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ANATASE-RUTILE TRANSFORMATION IN Fe/TiO_2, Th/TiO_2 AND Cu/TiO_2 CATALYSTS AND ITS POSSIBLE ROLE IN METAL-SUPPORT INTERACTION **

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Supported catalysts, metal-support interaction, rutile, anatase.

Based on *in-situ* Mössbauer and X-ray diffraction studies, it is shown that in the Fe/TiO_2 catalyst, the anatase-rutile transformation of the TiO_2 support is facilitated by the Fe^{2+} ions formed during the reduction. The transformation occurs at lower temperatures in Th/TiO_2 and Cu/TiO_2 compared to pure TiO_2. In general, the transformation of anatase to rutile seems to occur at or below the temperature (~ 770 K) at which strong-metal-support-interaction manifests itself.

1. Introduction

TiO_2 is generally used as the oxide support in catalyst systems where strong interaction occurs between the active transition metal particles and the support [1]. Accordingly, strong-metal-support interaction (SMSI) is found in catalysts such as Ni/TiO_2 and Rh/TiO_2. It has been observed that TiO_2 gets reduced in the SMSI state [2–4], accompanied by the formation of Ni–Ti [5] or Rh–Ti [6,7] bonds. There are also reports in the literature that TiO_2 employed for the preparation of the catalyst should initially be in the anatase form in order to obtain SMSI [8] and that the anatase-rutile transformation occurs at a temperature close to where the SMSI effect is observed [9–11]. Our recent investigation [10] of Ni/TiO_2 has shown that an intermediate ternary oxide, $NiTiO_3$ initially formed, undergoes reduction in hydrogen above 770 K giving rise to Ni metal and the rutile phase of TiO_2; SMSI also manifests itself above 770 K in this catalyst. These changes occur when the catalyst is prepared by the wet-impregnation method. We considered it to be of importance to investigate other catalyst

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systems containing the TiO_2 support alleged to exhibit the SMSI effect. Besides Rh/TiO_2 where the effect is well-documented [1], there are indications that Fe/TiO_2 [11] and Cu/TiO_2 [12] show anomalous chemisorption behaviour ascribable to SMSI when the catalysts are reduced around 770 K. We have investigated Fe/TiO_2, Rh/TiO_2 and Cu/TiO_2 catalyst systems employing *in-situ* Mössbauer spectroscopy and X-ray diffraction (XRD) with particular interest to explore the changes in the state of iron occurring while processing Fe/TiO_2 catalysts and also the occurrence of the anatase-rutile transformation during the calcination or the reduction process.

2. Experimental

We prepared two types Fe (10 wt%)/TiO_2 catalysts by the wet-impregnation method. The catalyst designated I was prepared using commercial TiO_2 (P-25 Degussa) as the support material. XRD analysis showed that the starting TiO_2 contained 70% anatase and 30% rutile. The required quantity of Fe(III) nitrate solution was added to the support and the slurry dried slowly in an air oven over a period of 48 hours. The resulting material was reduced in H_2 at different temperatures for reduction studies. In the second preparation, instead of commercial TiO_2, oven-dried TiO_2 gel prepared by the addition of $TiCl_4$ to cold water in a N_2 atmosphere [13] was used as the starting material. Catalyst II was prepared with the oven-dried gel by the same procedure as I and subjected to reduction at different temperatures.

Mössbauer measurements on the Fe/TiO_2 catalysts were carried out with a *in-situ* cell where reduction could be carried out in a H_2 atmosphere. The spectra were generally recorded after 20 hrs. of reduction at the desired temperature. Mössbauer spectra were recorded using a constant-acceleration, microprocessor-based spectrometer, built in this laboratory. A non-linear least-squares curve fitting procedure was used to achieve the best fit to the experimental data. X-ray diffraction patterns of the reduced catalysis were recorded using a JEOL powder diffractometer, with a step scan of 1°/cm, in order to estimate the proportion of anatase. The fraction of anatase phase was estimated using the formula available in the literature [14]. We studied the anatase-rutile transformation of pure TiO_2 prepared by the gel route as well, in order to assess the effect of the transition metal ions.

