Influence of the support on CO_2 methanation over Ru catalysts: an FT-IR study

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The hydrogenation of CO_2 to methane has been investigated over Ru catalysts supported on zeolite (H-ZSM-5) and on silica. *Supported Ru catalysts were very active for the hydrogenation of CO_2.* Ru/ZSM-5 was more selective to methane than Ru/SiO_2. On the basis of FT-IR spectra of CO and CO_2 adsorbed on the catalysts, it has been suggested that this behaviour can be related to a higher positive polarization of ruthenium on the zeolite. This leads to a weaker Ru–CO bond on the H-ZSM-5-supported sample with a corresponding increase of the hydrogen surface coverage that favours the transformation of the intermediate CO to methane.

Keywords: methanation, carbon dioxide, H-ZSM-5, ruthenium, FT-IR spectroscopy

1. Introduction

In recent years carbon dioxide is regarded as a potentially cheap source of more valuable carbon-containing products. Several articles have appeared in the literature regarding the selective hydrogenation of CO_2 to methane (CO_2 methanation: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) [1–14]. Among all catalysts reported, Ru, Rh, and Ni supported on metal oxides exhibit the highest activity [1–4]. Ruthenium has been reported to be the most selective catalyst towards the formation of methane [1,3]. It has been also shown [2,4–7] that the chemical nature of the support influences strongly the CO_2 methanation reaction. Over Rh catalysts it has been observed that the activity on different supports was in the order $TiO_2 > Al_2O_3 > SiO_2$. This behaviour has been attributed to a different extent of electronic interaction between Rh and the support [2].

The present paper reports an FT-IR study of CO adsorbed on supported Ru catalysts that have been tested in CO_2 methanation with the purpose to better clarify the influence of the support on the catalytic behaviour of ruthenium. CO_2 has been also used as probe molecule for the FT-IR experiments in order to obtain more insight on the reaction mechanism.

2. Experimental

Ru-supported samples were prepared by wet impregnation of the support with aqueous solution of $Ru(NO)(NO_3)_3$. The supports used were two commercial silica gels supplied by Grace (silica SE with a surface area of 490 m^2/g and silica SA with 25 m^2/g) and an H-ZSM-5 zeolite supplied by PQ (SiO_2/Al_2O_3 ratio of 30 and surface area of 410 m^2/g).

Chemisorption of CO was measured in a conventional pulse system operating at room temperature. Pulses of a mixture of 10 vol% CO in He were used. Before chemisorption experiments all samples have been reduced in H_2 for 1 h at 673 K, cooled to 443 K in flowing H_2, held in He at this temperature for 1 h to permit H_2 desorption, and then cooled in flowing He down to RT. Under these conditions negligible amounts of CO were found to chemisorb on the supports [15,16]. Chemisorption of CO, instead of H_2, was used in order to overcome the slow rate of hydrogen uptake on Ru [17].

Code, support used, chemical composition and CO/Ru ratio of the samples are reported in table 1.

The reaction was carried out in a tubular microreactor at atmospheric pressure. Before catalytic tests all samples were reduced in flowing H_2 at 400 °C. A reactant mixture of CO_2 (5.5%), H_2 (55%) and He (39.5%) has been always used. The reaction products were analysed on line by a gas chromatograph (equipped with a packed column with 3% Octoil S on silica and with a TCD detector) and by a quadrupole mass spectrometer (VG quadrupoles). Methane and carbon monoxide were the only products obtained.

FT-IR spectra were performed on a Perkin Elmer System 2000, with a resolution of 2 cm^{-1}, equipped with a MCT detector. Data are reported as difference spectra obtained by subtracting the spectrum on the sample recorded before the interaction with CO or CO_2 and are normalized to the same amount of catalysts per cm^2 (25 $mg\,cm^{-1}$).

Table 1
Chemical composition and CO/Ru ratio of Ru samples.

