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Strong metal support interaction state in the Fe/TiO$_2$ system – an XPS study

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Strong metal support interaction with supported group VIII metals is associated with the phase transformation of the support employed. The reduced uptake of hydrogen and the enhanced reactivity in CO hydrogenation in these systems are associated with the geometrical dispersion of the metal species, which is identified to have arisen from the formation of a ternary oxide phase and its subsequent reorganization under high temperature reduction conditions. XPS experimental evidence is provided for this postulate.

1. Introduction

In our previous communication [1], it was reported that in the iron on TiO$_2$ system the metal support interaction, deduced by H$_2$/CO chemisorption at room temperature, is dependent on the nature of the support sample used. It has also been reported [2] that the anatase form of the support is preferred, since the anatase to rutile transformation occurs at temperatures close to where the strong metal support interaction (SMSI) effect is observed and may facilitate the onset of the SMSI state. It has been proposed [3] that the formation of a solid state intermediate, such as ternary oxides (Bickley *et al.* [4] have proposed that pseudo-brookite is formed from the reaction between segregated α-Fe$_2$O$_3$ and saturated iron-doped titanium dioxide with an increase of firing temperature) involving the supported metal and TiO$_2$ or at least a surface intermediate, may be enhanced in the phase transition regime, which during the subsequent high temperature reduction leads to encapsulation of metal particles in the support to form a composite structure that can manifest the properties of the SMSI state. Sankar *et al.* [3] have shown that the presence of metal catalyses the phase transformation and thus facilitates the onset of the SMSI state. Bickley *et al.* [5] have examined the Fe/TiO$_2$ system by X-ray photoelectron and diffuse reflectance spectroscopic measurements, and have shown that iron-rich surfaces commenced even at 773 K, because of the lower solubility limit of iron in rutile phase (ca. 3% at 923 K) and the phase transition (anatase to rutile) being perceptible at lower temperatures in this system. In view of these reports, it was considered desirable to examine the Fe/TiO$_2$ system by X-ray photoelectron spectroscopy, with the objective of delineating the differences observed between the commercial support as well as the support obtained from the gel route. The specific questions addressed in this paper are:

1. whether the phase transformation of the support is a prerequisite for the SMSI state?
2. what are the driving forces that control the effective dispersion of the metal on a given support?
3. is the surface ternary oxide phase a necessary precursor to the SMSI state?

2. Experimental procedure

Two types of titania-supported iron catalysts were prepared by the wet impregnation method from a solution of iron(III) nitrate. The 9.5% Fe/TiO$_2$ catalyst was prepared using commercially available TiO$_2$ (Baker, UK) as support, indicated as TiO$_2$(C). The composition of TiO$_2$ was 97% anatase and 3% rutile. The 9.2% Fe/TiO$_2$ catalyst was prepared using oven-dried TiO$_2$ gel, indicated as TiO$_2$(G), and prepared by hydrolysis of TiCl$_4$ [3]. The weight loadings were determined volumetrically. The catalysts were dried at 110 °C overnight, and stored in a vacuum desiccator. The catalysts were subjected to reduction in flowing hydrogen at different temperatures prior to chemisorption, XRD and XPS studies.

H$_2$ chemisorption measurements were made in a conventional, all-glass, static volumetric system. Extents of reduction were measured by volumetric oxidation at 355 °C [6]. The XRD powder patterns were recorded in a Philips X-ray diffractometer. The fraction of anatase in the sample was determined using the expression: $f_A = (1 + 1.26 I_R/I_A)^{-1}$, where I_R and I_A are the highest intense peaks of rutile and anatase, respectively [7]. XP spectra were recorded with an ESCALAB Mk II spectrometer working with constant pass energy of 50 eV, using Mg$K\alpha$ radiation as the excitation source and taking binding energy (BE) reference at the C 1s line as 284.6 eV. The samples, in the form of pellets, after pretreatment in H$_2$ at different temperatures and evacuation to 1.333×10^{-6} Pa, were loaded into the spectrometer for recording the XP spectra. In order to obtain the concentration profiles in the subsurface layers, the samples were sputtered with argon ions for 2, 5 and 10 min. The surface area of

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the freshly reduced samples was measured by the BET method in a Carlo Erba sorptometer. Prior to measurement the samples were degassed at 393 K.