We prepared two Fe(10 wt%)/Al_2O_3 catalysts for a comparative study. Fe/Al_2O_3(I) catalyst was prepared by the wet-impregnation method by taking Fe(III) nitrate solution and γ-Al_2O_3 calcined at 570 K. The second catalyst, Fe/Al_2O_3, was prepared by using γ-Al_2O_3 calcined at 770 K. The oven-dried catalysts were further calcined at 770 K for 3 hrs. before carrying out the reduction at 770 K for 20 hrs in a hydrogen atmosphere in the *in-situ* Mössbauer cell.

Rh/TiO_2 and Cu/TiO_2 catalysts were prepared by the wet-impregnation method using the commercial TiO_2 (P-25 Degussa) and the appropriate quantity of the Rh/Cu nitrate solution. Oven-dried Rh/TiO_2 and Cu/TiO_2 catalysts were calcined at desired temperatures for 5 hrs and XRD measurements carried out.

3. Results and discussion

Mössbauer spectra of the Fe/TiO_2(I) catalyst subjected to reduction at different temperatures are shown in fig. 1. We see that the sample as prepared shows a doublet, characteristic of Fe^{3+} as in Fe_2O_3. On the reduction at a relatively low temperature (620 K), we see evidence for the formation of lower oxides of iron in mixture with metallic iron (Fe^0) and unreduced Fe_2O_3 (fig. 1b). A sample reduced at 700 K shows predominantly Fe^0 and only a small amount of unreduced Fe^{2+} (see fig. 1c). Complete reduction occurs at 770 K as can be seen

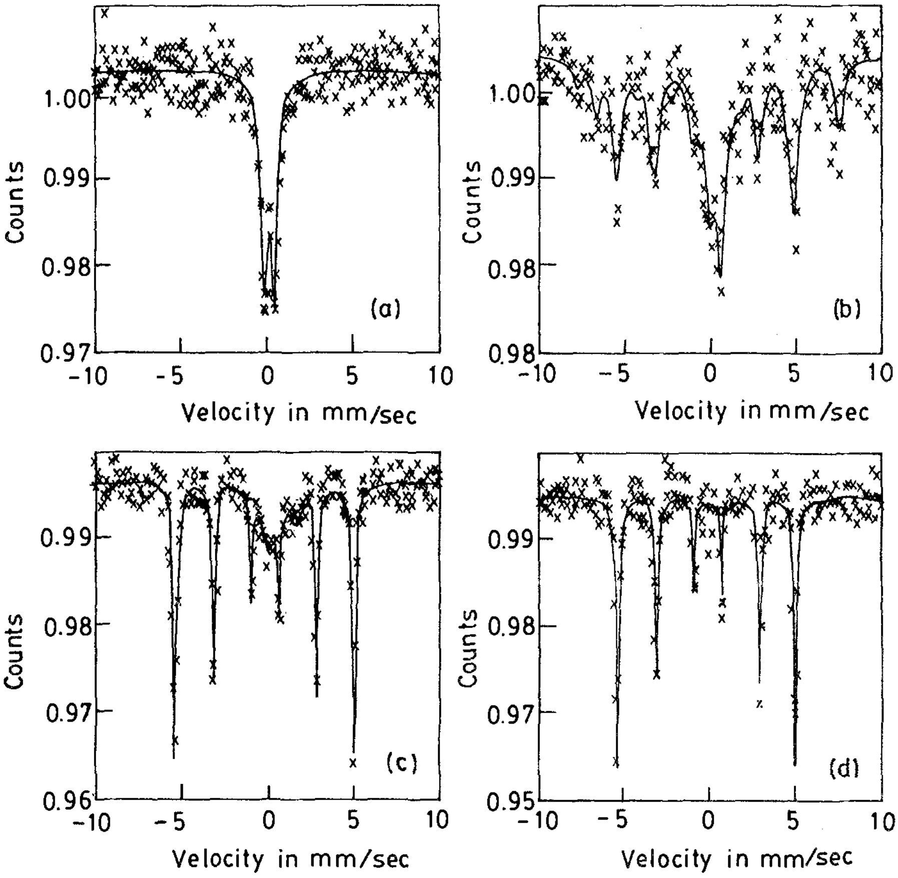

Fig. 1. Mössbauer spectra of Fe/TiO_2(I) prepared from commercial TiO_2: (a) oven-dried sample; (b), (c) and (d) are catalysts reduced in hydrogen at 620 K, 700 K and 780 K respectively.