Code	Support	Ru (wt%)	CO/Ru
SE100N	silica SE	2.0	0.96
Z100N	H-ZSM-5	2.0	0.55
SA100N	silica SA	2.0	0.24

For the FT-IR spectra, the powdered samples were pressed into self-supporting discs, reduced in H_2 at 673 K, cooled to 443 K in flowing H_2, held in He at this temperature for 1 h to permit H_2 desorption, and then cooled in flowing He down to RT.

3. Results and discussion

The FT-IR investigation of adsorbed CO and CO_2 has been carried out on Ru catalysts supported on silica (SE100N) and on H-ZSM-5 zeolite (Z100N) that have been previously tested in the catalytic hydrogenation of CO_2. The catalytic tests carried out at 623 K have shown that the two investigated Ru samples have a comparable activity in terms of velocity per gram of Ru (SE100N $= 5.41 \times 10^{-4}$ mol s^{-1} (g Ru)$^{-1}$, Z100N $= 4.90 \times 10^{-4}$ mol s^{-1} (g Ru)$^{-1}$) while the turnover frequency is slightly higher for the Z100N sample (SE100N $= 0.057$ mol s^{-1} Ru$_s^{-1}$, Z100N $= 0.090$ mol s^{-1} Ru$_s^{-1}$). On both the investigated catalysts methane and CO were the only products formed. No deactivation has been observed during ten hours of operation, indicating that in the presence of hydrogen no irreversible coking was taking place.

Figure 1 shows the selectivity to CO and CH_4 as a function of conversion. On increasing the conversion levels the selectivity to CO decreases. This decrease is much more relevant on the Z100N sample where no CO is formed for conversions higher than 20%.

These results are in agreement with literature data [3,4,7–9], which have shown that the methanation of CO_2 is a consecutive reaction that proceeds through the dissociation of CO_2 to adsorbed CO and then following the same reaction pathway as CO hydrogenation.

In order to verify if the different selectivity of the two Ru catalysts could be ascribed to the different metal dispersion (table 1), a silica-supported sample with a much lower Ru dispersion (SA100N) has been tested and the results reported for comparison in figure 1. It can be observed that the SA100N sample exhibits a CO selectivity similar to that measured on SE100N. Ru supported on H-ZSM-5 (Z100N), which has a metal dispersion intermediate between SA100N and SE100N, shows, instead, a selectivity to CO much lower than the silica-supported samples. This suggests that an effect of the support must be considered to account for the much lower CO selectivity observed on the Z100N catalyst.

Figures 2 and 3 show the FT-IR spectra of CO adsorbed at room temperature on SE100N (figure 2) and Z100N (figure 3) after admission of 25 mbar of CO and outgassing at room temperature at 2 mbar (spectrum (a)) and at increasing outgassing temperatures (spectra (b)–(e)).

On SE100N (figure 2), a main band at 2040 cm^{-1} has been observed. This band can be assigned to CO linearly adsorbed on Ru^0 [16]. A shoulder at 2080 cm^{-1} and a band at 2142 cm^{-1} are also present, due to CO adsorbed on Ru$^{\delta+}$ (respectively, Ru$^{\delta+}$–CO and Ru$^{\delta+}$(CO)$_3$ species) [16]. Moreover, it is possible to note a shoulder at around 2000 cm^{-1}, due to CO adsorbed on isolated Ru^0 atoms [16]. The intensity of all bands decreases continuously on evacuation at increasing temperatures (spectra (b)–(e)). At 573 K (spectrum (e)), all CO bands practically disappear thus showing that at this temperature CO is almost completely desorbed from the metal surface.

