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Strong metal–support interaction in Ni/TiO_2 catalysts: in situ EXAFS and related studies

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In situ EXAFS and X-ray diffraction investigations of Ni/TiO_2 catalysts show that $NiTiO_3$ is formed as an intermediate during calcination of catalyst precursors prepared by the wet-impregnation method; the intermediate is not formed when ion-exchange method is used for the preparation. On hydrogen reduction, $NiTiO_3$ gives rise to Ni particles dispersed in the TiO_2(rutile) matrix. The occurrence of the anatase–rutile transformation of the TiO_2 support, the formation and subsequent decomposition/reduction of $NiTiO_3$ as well as the unique interface properties of the Ni particles are all factors of importance in giving rise to metal–support interaction. Active TiO_2(anatase) prepared from gel route gives an additional species involving Ni^{3+}.

Keywords: SMSI; strong metal–support interaction; Ni/TiO_2 catalyst; EXAFS of catalysts

1. Introduction

There has been considerable effort to understand the nature of interaction between reducible oxide supports such as TiO_2 and the dispersed transition metals [1–3]. Such catalysts displaying strong metal–support interaction (SMSI) exhibit suppression of chemisorption of H_2 and CO [4]. One of the widely accepted models for the SMSI state is the decoration model [2,5,6] according to which a progressive reduction of the surface of the oxide support leads to the burial of metal particles, probably involving complex interaction at the interface. The nature of this interaction is, however, not entirely understood [7,8]. Recent studies of TiO_2-supported catalysts have shown that the anatase–rutile transformation of TiO_2 occurs around the temperature where SMSI effect manifests itself [9–11]. We have been interested in understanding the SMSI state in the Ni/TiO_2 catalysts and its possible relation to the anatase–rutile transformation

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of the TiO_2 support. For this purpose we have carried out in situ EXAFS and X-ray diffraction measurements on Ni/TiO_2 catalysts prepared with commercial Degussa TiO_2 (50 m^2/g) as well as with TiO_2 gel possessing a higher surface area (85 m^2/g). We have compared the Ni/TiO_2 catalysts prepared by both the wet-impregnation and the ion-exchange methods since the latter method is not expected to favour the SMSI state [12]. We have also measured EXAFS spectra at different temperatures in order to understand the nature of Ni particles present in the SMSI state.

2. Experimental

The commercial Degussa TiO_2 contained 75% anatase and 25% rutile, while the TiO_2 gel prepared by a hydrothermal process involving hydrolysis of $TiOCl_2$ was entirely in the anatase form. In the wet-impregnation method, TiO_2 was slurried with nickel nitrate solution containing the required amount of nickel. After adding a small quantity of acetone, the slurry was ground and dried for 1 h under vacuum. In the ion-exchange method, TiO_2 was refluxed at 373 K for 20 h in an ammoniacal solution of nickel nitrate (pH = 11). After the blue solution turned clear, the mixture was filtered hot and dried at 373 K. The catalyst samples were calcined in air at different temperatures and then subjected to hydrogen reduction at 573 K (low-temperature reduction) and 823 K (high-temperature reduction) for 6 h in the EXAFS in situ cell. X-ray diffraction measurements were carried out with a Jeol diffractometer.

EXAFS spectra were recorded at room temperature using a Rigaku spectrometer attached to a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). The precursor catalysts were pressed into self-supporting wafers and the thickness of the wafer was adjusted so that the edge jump (μ.d) in the EXAFS was 1.0 in every case. Fourier transforms (FT) of the EXAFS data were obtained with $k_{min} \approx 3.5$ and $k_{max} \approx 12.75$ Å^{-1} after weighting the data by k^3. Curve fitting analysis was carried out using a multiphasic model involving the additive relationship of EXAFS function [13]. The amplitude and phase functions of Ni–Ni and Ni–O atom pairs were extracted from the inverse-transformed data of the reference compounds, Ni metal ($N_{Ni-Ni} = 12$; $R_{Ni-Ni} = 2.48$ Å) and NiO ($N_{Ni-O} = 6$; $R_{Ni-O} = 2.08$ Å). In order to perform low-temperature EXAFS measurements, the reduced catalyst samples were transferred to an indiginously designed sample cell without exposure to air. Temperatures down to 25 K were attained using an Air Products cryogenic refrigeration system.