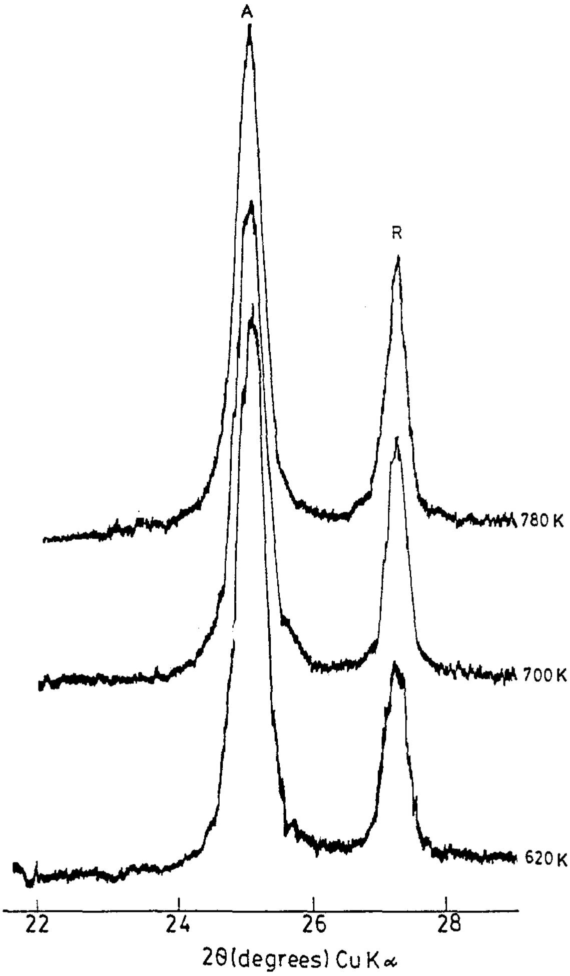

Fig. 2. XRD patterns of Fe/TiO$_2$(I) reduced at different temperatures. Reflections due to the anatase and rutile forms of TiO$_2$ are marked A and R respectively.

from the characteristic six-finger spectrum in fig. 1d. XRD patterns of the Fe/TiO$_2$(I) catalyst reduced at different temperatures are shown in fig. 2. The fraction of rutile in the support does not change significantly up to 770 K. The anatase-rutile transformation seems to become marked only above 770 K (table 1). It is noteworthy that the SMSI effect also manifests itself when the reduction is carried out around 770 K.

In fig. 3 we show the Mössbauer spectra of the Fe/TiO$_2$(II) catalyst prepared from the TiO$_2$ gel. This catalyst shows Fe^{3+} in the oven-dried sample similar to Fe/TiO$_2$(I). The TiO$_2$ support is, however, present entirely in the anatase form in this catalyst prepared as can be seen from fig. 4. On reduction at 620 K, a small amount of Fe^{2+} is formed. The formation of Fe^{2+} becomes significant when the catalyst is reduced at 700 K, with the proportion of Fe^{2+} and Fe^{3+} becoming

Table 1
Mössbauer and XRD results of Fe/TiO$_2$ catalysts

Reduction temperature (K)	Fe/TiO$_2$(I)		Fe/TiO$_2$(II)	
	oxidation state of iron	% rutile	State of iron	% rutile
300 K	3+	30	3+	0
620 K	3+ [a], 2+ [b], 0	30	3+, 2+	10
700 K	2+, 0 [c]	31	3+, 2+	45
750 K	–	–	2+	49
780 K	0	36	0	58

[a] 3+ from unreduced Fe$_2$O$_3$ as well as Fe$_3$O$_4$.

[b] 2+ from Fe$_3$O$_4$ and FeO; 0 refers to metallic iron.

[c] about 80% metallic iron.