On Z100N (figure 3), admission of CO and outgassing at RT at 2 mbar leads to a spectrum approximately with the same series of bands (CO on Ru^0 and Ru$^{\delta+}$–(CO)$_n$

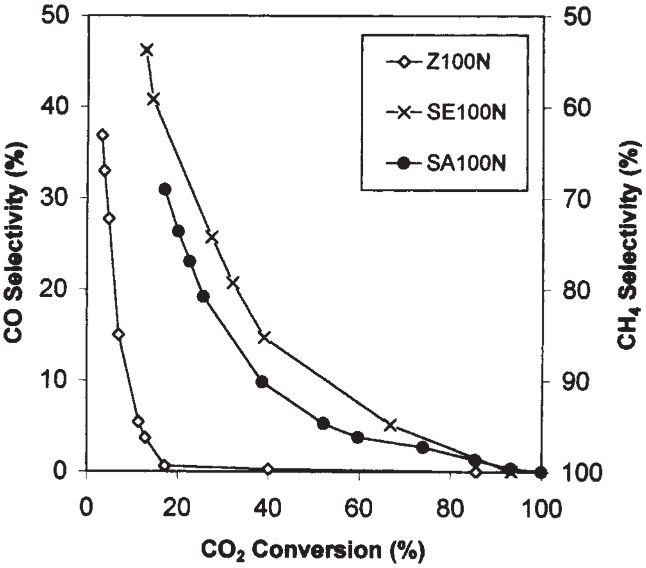

Figure 1. CO and CH_4 selectivity as a function of conversion level measured at 623 K.

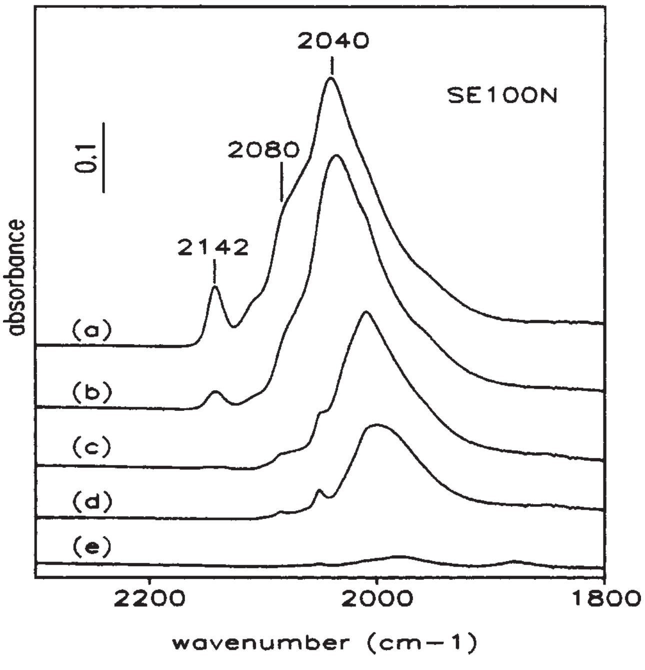

Figure 2. FT-IR spectra recorded after admission of 25 mbar of CO and outgassing at room temperature (spectrum (a)), 373 K (spectrum (b)), 473 K (spectrum (c)), 523 K (spectrum (d)) and 573 K (spectrum (e)) on the SE100N sample.