3. Results and discussion

The XRD patterns of 9.5% Fe/TiO_2(C) and that of 9.2% Fe/TiO_2(G) reduced at 673 and 773 K are given in Fig. 1. The data extracted from Fig. 1 are given in Table I, together with the values of BET surface area of the samples reduced at different temperatures and the extent of reduction of iron at various temperatures of reduction. Hydrogen chemisorption data for these two systems are given in Table II. It is seen from Fig. 1 and Table I that anatase to rutile transformation does not occur even at 500 °C in the case of commercial TiO_2, and the complete onset of the SMSI state accordingly requires higher temperatures (525 °C), whereas in the case of the TiO_2(G) sample the SMSI state is completely discernable even at 500 °C and the support contains a considerable amount of the rutile phase (ca. 15%). One striking observation is that activated adsorption of hydrogen is discernable for the Fe/TiO_2(C) system, while such behaviour is absent for a Fe/TiO_2(G) sample. This difference presumably arises from better dispersion of the metallic particles (see below) in this case due to the preparative conditions employed. However, this observation must be extended to other group VIII metals, which are expected to exhibit activated hydrogen adsorption, to substantiate that preparative procedures have a pronounced effect on the presence or absence of an activated adsorption state. Another difference between TiO_2(C) and TiO_2(G) is that metal dispersion seems to be more favourable in the TiO_2(G) support, which is in agreement with the observations of Bickley *et al.* [8]. Bickley *et al.* [8] observed that at low nominal composition of Fe ($< 1\%$) , the Fe^{3+} ions are well dispersed in the lattice of the co-precipitated sample. At higher loadings of Fe ($> 5\%$) systems become multiphasic, with the formation of the α-Fe_2O_3 phase at low temperatures (923 K) and Fe_2TiO_3 at higher temperatures (> 1073 K) . Since the solubility limit of Fe^{3+} ions in the anatase phase of TiO_2 is a facile process, and is limited (ca. 3%) in the case of rutile phase, the segregation of Fe_2O_3 could mean that the anatase to rutile phase transformation could occur in this temperature range itself in the presence of iron oxide, which is commonly identified as the catalytic role of the metal ions in phase transformations. The extent of reduction to the metallic state is considerably higher in the case of the commercial support as compared to the gel sample, where the extent of reduction is only ca. 25% even at 500 °C. It has been reported that in TiO_2-supported systems the anatase to rutile phase transformation occurs at a lower temperature as compared to pure anatase because of the catalytic effect of the transition metal ions [5, 9]. However, it should be remarked that the ease of phase transformation also depends on the nature of the TiO_2 precursor used in preparing the support. In the case of the commercial titania the supported metal (in this case Fe) is well dispersed and hence could undergo extensive reduction to its metallic state, but it still did not promote the anatase to rutile transformation since the extent of rutile phase was of the order of 5%, which remained constant at all temperatures of reduction. In the case of TiO_2(G) the precursor Fe^{3+} ions were not only uniformly distributed completely on the surface of the support but were also probably considerably distributed inside the support, and hence the extent of reduction was considerably small (limited to only 25% even after reduction at 500 °C), though one could observe 10–15% of the rutile phase in the support. It should be pointed out that the catalytic effect of the transition metal or ions is effectively felt in the phase transformation reaction only when the transition metal ion precursors are effectively dissolved in the support phase. This observation is in agreement with the results of Bickley *et al.* [5]. Secondly, the fact that complete onset of the SMSI state is observed in the case of the TiO_2(G) sample, even at 500 °C, lends further support that the onset of SMSI state is connected with the phase transition of the support. However, it is uncertain whether the resultant SMSI state is