3. Results and discussion

In fig. 1a we show the FTs of Ni(10 wt%)/(TiO_2(Degussa) calcined at different temperatures. We see two distinct peaks at 1.4 and 1.9 Å correspond-

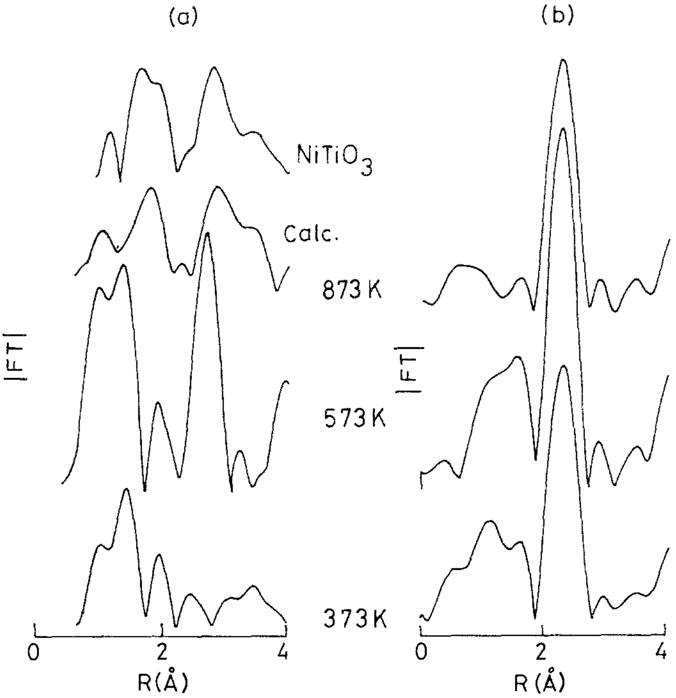

Fig. 1. Fourier transforms (FT) of the Ni K-EXAFS of Ni(10 wt%)/TiO$_2$(Degussa) prepared by the wet impregnation method. (a) Samples calcined at different temperatures; FT of bulk NiTiO$_3$ is also shown. (b) Catalyst after reduction at 823 K.

ing to Ni–O distances of 1.75 and 2.15 Å in the samples calcined at 373 and 573 K. An additional peak at 2.66 Å due to Ni–Ni coordination as in NiO is also seen in the FT of the sample calcined at 573 K. The FT of the catalyst calcined at 873 K, however, resembles that of the bulk NiTiO$_3$ prepared by heating a mixture of NiO and TiO$_2$ gel at 1350 K for 24 h. We have shown the FT of NiTiO$_3$ in fig. 1a for purpose of comparison. X-ray diffraction patterns of Ni/TiO$_2$ calcined at 873 K or higher do indeed show the presence of NiTiO$_3$ on the surface with the most intense reflection at $d = 2.705$ Å [10].

FTs of the Ni(10 wt%)/TiO$_2$(Degussa) catalysts subjected to reduction at 823 K (after precalcination at different temperatures) are shown in fig. 1b. All the FTs show a main feature at 2.22 Å due to Ni–Ni coordination as in Ni metal, the intensity varying with the calcination temperature prior to reduction. Curve fitting using the Ni–Ni parameters from Ni metal gave coordination numbers of 10, 12 and 9 at a distance of 2.45 Å for the catalyst samples pre-calcined at 373, 573 and 873 K, respectively. The initial increase in the coordination number may be due to sintering during calcination of the easily reducible NiO-like species. In the case of the sample calcined at 873 K, we notice that the NiTiO$_3$ particles decompose to well dispersed Ni metal and TiO$_2$ after reduction at 823 K. X-ray diffraction measurements show that the TiO$_2$ so formed exists in the rutile