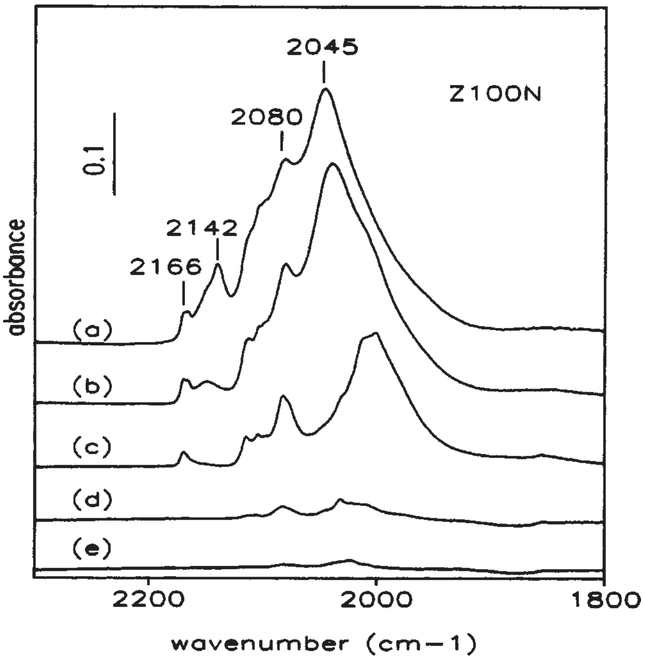

Figure 3. FT-IR spectra recorded after admission of 25 mbar of CO and outgassing at room temperature (spectrum (a)), 373 K (spectrum (b)), 473 K (spectrum (c)), 523 K (spectrum (d)) and 573 K (spectrum (e)) on the Z100N sample.

species) [15]. However, it must be noted that on Z100N the percentage of CO adsorbed on $Ru^{\delta+}$ (frequencies in the region 2080–2142 cm^{-1}) [15] is quite higher than on SE100N. On Z100N, a new band at 2166 cm^{-1} is also present. According to literature data [15,18] this band can be attributed to $Ru^{2+}(CO)_n$ species, formed as a result of an ionic exchange with the protons of the zeolite.

The presence of a higher amount of $Ru^{\delta+}$ species on the H-ZSM-5-supported sample (compared to the silica-supported one) suggests that Ru interacts strongly with the zeolitic support, possibly through the reaction of the OH groups of the zeolite with Ru, with formation of oxidized Ru particles. A strong metal–support interaction on H-ZSM-5-supported metal catalysts has been previously reported by several authors [15,19,20]. Moreover, the formation of H_2 by interaction of the metal with the zeolite has been also detected on metal-supported zeolite [20].

The FT-IR spectra recorded on Z100N after admission of CO and outgassing at increasing temperatures (figure 3) show that on the H-ZSM-5-supported sample CO desorbs at a lower temperature than when silica is used as support (compare the two spectra (d) of figures 2 and 3 after outgassing at 523 K). This different behaviour clearly indicates that on Z100N, CO is bound to the atoms of Ru on the surface less strongly than on SE100N.

The above reported FT-IR experiments indicate that the support strongly influences the electronic state of Ru, playing an important role in determining the catalytic behaviour of Ru in the hydrogenation of CO_2 to methane. On the basis of these results it is possible to suggest that the lower CO selectivity observed on the Z100N sample compared to SE100N (see figure 1) could be related to a more oxidized electronic state of ruthenium on the zeolite. The more positive Ru particles lead to a weaker Ru–CO bond, also in accordance to the results of Doi et al. [21]. Since CO and H_2 has been reported to compete for the same adsorption sites in CO hydrogenation [9,21,22], it is likely that a lower CO coverage on Ru increases the concentration of hydrogen on the surface (i.e., the H_2/CO ratio) and consequently the overall rate of CO_2 methanation. Kinetic studies [2,3,5,12] have shown, in fact, a strong dependence of CO_2 methanation on H_2 partial pressure. The competitive effect of the adsorption of CO is confirmed by the fact that the presence of gas phase CO in the feed has been found to slow significantly the rate of CO_2 hydrogenation [2,4,8]. This is also in agreement with the fact that the CO_2/H_2 reaction occurs on Ru or Rh much faster and with a lower activation energy than CO hydrogenation [2,3,9,12,14,23]. Zhang et al. [12,13] have also reported a positive influence of doping Rh/TiO_2 catalysts by W^{6+} and attributed the increased activity of the doped systems to an enhanced hydrogen adsorption capacity and a weakening of the Rh–CO bond due to the presence of the W^{6+} cations.