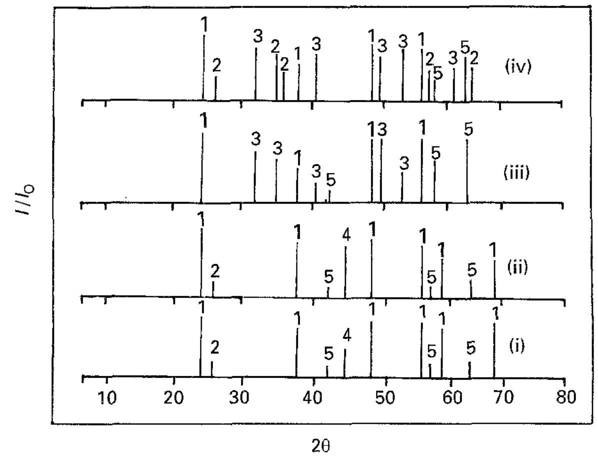

Figure 1 XRD patterns for samples of: 9.5% Fe/TiO_2(C) reduced at (i) 400 °C and (ii) 500 °C; 9.2% Fe/TiO_2(G) reduced at (iii) 400 °C and (iv) 500 °C. 1, TiO_2-A; 2, TiO_2-R; 3, $FeTiO_3$; 4, α-Fe; 5, Fe_3O_4.

TABLE I XRD and BET surface area data for Fe/TiO_2 catalysts

Reduction temp. (°C)	9.5% Fe/TiO_2 (C)			9.2% Fe/TiO_2 (G)		
	Reduction (%)	Rutile (%)	S_{BET} (m^2/g^{-1})	Reduction (%)	Rutile (%)	S_{BET} ($m^2 g^{-1}$)
–	–	–	17	–	–	105
400	70	3	16	22.0	–	42
450	75	3	–	23.5	–	–
500	76	3	15	25.5	13	33

TABLE II Hydrogen chemisorption data for Fe/TiO_2 catalysts

Temperature	Hydrogen uptake (μ mol g^{-1} of catalyst)			
	9.5 Fe/TiO_2 (C)		9.2% Fe/TiO_2(G)	
(°C)	RT	100 °C	RT	100 °C
400	6.4	12.0	5.6	5.7
450	3.3	6.0	6.3	6.6
500	1.4	4.2	0.0	0.0
525	0.0	0.0	–	–
400[a]	6.4	12.0	5.6	5.7

[a] 525 (R) → 350 (O) → 400 (R).