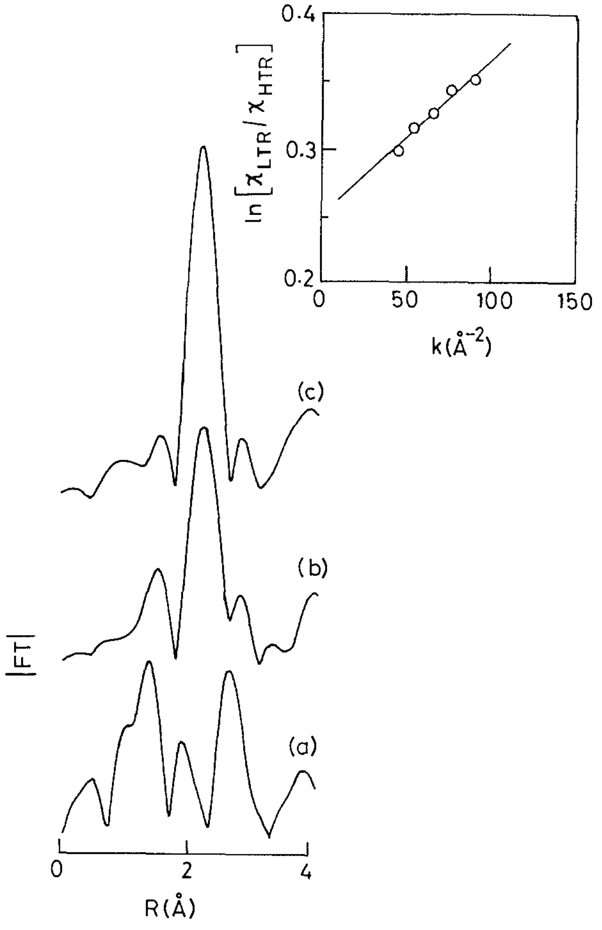

Fig. 2. Fourier transforms of the Ni K-EXAFS of Ni(10 wt%)/TiO_2(Degussa) prepared by the wet impregnation method. (a) Reduced at 823 K and reoxidized at 673 K; (b) after reduction at 573 K (LTR); (c) after reduction at 823 K (HTR). Inset shows the amplitude ratio plot for the catalyst reduced at 823 K.

phase. That is, part of the TiO_2 support present as anatase initially transforms to rutile. X-ray diffraction measurements also show that $NiTiO_3$ is initially formed by the interaction of Ni^{2+} with anatase form of TiO_2.

We have also examined the EXAFS of Ni(10 wt%)/TiO_2(Degussa) catalyst reduced at 823 K after exposure to air at 673 K. The peaks in the FT of the reoxidized catalyst (fig. 2a) are intermediate between those of the catalysts calcined at 573 and 873 K (see fig. 1a) suggesting that the reoxidized sample contains well dispersed $NiTiO_3$. We have subjected this catalyst to a low-temperature reduction at 573 K (LTR) and a high-temperature reduction at 823 K (HTR) in order to understand the differences in the normal and the SMSI states. In both the cases the FTs show a prominent peak corresponding to

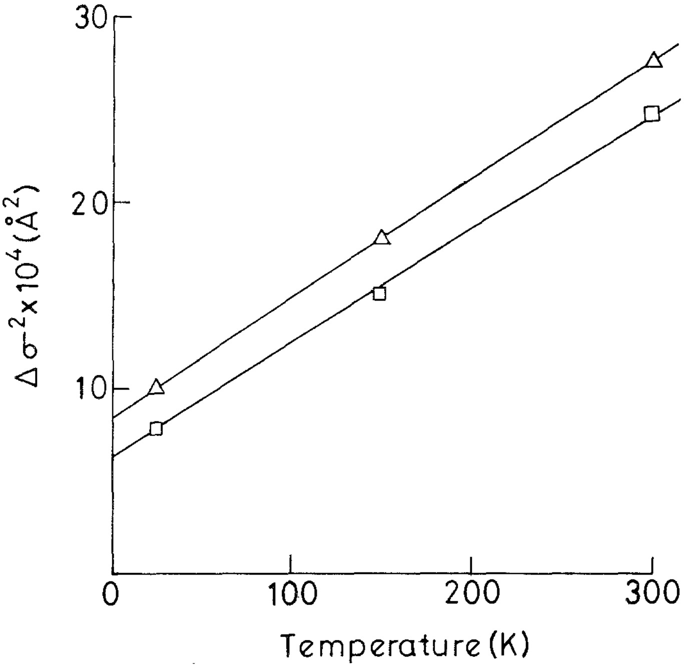

Fig. 3. Variation of $\Delta\sigma^2$ with temperature for Ni(10 wt%)/TiO$_2$(Degussa) subjected to HTR. Nickel metal at 25 K was used as the reference. (△) Wet impregnated; (□) ion-exchanged.

