NO adsorption at RT yielded the same nitrosyl bands but more intense than those observed on s.o. samples. On all ZFe, containing up to 3.8 Fe atoms nm^{-2}, the band had nearly identical shape (Fig. 2), whereas on the sample ZFe5.7, the band shape was more asymmetric, with a tail towards

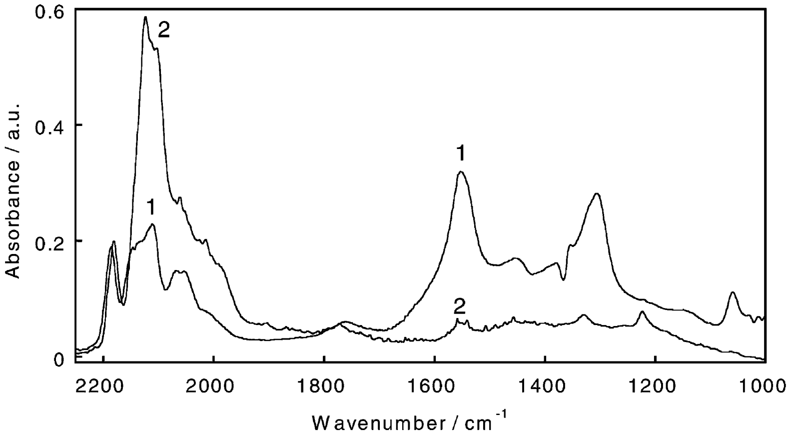

Fig. 1. IR spectra of carbonyls and carbonates formed on ZFe2.8 by CO adsorption at RT (80 Torr). After s.o. treatment (spectrum 1); after heating in H_2 at 653 K and evacuating at 773 K (spectrum 2).

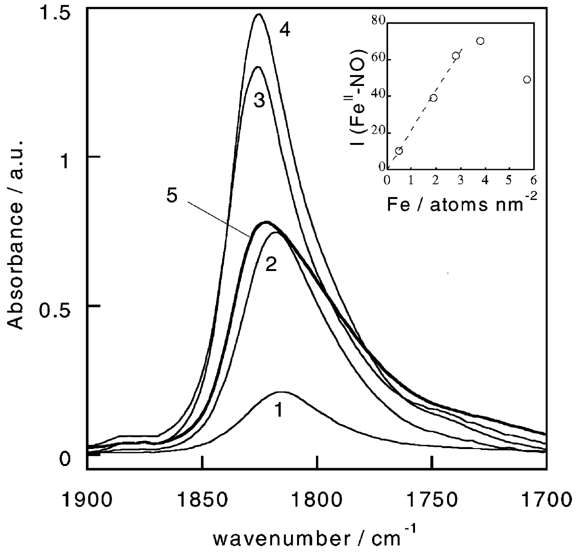

Fig. 2. IR spectra of iron nitrosyls formed by NO adsorption at RT (20 Torr) on s.o. ZFe samples: ZFe0.5 (spectrum 1); ZFe1.9 (spectrum 2); ZFe2.8 (spectrum 3); ZFe3.8 (spectrum 4); ZFe5.7 (spectrum 5). Inset: integrated intensity of iron nitrosyls (cm^{-1}) as a function of iron-content (atoms nm^{-2}).

lower wavenumbers (Fig. 2, spectrum 5), indicating a different distribution of iron species, consistent with the presence of Fe_2O_3. On s.o. ZFe samples, the integrated intensity of nitrosyls proportionally increased with the iron-content on samples up to 2.8 atoms nm^{-2}, increased further, but less markedly, up to 3.8 atoms nm^{-2}, and decreased on the sample with 5.7 Fe atoms nm^{-2} (inset in Fig. 2).

The linear dependence of the integrated intensity of iron carbonyls and nitrosyls on the iron-content in samples containing up to 2.8 Fe atoms nm^{-2} suggests that in these samples a large fraction of iron was highly dispersed on the ZrO_2 surface. This result is consistent with DRS data showing that in ZFe samples with an iron-content $\geq$ 2.8 atoms nm^{-2} Fe_2O_3 particles form.

3.3. Redox cycles and volumetric CO adsorption

The ZFe2.8 s.o. sample consumed no oxygen on heating in O_2 at 773 K, $(e/Fe)_{O_2} = 0$. Hence evacuation at 773 K of ZFe samples did not reduce Fe^{3+}. Heating the sample with H_2 at 653 K reduced all Fe^{3+} to Fe^{2+}, $(e/Fe)_{H_2} = 1 \pm 0.1$. A subsequent heating with O_2 a 773 K restored the Fe^{3+}, $(e/Fe)_{O_2} = 1 \pm 0.1$.