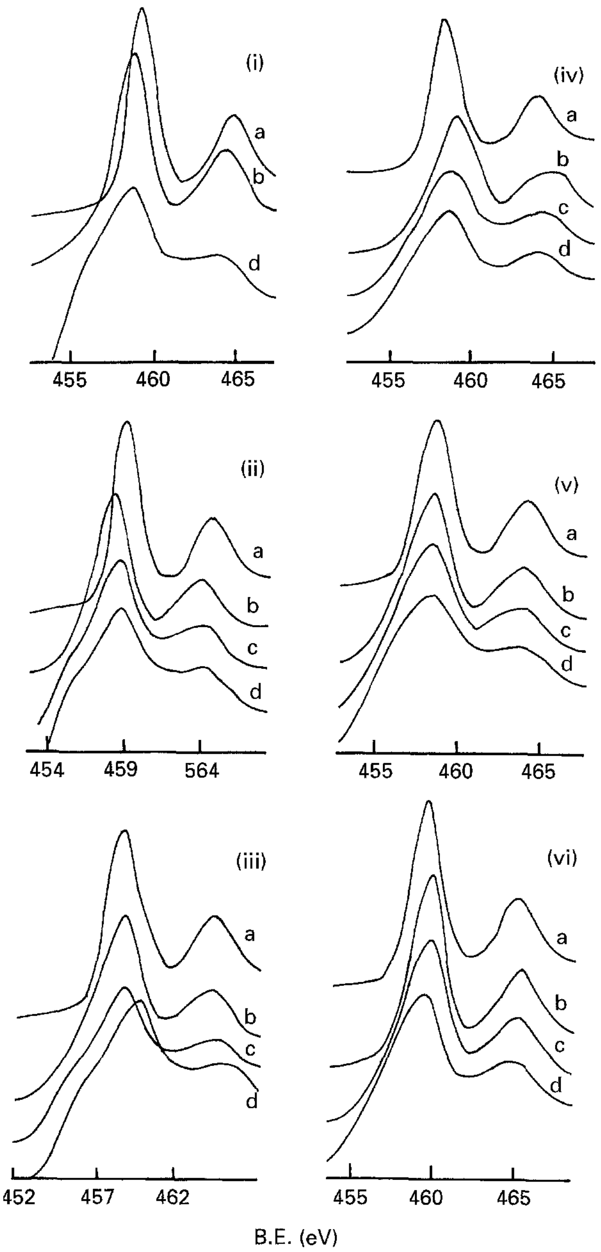

Figure 2 Ti 2p XP spectra of Fe/TiO_2 catalysts: (i)–(iii) commercial, reduced at 400, 450 and 500 °C; (iv)–(vi) gel, reduced at 400, 450 and 500 °C. a, As received; b–d, submitted to Ar^+ etching for 2, 5 and 10 min, respectively.

a result of the heat quantities involved in the phase transition [10] or the structural features of the phases formed. The catalytic effect in the phase transformation was associated with the formation of well characterized intermediate ternary oxide species either in the bulk or at least on the surface. It is interesting to note that Bickley *et al.* [5] propose that the reaction between segregated α-Fe_2O_3 and the region of TiO_2 saturated with Fe will lead to pseudo-brookite phase formation. Therefore, the complex ternary oxide formation in the supported metal systems is dependent on various factors, like the segregation of the metal precursor, the dissolution of the metal ions in the phases of the support and the proximity of these two regions of the solid for a facile reaction. It can, therefore, be proposed that the failure to observe the ternary oxide phase in some of the group VIII metals supported on TiO_2 has to be associated with the limitations associated with segregation of the metallic oxide phase as well as the extent of dissolution of the metal ions in the two phases of the TiO_2 support. It may be possible that during the high temperature reduction the dissolved active transition metal ions are included in the support material, thus favouring ternary oxide phase formation. This may lead to complete wetting of the metallic particles which are subsequently formed on reduction of the ternary oxide by the support phase. The phase transformation can favour such a dissolution reaction, either by providing the necessary activation energy for the diffusion of the metallic species or by the geometrical factor wherein the transformed phase is more amenable to the dissolution of the metallic species. It may be possible that both factors contribute and, depending on the nature of the precursor used for the support preparation, one or the other will have a predominant role. In the case of the gel sample, since the extent of the phase transformation is only of the order of 15%, we feel that a geometrical factor may have had a predominant role in the formation of ternary oxide intermediate phase favourable for the SMSI state. However, identification of the ternary phase in supported systems (by XRD) would have been difficult, especially since the extent of metal loading is often very much less than 5%. Even then, in the case of the Fe/TiO_2 and Fe/La_2O_3 systems, it has been reported by Lakshmi [11] that ternary phases like Fe_2TiO_3 and $LaFeO_3$ could be seen by XRD when reduced at 550 and 725 °C, respectively. She attempted to identify the ternary precursor phase from the energy separation between the main La $3d_{3/2}$ photo-emission peak and the satellite which is of the order of 2.7 eV. Berthou *et al.* [12] reported that E is of the order of 4.0–4.5 eV for La_2O_3, while it is of the order of 3.0–3.5 eV for $La(OH)_3$; a value of 2.5–3.0 eV is observed for compounds such as $LaCrO_3$, $LaMnO_3$ and $LaNiO_3$.