Ni–Ni coordination as in Ni metal (figs. 2b and 2c). We have investigated the amplitude of the inverse transformed data of the peak due to Ni–Ni in the case of the catalyst subjected to HTR relative to that of the catalyst subjected to LTR. The amplitude ratio, $\chi_{\mathrm{LTR}}/\chi_{\mathrm{HTR}}$, is plotted against k^2 in the inset of fig. 2. The catalyst subjected to HTR shows a positive (relative) Debye–Waller factor ($\Delta\sigma^2 = 6 \times 10^{-4}$ Å^2 derived from the slope of the plot), suggesting higher disorder of the metal particles. Kuroda et al. [14] have made a similar observation in the case of the Ru/TiO$_2$ catalyst in its SMSI state. The increased disorder in the HTR sample (the SMSI state) may be related to the differences in the interface between the metal particles and the oxide support.

We have examined the temperature variation of the disorder parameter of Ni(10 wt%)/TiO$_2$(Degussa) catalysts prepared by both the wet-impregnation and the ion-exchange methods and subjected to HTR by making use of the spectrum of bulk Ni at 25 K as the reference. In fig. 3 we show the plots of $\Delta\sigma^2$ with temperature for both the catalysts. The variation of $\Delta\sigma^2$ is nearly linear in the 25–300 K regime with the wet-impregnated catalyst showing a higher value at any given temperature. It is to be noted that $\Delta\sigma^2$ has contributions from dynamic as well as static disorder, the former being temperature-dependent and decreasing on lowering temperature. The contribution from static disorder is, however, expected to be almost temperature independent. We have extrapo-

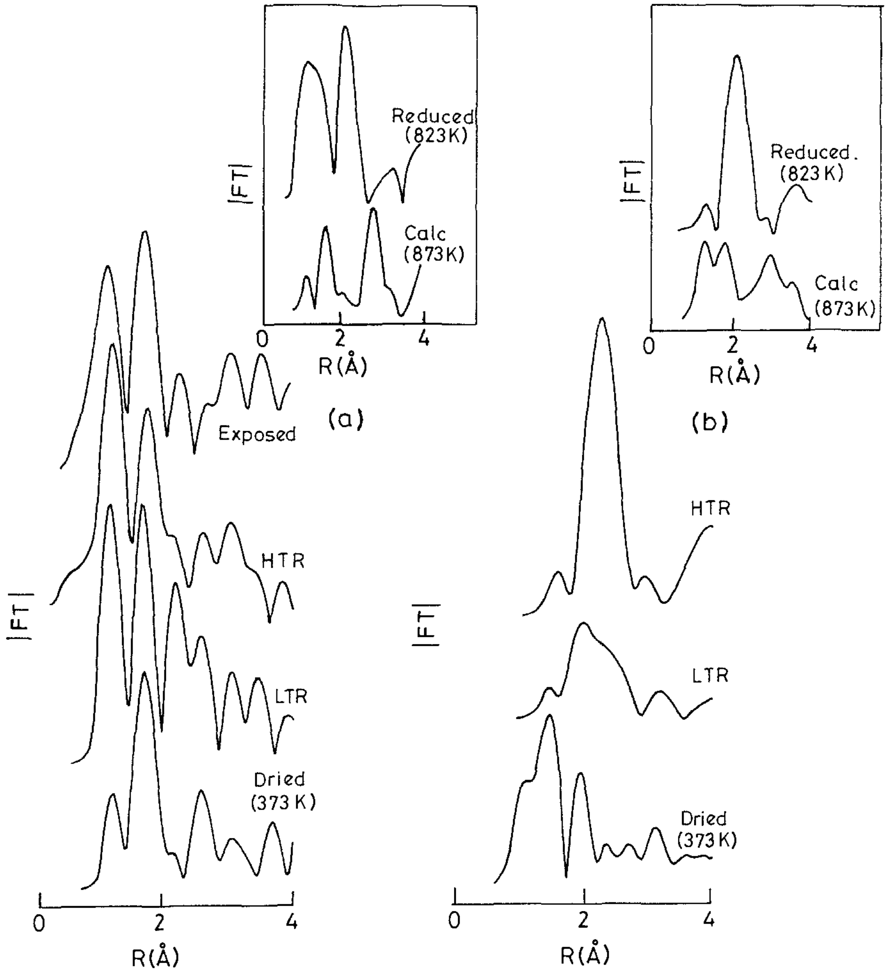

Fig. 4. Fourier transforms of the Ni K-EXAFS of Ni(5 wt%)/TiO_2(gel). (a) Catalyst prepared by wet impregnation, in dried and reduced conditions, and after exposure of the HTR sample to air at room temperature; (b) catalyst prepared by ion-exchange, in dried and reduced conditions. Insets show the FTs of catalyst calcined at 873 K followed by reduction at 823 K.