Therefore, it can be concluded that on the Z100N sample a decrease in the electron density of the Ru surface aggregates favours the second step of CO_2 methanation, i.e., the CO/H_2 reaction, strongly affecting the selectivity towards the formation of the intermediate carbon monoxide. This hypothesis is confirmed by the results of the catalytic activity measurements of CO hydrogenation carried out at 623 K on Z100N and on SE100N. Turnover numbers measured on Z100N were, in fact, about 5 times higher than on SE100N [24].

Figure 4 shows the spectra of CO_2 adsorbed at room temperature on SE100N (spectrum (a)) and on Z100N (spectrum (b)) after admission of 25 mbar of CO_2. In the spectrum (a) it is possible to observe two main bands respectively at 2343 cm^{-1}, attributed to the asymmetric stretching (ν_3 mode) of gaseous CO_2 which interacts with the support [25], and at 1426 cm^{-1}, due to a symmetric carbonate species [3,9,25]. This latter band is absent in the spectrum of the support alone (SiO_2), so indicating the participation of Ru in the formation of the carbonate species. A small band at 1620 cm^{-1} is also present, and it is probably due to traces of water in the feed.

In the spectrum of CO_2 adsorbed on the Z100N sample (spectrum (b)) bands are present at 2347, 1984, 1620, 1426 and 1380 cm^{-1} (after admission of CO_2 on the H-ZSM-5 alone only the bands at 2347 and 1380 cm^{-1} have been detected). The main band of the spectrum is the band at 2347 cm^{-1} (asymmetric stretching of CO_2) which is much more intense than the corresponding one on SE100N, indicating a higher amount of CO_2 interacting with the zeolite. The interaction probably involves the OH groups of the zeolite, as confirmed by the negative band (not shown in the figure) in the OH stretching region at 3610 cm^{-1}. This interaction with the zeolite induces a loosing of the CO_2 molecular symmetry, leading to the activation of the

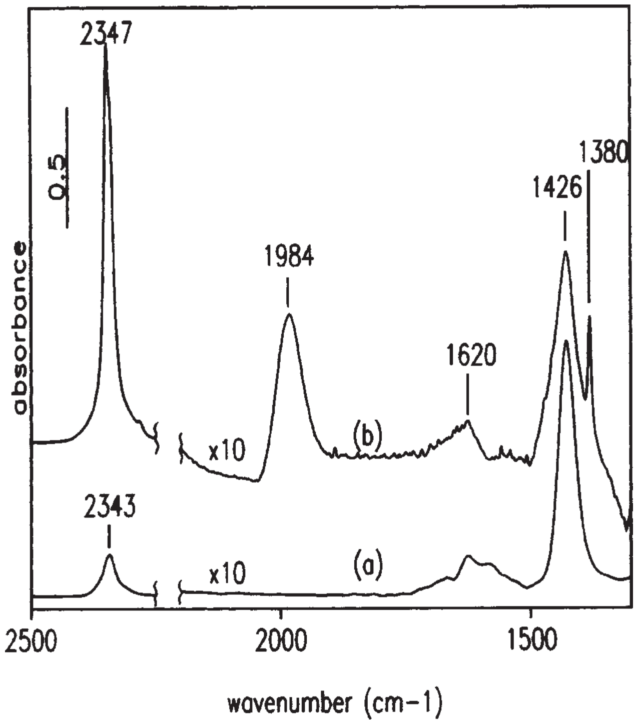

Figure 4. FT-IR spectra recorded at room temperature after admission of 25 mbar of CO_2 on SE100N (spectrum (a)) and Z100N (spectrum (b)).