Since, in the literature, the formation of intermediate ternary oxide phases as a precursor for the SMSI state has not been explicitly identified, we have examined the Fe/TiO_2 system of our samples (both commercial and gel support) by X-ray photoelectron spectroscopy. The Ti 2p emissions, after reduction at various temperatures, as well as after etching for 2, 5 and 10 min are given in Fig. 2 (roughly, our etching conditions correspond to removal of 1.8 nm min^{-1}). It is seen from Fig. 2 that the Ti 2p level has a BE of 458.75 + 0.5 eV. It is normally argued that the reduced phases of titania, like Ti_3O_5, are related to the

TABLE III XPS BE shifts in eV between O 1s and Ti 2p for Fe/TiO_2 fresh and argon sputtered catalysts

Catalysts	Reduction temp. (°C)	BE Fresh	ET2[a]	ET5	ET10
9.5% Fe/TiO_2 (C)	400	72.25	71.75	–	72.0
	450	71.50	72.50	72.00	72.25
	500	71.50	71.75	72.00	72.75
9.2% Fe/TiO_2 (G)	400	71.75	71.75	72.75	72.00
	450	72.75	72.75	72.75	72.75
	500	71.50	71.75	72.00	72.75

[a]After 2 min sputtering.

TABLE IV The I_o/I_{Ti} ratios for fresh and sputtered Fe/TiO_2 catalysts

Catalysts	Reduction temp. (°C)	I_O/I_{Ti} Fresh	ET2	ET5	ET10
9.5% Fe/TiO_2(C)	400	6.37	4.00	–	2.25
	450	5.23	4.23	5.16	4.64
	500	5.33	3.94	3.46	2.69
9.2% Fe/TiO_2(G)	400	13.19	7.42	7.84	7.12
	450	9.08	7.97	5.46	4.14
	500	6.69	5.15	3.75	4.07

rutile structure [13] and that formation of such phases could also be responsible for the onset of the SMSI state. Since the absolute BE values for Ti 2p levels probed in our samples do not give any clue towards the formation of reduced Ti species, the separation between the O 1s level and the Ti 2p level (BE) has been computed from the XP spectra obtained. This BE value should be ca. 71.5 eV for TiO_2, while it is 73.4 eV for Ti_2O_3, 75.0 eV for TiO and 77.0 eV for metallic Ti [14]. The data summarized in Table III show that the BE values are always ca. 71.5 eV, showing that the majority of the Ti species probed by our XPS measurements are present in the + 4 oxidation state. Since full width at half maximum (FWHM) values also could not be used to obtain clues for the presence of other oxidation states of Ti, the I_O/I_{Ti} ratio was considered. The data generated, given in Table IV, indicate that other oxidation states of Ti other than + 4 might be present on the surface layers, but the extent of such species appears to be small. The Fe 2p spectra for the two support samples are given in Fig. 3. From the BE values given in Table V, one can infer [15, 16] that Fe is present at the top surface layers in the oxidized form and in the inner surfaces (as deduced from the Fe 2p peaks after etching for definite time intervals), the presence of reduced forms of Fe can be noted. For example, in the case of the Fe/TiO_2(C) sample, reduced at 500 °C, it can be inferred that the majority of the Fe is present as Fe^{2+} at the top surface, and just after 2 min etching Fe(0) is already noticed and after 10 min etching only