lated the plots to 0 K to determine the static disorder. The catalyst prepared by wet-impregnation shows a higher static disorder (8.5×10^{-4} Å^2) compared to that prepared by ion-exchange (6.25×10^{-4} Å^2). This suggests that greater static disorder may be introduced because of the strong interaction of the Ni particles with the decorating oxide species present in the SMSI state of the catalyst.

We have investigated Ni(5 wt%)/TiO_2(gel) in some detail since the higher surface area of the gel was expected to favour greater interaction between nickel and the oxide support thereby affecting the nature of the nickel species as well as the interface properties. In fig. 4a we show the FTs of wet-impregnated Ni(5 wt%)/TiO_2(gel) dried at 373 K along with the FTs of the samples reduced at

Table 1
Structural parameters from Ni K-EXAFS of Ni(5 wt%)/TiO_2(gel) catalyst

Catalyst	Atom pair	N	R (Å)	$\Delta\sigma^2$ (Å^2)
wet-impregnated				
1 dried	Ni–O	2	1.6	0.0
	Ni–O	6	2.04	0.0004
	Ni–Ni	3	2.92	0.0005
2 reduced at 573 K	Ni–O	4	1.59	0.0
	Ni–O	6	2.0	0.0
	Ni–Ni	3	2.44	0.0
	Ni–Ni	3	2.86	0.0
3 reduced at 773 K	Ni–O	5	1.62	0.0
	Ni–O	5	2.06	0.0004
	Ni–Ni	1	2.4	0.0002
4 exposed to air	Ni–O	3	1.58	0.0
	Ni–O	6	2.05	0.0
	Ni–Ni	2	2.49	0.0
ion-exchange				
1 dried	Ni–O	5	1.76	0.0005
	Ni–O	2	2.12	0.0
2 reduced at 573 K	Ni–O	2	2.16	0.001
	Ni–Ni	5	2.48	0.001
3 reduced at 773 K	Ni–Ni	9	2.52	0.0004

573 K (LTR) and 823 K (HTR). The FT of the dried sample shows two peaks at 1.2 and 1.66 Å corresponding to Ni–O coordinations of 2 and 6 at distances of 1.6 and 2.05 Å respectively (table 1). The Ni–O distance of 2.05 Å is similar to that in NiO while the 1.6 Å distance is rather unique. Curve fitting of the third peak at 2.54 Å gave a Ni–Ni coordination of 3 at 2.92 Å due to Ni–Ni distance as in NiO. The Ni–O distance of 1.6 Å can arise from the presence of Ni^{3+} species. Formation of Ni^{3+} in defect nickel oxides as well as in the surface oxidation of nickel is known. It has indeed been suggested that Ni^{3+}–O^{1-} or Ni^{3+}–O_2^{2-} is the likely species to be found in such cases [15]. The 1.6 Å distance is consistent with Ni^{3+}–O^{1-} type species and furthermore Ni^{3+} species is likely to be formed on an active gel surface.