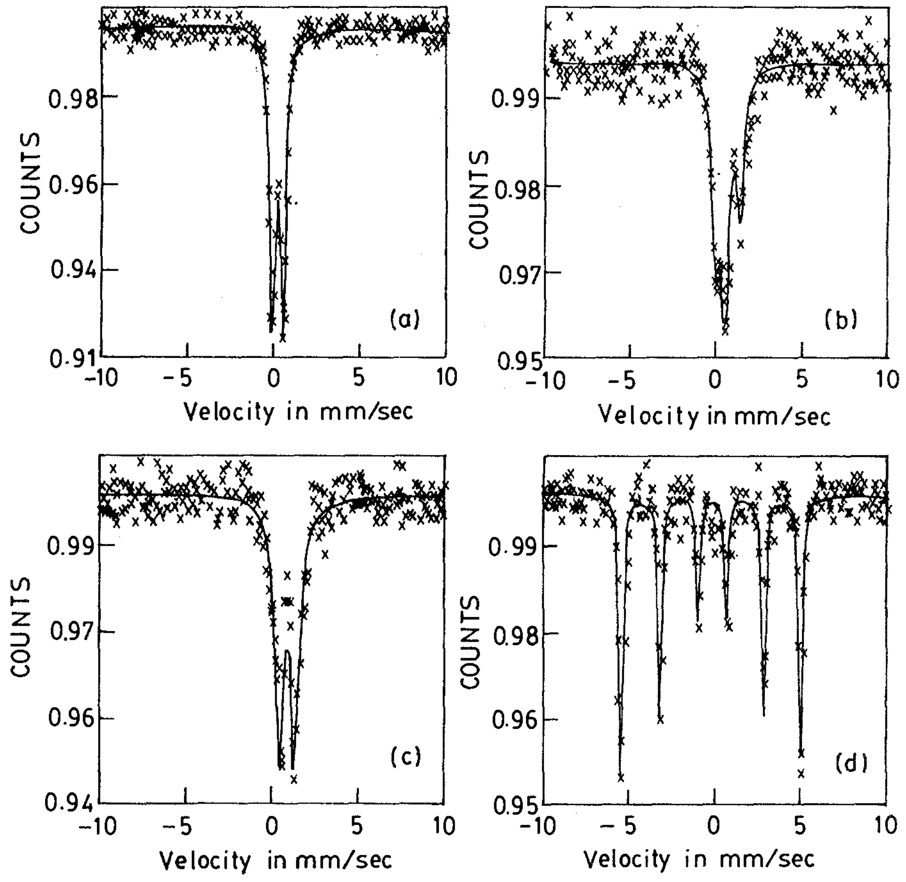

Fig. 3. Mössbauer spectra of Fe/TiO$_2$(II) prepared by the gel route: (a) oven-dried sample; (b), (c) and (d) are catalyst reduced in hydrogen at 700 K, 750 K and 780 K respectively.

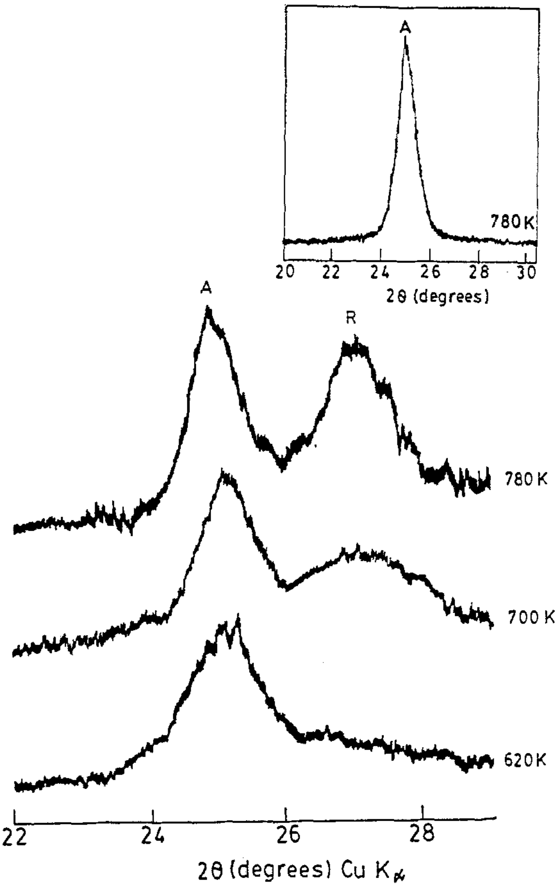

Fig. 4. XRD patterns of Fe/TiO$_2$(II) catalyst reduced at different temperatures. Notice the transformation of anatase to rutile occur even at 750 K. Inset shows the XRD pattern of pure TiO$_2$ gel heated to 780 K in hydrogen atmosphere.

equal (see fig. 3b). The catalyst reduced at 750 K shows only features characteristic of Fe^{2+} (fig. 3c). It is significant that there is no metallic iron in the Fe/TiO$_2$(II) sample reduced at or below 750 K unlike in the case of Fe/TiO$_2$(I). Complete reduction of Fe/TiO$_2$(II) to metallic iron occurs when it is reduced above 770 K (see fig. 3d).