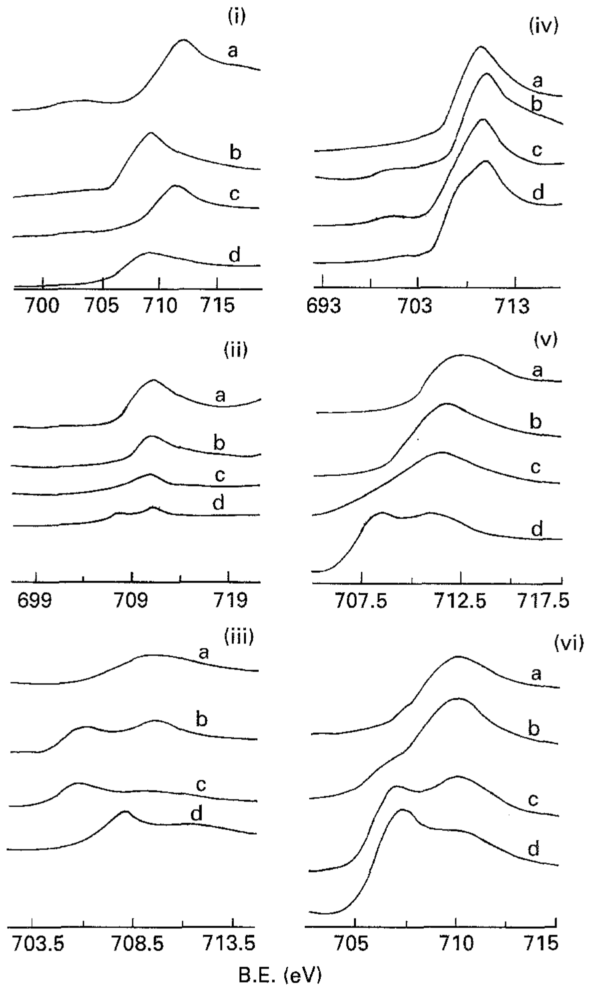

Figure 3 Fe 2p XP spectra of Fe/TiO_2 catalysts: (i)–(iii) commercial, reduced at 400, 450 and 500 °C; (iv)–(vi) gel, reduced at 400, 450 and 500 °C. a, As received; b–d, submitted to Ar^+ etching for 2, 5 and 10 min, respectively.

TABLE V The Fe 2p BE values for fresh and sputtered Fe/TiO_2 catalysts

Catalysts	Reduction Temp. (°C)	BE (eV) Fresh	ET2	ET5	ET10
9.5% Fe/TiO_2(C)	400	711.5	710.5	–	709.5
	450	710.0	710.0	710.5	710.75
	500	709.75	706.25 709.50	706.25 709.50	708.25
9.2% Fe/TiO_2(G)	400	709.5	709.0	709.25	708.75
	450	710.0	709.5	707.0 709.5	707.0 710.0
	500	712.25	711.5	711.5	708.25 711.00

TABLE VI The I_{Fe}/I_{Ti} ratios for fresh and sputtered Fe/TiO_2 catalysts

Catalysts	Reduction temp. (°C)	I_{Fe}/I_{Ti}			
		Fresh	ET2	ET5	ET10
9.5% Fe/TiO_2(C)	400	0.16	0.08	–	0.07
	450	0.14	0.05	0.03	0.03
	500	0.13	0.09	–	0.07
9.2% Fe/TiO_2(G)	400	0.18	1.49	2.35	0.64
	450	0.51	1.03	1.15	1.03
	500	0.40	0.33	–	0.35

metallic Fe is observed. On the contrary, in the case of the TiO_2(G) sample, Fe in the top layers is present as Fe^{3+} and the presence of the + 3 oxidation state is persistent even after etching for 10 min. This experimental observation has been taken to mean that Fe ion diffusion is a facile process in the TiO_2(G) sample as compared to the TiO_2(C) support. In order to examine this point further, we computed the relative values of I_{Fe}/I_{Ti} as a function of etching time. It can be seen from Table VI that the iron concentration is higher in the subsurface layers of TiO_2(G) sample as compared to the TiO_2(C) support. In addition, the variation of this ratio as a function of etching time, given in Fig. 4, shows a maximum in Fe concentrations in subsurface layers and this maximum shifts towards the surface layer with increasing temperature of reduction. On the contrary, in the case of the TiO_2(C) support, subsurface concentrations of Fe are always lower, and independent of the temperature of reduction and decrease with increasing depths in the subsurface layers. It is interesting to compare our XPS results with those reported by Bickley *et al.* [5]. Bickley *et al.* also investigated the Fe/Ti ratio as a function of sputtering time (Fig. 6 of [5]) and observed an initial decrease in this ratio with an increase in sputtering time for the sample containing 5 at % of Fe, while this ratio remained constant with sputtering time for samples containing 0.5 and 1.0 at % of Fe. They have also concluded that enrichment of Fe at the surface could have occurred in the case of sample with 5 at % of Fe. However, the caution given by them that the distribution of Fe^{3+} species may not be completely uniform within the particles (inhomogeneous solid solution formation), irrespective of the extent of iron loadings, should be noted. It can be inferred that Fe ion diffusion is a facile process in the case of the TiO_2(G) sample as compared to the TiO_2(C) support. The extensive diffusion of Fe ions and consequent interaction with titania to form a ternary oxide phase may be the reason for the low extent of reduction of Fe in the TiO_2(G) sample. In the case of the TiO_2(C) sample, most of the Fe ions are present on the surface and are reduced to give rise to bigger particles. Because of the diffusion of Fe ions, which seem to be predominant at 500 °C or higher, the Fe species are completely dissolved in the surface layers of the gel support and hence the surface ternary oxide intermediate formed resists reduction to the metallic Fe state. This may be the reason why most of the Fe is present as Fe^{3+} in the gel sample, as deduced from the BE of the 2p emission of Fe. In the case of the gel sample, the Fe:Ti ratio of the freshly reduced samples increases with increasing reduction temperature (See Fig. 4b). Since the extent of solubility of Fe^{3+} ions in the rutile phase is less compared to that of anatase phase, and as increasing amounts of the rutile phase are formed with an increase in reduction temperature, the segregated Fe species gives rise to a higher Fe:Ti ratio. This result is in agreement with the observations of Bickley *et al.* [5]. From these results it can be hypothesized that for an effective SMSI state to form, it may be necessary that the metal ion precursors are completely wetted by the support and the support phase should be amenable to structural changes (either phase transformation or formation of reduced phases) which can favour the dissolution of the metal ion precursors. Under these circumstances, the dissolved metal ions, at least at the local level, react with the geometrically favourable support phase to give rise to an intermediate phase which resists rapid reduction to the metallic state or creates a configuration where the supported metal is completely concealed by the support phase. Supports which do not permit the dissolution of precursor metal ions will not exhibit the SMSI state, as the metal particles will be formed and dispersed on the surface without complete wetting of the metallic particles by the support phase.