On reduction at 573 K, Ni(5 wt%)/TiO_2(gel) gives rise to a peak at 2.22 Å due to Ni–Ni coordination of the nickel metal. This is accompanied by an increase in the magnitude of the peak corresponding to an Ni–O distance of 1.6 Å while that at 2.05 Å remains unaffected. This behaviour is due to the multiphasic nature of the system wherein the nickel atoms are present in three different species – Ni–O as in NiO, Ni metal particle and Ni^{3+}–O surface species. The coordination numbers obtained from the analysis, however, correspond to the relative proportions of the different species. The intensity of the 2.05 Å peak decreases on HTR at 823 K along with a slight increase in the magnitude of the 1.6 Å peak. Surprisingly, there is a slight decrease in the magnitude of the nickel metal peak as well (see table 1). We have ensured by careful analysis that these changes are not artifacts arising from poor background subtraction in processing the EXAFS data. Accordingly, the intensity of the white-line also changes with the intensity of the 1.6 Å peak on HTR. It is not clear as to how the short Ni–O distance of 1.6 Å is related to SMSI since such a distance is not seen in the catalyst prepared by Degussa TiO_2. It is noteworthy, however, that the reduced Ni(5 wt%)/TiO_2(gel) catalyst when exposed to air shows an increase in the intensity of the peak at 2.22 Å (due to the Ni metal) and also of the 2.05 Å Ni–O peak. Using in situ X-ray diffraction, Jiang et al. [16] have provided evidence for the encapsulation of metal particles by the TiO_2 support after high-temperature reduction and their reappearance upon exposure to air. What is interesting is that the Ni(5 wt%)/TiO_2(gel) catalyst calcined at a still higher temperature of 873 K shows the formation of $NiTiO_3$ (see inset of fig. 3a), which on reduction gives a higher proportion of nickel metal (via the decomposition of $NiTiO_3$). X-ray diffraction measurements show that TiO_2(rutile) is formed accompanying the reduction.

Unlike the Ni(5 wt%)/TiO_2(gel) catalyst prepared by the wet-impregnation method, the one prepared by the ion-exchange method readily gives nickel metal on reduction as shown in fig. 4b with no evidence for the presence of any unreduced species. Even calcination at 873 K fails to produce $NiTiO_3$ in this catalyst (see inset of fig. 4b).

The present study of the Ni/TiO_2 catalysts shows that the wet-impregnation method generally favours the formation of the $NiTiO_3$ intermediate during calcination. It seems likely that such an intermediate species is involved in the SMSI state since the ion-exchange method of preparation does not give rise to this species. Reduction of $NiTiO_3$ is likely to give rise to nickel particles with distinctly different interface properties since the anatase–rutile transformation of the support occurs during the decomposition/reduction of $NiTiO_3$. It may be recalled that the rutile phase of TiO_2 is more dense than the anatase phase. When active TiO_2 (anatase) is used as the support, an additional species involving Ni^{3+} is seen on the surface; the role of this species in SMSI is not clear at present.

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References

[1] S.J. Tauster, S.C. Fung, R.T.K. Baker and J.A. Horsley, Science 211 (1981) 1121.
[2] G.L. Haller and D.E. Resasco, Adv. Catal. 36 (1989) 173.

[3] H. Yoshitake and Y. Iwasawa, J. Phys. Chem. 96 (1992) 1329.
[4] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.
[5] J. Santos, J. Phillips and J.A. Dumesic, J. Catal. 81 (1983) 147.
[6] M.G. Sanchez and J.L. Gazquez, J. Catal. 104 (1987) 120.
[7] L. Wang, G.W. Qiao, H.G. Ye, K.H. Kuo and Y.X. Chen, in: *Proc. 9th Int. Congress on Catalysis*, Vol. 3, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. Canada, Ottawa, 1988) p. 1253.
[8] A.R. Gonzalez-Elipe, A. Fernandez, J.P. Espinos and G. Munuera, J. Catal. 131 (1991) 51.
[9] D.E. Resasco, PhD Thesis, Yale University, New Haven, CT, USA (1983).
[10] G. Sankar, C.N.R. Rao and T. Rayment, J. Mater. Chem. 1 (1991) 299.
[11] G. Sankar, K.R. Kannan and C.N.R. Rao, Catal. Lett. 8 (1991) 27.
[12] H.C. Zurloye, J.A. Faltens and A.M. Stacy, J. Am. Chem. Soc. 108 (1986) 8104.
[13] G.U. Kulkarni, G. Sankar and C.N.R. Rao, Z. Phys. B73 (1989) 529.
[14] H. Kuroda, T. Yokoyama, K. Asakura and Y. Iwasawa, Faraday Discussions Chem. Soc. 92 (1991).
[15] A.R. Gonzalez-Elipe, J.P. Holgado, R. Alvarez and G. Munuera, J. Phys. Chem. 96 (1992) 3080.
[16] X.Z. Jiang, B.H. Song, Y. Chen and Y.W. Wang, J. Catal. 102 (1986) 257.