The adsorption of CO at RT was measured on s.o. ZFe2.8 after reduction with H_2 at 653 K. As assessed by IR, CO adsorption on reduced samples yielded only iron and zirconium carbonyls: no carbonates formed. The amount of Fe–CO, calculated from the amount of adsorbed CO, corresponded to 45% of analytical iron.

3.4. Catalytic activity for NO reduction with C_3H_6 in the presence of O_2

In the temperature range 473–773 K, all catalysts, including pure ZrO_2, were stable and active as a function of the time on stream throughout experiments lasting up to about 10 h.

Pure ZrO_2 was active above 623 K (Fig. 3a and b). As the temperature increased from 623 to 773 K, the selectivity S_{SCR} decreased from 80 to 50%. At temperature above 673 K, S_{N_2} was higher than 90%. Up to 673 K, S_{CO_2} was 100%, but at higher temperature it decreased to 60%.

ZFe samples were active above 523 K. On all ZFe samples, NO conversion reached a maximum as a function of temperature. As the iron-content in the sample increased, NO reached the maximum conversion at a lower temperature. NO conversion slightly increased with Fe-content in the region 523–623 K, whereas it markedly decreased in the region 623–773 K (Fig. 3a). Conversely, the C_3H_6 conversion monotonically increased with temperature, reaching 100% at the temperature yielding the maximum NO conversion (Fig. 3b). Accordingly, the selectivity S_{SCR}, decreased with temperature and with iron-content. In particular, on ZFe0.5, $S_{SCR} = 60\%$ at 573 K and 20% at 773 K, and on ZFe5.7 $S_{SCR} = 40\%$ at 523 K and 10% at 723 K. S_{N_2} was nearly independent of Fe-content and increased with temperature from 70% at 523 K to 100% above 623 K. Whereas ZrO_2 produced a large amount of CO at temperature above 673 K, on all ZFe samples with Fe-content above 1.9 Fe atoms nm^{-2}, S_{CO_2} was always 100%. On ZFe0.5, S_{CO_2} increased from 80% at 523 K to 100% at 723 K.

3.5. The dependence of rates on iron-content

The rate r_{NO} increased with iron-content up to 2.8 atoms nm^{-2}, and increased only slightly at higher iron-content (Fig. 4a). The rate r_{comb}

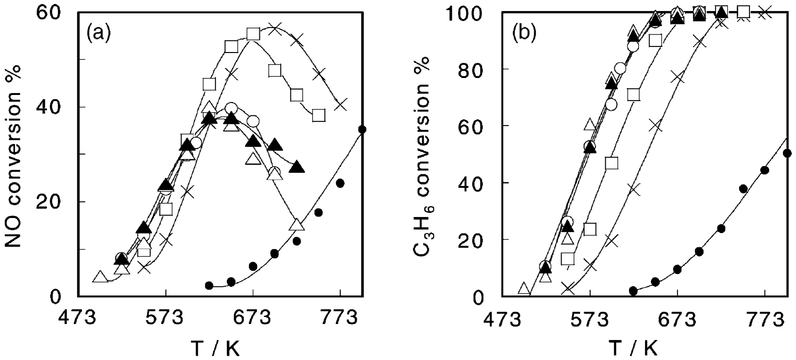

Fig. 3. NO conversion (a) and C_3H_6 conversion (b) as a function of temperature. Catalysts: ZrO_2 (●); ZFe0.5 (×); ZFe1.9 (□); ZFe2.8 (○); ZFe3.8 (△); ZFe5.7 (▲). Reactant mixture: NO = 4000 ppm, C_3H_6 = 4000 ppm; O_2 = 2%.

increased nearly exponentially with Fe-content up to 2.8 Fe atoms nm^{-2}, and increased no further on more concentrated samples (Fig. 4b). Active sites for NO reduction apparently differ from those for propene combustion. The dependence on iron-content suggests that only isolated iron, prevailing in dilute ZFe, is active for NO reduction, whereas iron on the surface of segregated iron oxide, prevailing in concentrated ZFe, is active for C_3H_6 combustion.