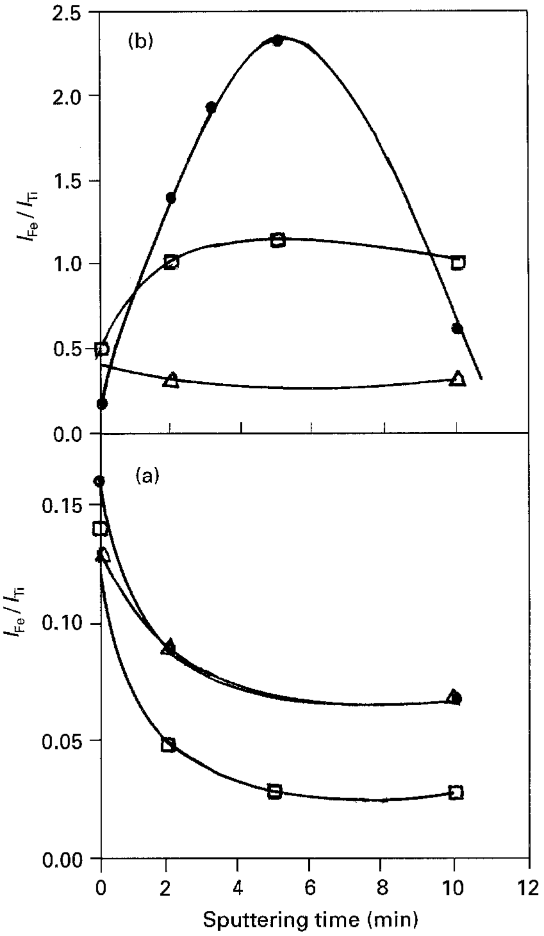

Figure 4 Variation of I_{Fe}/I_{Ti} as a function of sputtering time for Fe/TiO_2 catalysts reduced in H_2 at various temperatures (°C) : ●, 400; □, 450; △, 500. (a) Commercial; (b) gel.

It must be remarked that the model proposed in this paper is not completely new. Earlier reports [17] treated this model in terms of the encapsulation of the metal particles by the support. Recently, the explanation of the formation of the ternary oxide intermediate species as the cause for the SMSI state has gained importance [18]. However, in this communication we have identified factors responsible for the formation of at least a surface ternary oxide intermediate species, which can be advantageously used for predicting the SMSI state in supported systems.

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