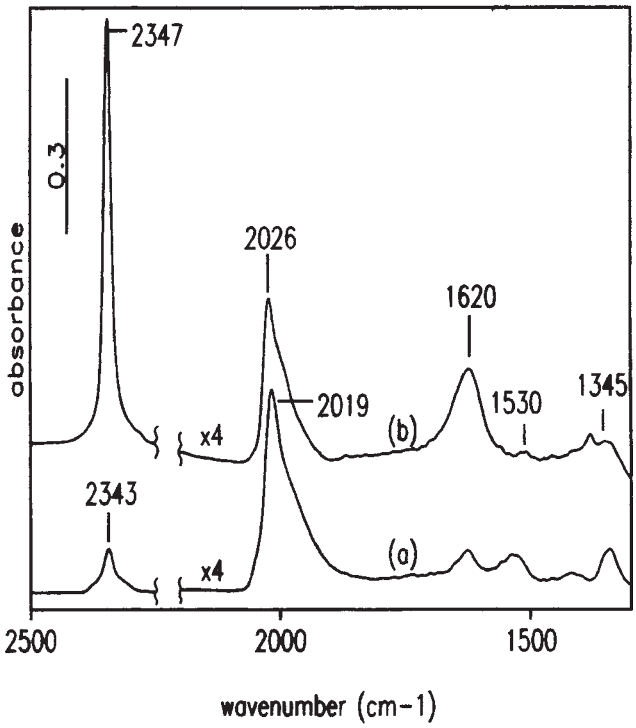

Figure 5. FT-IR spectra recorded at room temperature after admission of a mixture of 25 mbar of CO_2 and 65 mbar of H_2 on SE100N (spectrum (a)) and Z100N (spectrum (b)).

stretching ν_1 mode, as confirmed by the appearance of the band at 1380 cm^{-1} [26,27]. The attribution of this band to formate species can be excluded by considering that it disappears very easily upon outgassing at room temperature. The other two bands, observed in the spectrum (b) at 1426 and 1984 cm^{-1}, can be respectively attributed to a symmetric carbonate species and to CO linearly adsorbed on isolated Ru^0 atoms. The presence on the Z100N sample of a band due to CO, after admission of CO_2 alone (i.e., in the absence of H_2), suggests the participation of the OH groups of the zeolite in the dissociation step of CO_2 to CO.

In figure 5 are reported the spectra recorded after admission at room temperature of a mixture of 25 mbar of CO_2 and 65 mbar of H_2 on SE100N (spectrum (a)) and on Z100N (spectrum (b)). In addition to the CO_2 bands, both on Z100N and SE100N it is possible to observe an intense band at around 2020 cm^{-1} assigned to CO linearly adsorbed on Ru^0. This band presents a lower frequency compared to the corresponding one observed on the same samples after admission of CO (figures 2 and 3). This red shift observed in the C–O stretching frequency in the presence of H_2 is likely due to the formation of hydrocarbonyl RuH(CO) species [3,10,28], so confirming the competition of CO and H_2 for the same Ru sites [10,28]. Figure 5 also shows that on both spectra are present bands at around 1345 and 1530 cm^{-1} (respectively, symmetric and asymmetric O–C–O stretching vibration of formate species [3,8,10]) and at 1620 cm^{-1} (O–H bending vibration of adsorbed water).

On the basis of these results it seems highly probable that both on H-ZSM-5 and silica-supported Ru catalysts the methanation of CO_2 proceeds with the same mechanism. The FT-IR spectra of figures 4 and 5 are in agreement with the reaction pathway reported in the literature [4,8,9] which assumes that CO_2 hydrogenation proceeds through the formation of formate species, which evolve to adsorbed CO and water. CO is then hydrogenated to methane with the same reaction pathway as that of CO hydrogenation.

4. Conclusions

On the basis of the obtained results the following conclusions can be drawn:

(a) Supported Ru resulted to be a very effective catalyst for CO_2 methanation. On Ru/ZSM-5 a higher selectivity to methane, compared to Ru/SiO_2, has been obtained.