3.6. The dependence of catalytic activity on the composition of the reactant mixture

The dependence of NO conversion on the C_3H_6-content in the mixture, was studied using a mixture containing C_3H_6 from 0 to 6000 ppm, NO = 4000 ppm, O_2 = 2% at T = 548 or 623 K. The rate of NO abatement linearly increased as the C_3H_6 partial pressure increased from 0 up to 4000 ppm (reaction order, $n = 0.9$–1.0), and increased little as the C_3H_6-content increased further.

The dependence of NO and C_3H_6 conversion on the O_2-content in the mixture, was studied using a mixture containing O_2 from 0 to 4%, NO = 4000 ppm, C_3H_6 = 4000 ppm. In the absence of O_2, ZFe catalysts were highly active for the C_3H_6 + NO reaction. The activity, however, decreased with time on stream because carbonaceous deposits formed on the catalyst surface. In agreement, we detected CO_2 production on heating these samples in O_2 at 773 K, after C_3H_6 + NO experiments. In the presence of O_2, the catalytic activity for the NO abatement was somewhat

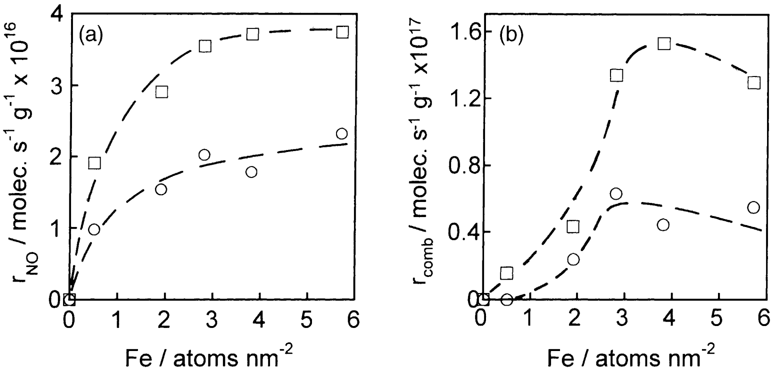

Fig. 4. Rates of NO abatement (a) and C_3H_6 combustion (b) (r (molecules s^{-1} g^{-1})) as a function of iron-content (atoms nm^{-2}) at T = 548 K (○), and T = 573 K (□).

lower but stable as a function of time on stream. With O_2-content in the range 1–4%, both NO and C_3H_6 conversion were independent of the O_2-content.

4. Conclusions

Low loading FeO_x/ZrO_2 samples with iron-content up to 2.8 atoms nm^{-2} contain a large fraction of isolated Fe^{3+} together with small iron oxide particles. On more concentrated samples segregated iron oxide prevails. Isolated iron in FeO_x/ZrO_2 is active and selective for NO reduction in the presence of O_2. Iron on the surface of small oxide particles is active for propene combustion, thus rendering the relevant FeO_x/ZrO_2 non-selective.

Acknowledgements

Financial support was provided by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Programmi di ricerca di interesse nazionale).

References

[1] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, H.H. Kung, Catal. Today 26 (1995) 169.

[2] S. Sato, H. Hirabayashi, N. Mizuno, M. Iwamoto, Catal. Lett. 12 (1992) 193.

[3] D. Pietrogiacomi, D. Sannino, S. Tuti, P. Ciambelli, V. Indovina, M. Occhiuzzi, F. Pepe, Appl. Catal. B 21 (1999) 141.

[4] V. Indovina, M. Occhiuzzi, D. Pietrogiacomi, S. Tuti, J. Phys. Chem. B 103 (1999) 9967.

[5] D. Pietrogiacomi, S. Tuti, M.C. Campa, V. Indovina, Appl. Catal. B 28 (2000) 43.

[6] E. Guglielminotti, J. Phys. Chem. 98 (1994) 4884;
E. Guglielminotti, J. Phys. Chem. 98 (1994) 9033.

[7] L.A. Boot, A. Jos van Dillen, J.W. Geus, A.M. van der Kraan, A.A. van der Horst, F.R. van Buren, Appl. Catal. A 145 (1996) 389.

[8] Y. Okamoto, T. Kubota, Y. Ohto, S. Nasu, J. Catal. 192 (2000) 412.

[9] A.B.P. Lever, Inorganic Electron Spectroscopy, 2nd Edition, Elsevier, Amsterdam, 1984, p. 450, Table 6.13.

[10] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, G. Vlaic, J. Catal. 158 (1996) 486.

[11] G. Centi, F. Vazzana, Catal. Today 53 (1999) 683.

[12] C. Morterra, L. Orio, Mater. Chem. Phys. 24 (1990) 247.