(b) A metal–support interaction occurs between Ru and the support, which modifies the electronic state of the active metal (Ru), strongly affecting the selectivity to CO. The quite higher selectivity to methane obtained on Ru/ZSM-5, compared to Ru/SiO_2, has been related to a higher positive polarization of Ru on the zeolite. A more oxidized Ru leads to a weaker Ru–CO bond with a corresponding increase in H_2 concentration, which favours the transformation of the intermediate CO to methane.

(c) Both on H-ZSM-5 and silica-supported Ru catalysts the methanation of CO_2 proceeds with the same mechanism, probably via hydrogen-assisted dissociation of CO_2 to some form of adsorbed CO, and then following the same reaction pathway as CO hydrogenation.

References

[1] G.D. Weatherbee and C.H. Bartholomew, J. Catal. 87 (1984) 352.
[2] F. Solymosi, A. Erdöhelyi and T. Bansagi, J. Catal. 68 (1981) 371.
[3] F. Solymosi, A. Erdöhelyi and M. Kocsic, J. Chem. Soc. Faraday Trans. I 77 (1981) 1003.
[4] M.A. Henderson and S.D. Worley, J. Phys. Chem. 89 (1985) 1417.
[5] A. Erdöhelyi, M. Pasztor and F. Solymosi, J. Catal. 98 (1986) 166.
[6] C.K. Vance and C.H. Bartolomew, Appl. Catal. 7 (1993) 169.
[7] T. Iizuka, Y. Tanaka and K. Tanabe, J. Catal. 76 (1982) 1.
[8] M.K. Prairie, A. Renken, J.G. Highfield, K. Ravindranathan Thamphi and M. Gratzel, J. Catal. 129 (1991) 130.
[9] I.A. Fisher and A.T. Bell, J. Catal. 54 (1996) 162.
[10] N.M. Gupta, V.S. Kamble, V.B. Kartha, R.M. Iyer, K. Ravindranathan Thamphi and M. Gratzel, J. Catal. 146 (1994) 173.
[11] F. Solymosi and H. Knözinger, J. Catal. 122 (1990) 166.
[12] Z. Zhang, A. Kladi and X.E. Verykios, J. Catal. 148 (1994) 737.
[13] Z. Zhang, A. Kladi and X.E. Verykios, J. Catal. 156 (1995) 37.
[14] M. Bowker, T.J. Cassidy, A.T. Ashcroft and A.K. Cheetham, J. Catal. 143 (1993) 308.
[15] C. Crisafulli, S. Scirè, S. Minicò, R. Maggiore and S. Galvagno, Appl. Surf. Sci. 99 (1996) 401.
[16] C. Crisafulli, R. Maggiore, S. Scirè and S. Galvagno, J. Chem. Soc. Faraday Trans. 90(18) (1994) 2809.
[17] C. Crisafulli, R. Maggiore, S. Scirè, L. Solarino and S. Galvagno, J. Mol. Catal. 63 (1990) 55.
[18] J.G. Goodwin and C. Naccache, J. Catal. 120 (1980) 1.
[19] J.Y. Shen, A. Sayari and S. Kaliaguine, Appl. Spectrosc. 46 (1992) 1279.
[20] J. Sarkani, J.L. d'Itri and W.M.H. Sachtler, Catal. Lett. 16 (1992) 241.
[21] Y. Doi, H. Miyake and K. Soga, J. Chem. Soc. Chem. Commun. 347 (1987).
[22] C.S. Kellner and A.T. Bell, J. Catal. 70 (1981) 418.
[23] B.A. Sexton and G.A. Somorjai, J. Catal. 46 (1997) 167.
[24] S. Scirè and C. Crisafulli, unpublished results.
[25] H. Knözinger, Adv. Catal. 25 (1976) 184.
[26] M. Forster and M. Schumann, J. Chem. Soc. Faraday Trans. I 85 (1989) 1149.
[27] J.C. Lavalley, Catal. Today 27 (1996) 377.
[28] N.M. Gupta, V.P. Londhe and V.S. Kamble, J. Catal. 169 (1997) 423.