The XRD patterns of the Fe/TiO$_2$(II) catalyst reduced at different temperatures (fig. 4) are revealing. The TiO$_2$ support, present only in the anatase form to start with, transforms to the rutile form at as low a temperature as 650 K. The transformation becomes marked around 700 K and higher (table 1). On the other hand, pure TiO$_2$ (anatase) prepared by the gel route does not undergo the anatase-rutile phase transformation when heated (or reduced) even at 780 K (see the inset to fig. 4). This observation suggests the important role of Fe^{2+} in facilitating the anatase-rutile transformation of the TiO$_2$ support. It is likely that the anatase-rutile transformation is not favoured in the Fe/TiO$_2$(I) catalyst,

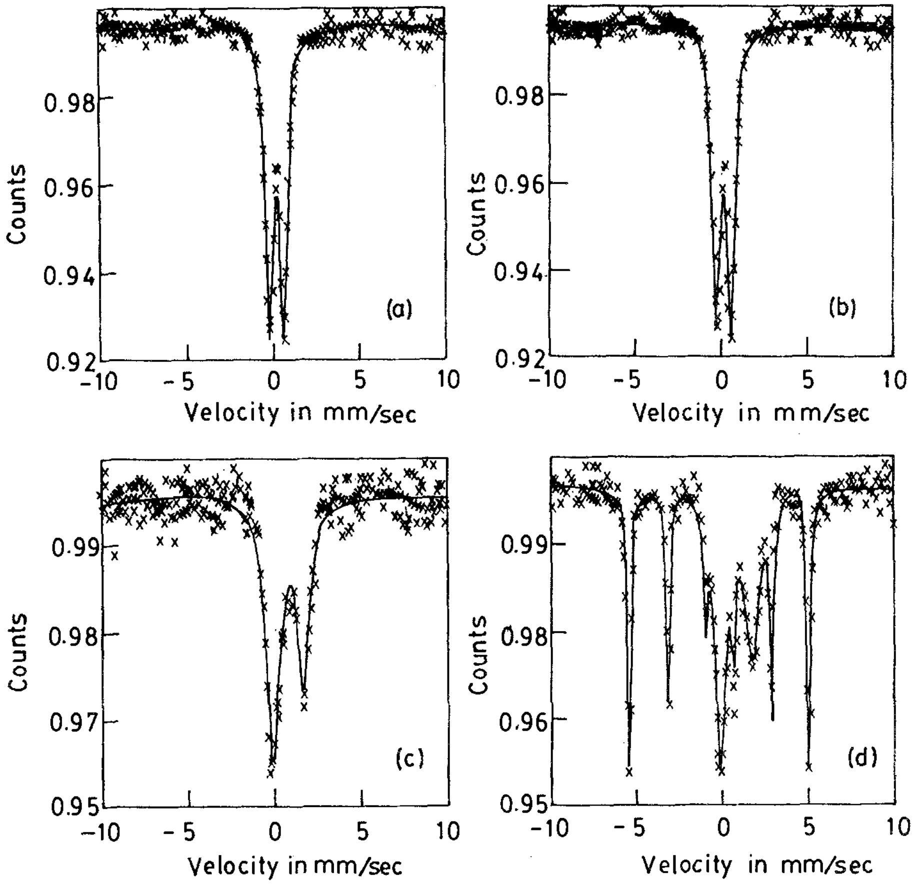

Fig. 5. Mössbauer spectra of Fe/Al_2O_3: (a) and (b), oven-dried samples of (I) and (II) respectively (see text for details); (c) and (d), (I) and (II) respectively reduced in hydrogen at 770 K.

because Fe^{3+} is reduced almost directly to Fe^0 with marginal formation of Fe^{2+} en route and also because the interaction of the Fe^{2+} so formed with the TiO_2 surface is negligible due to the lower surface area of the commercial TiO_2 (50 m^2/gm) (compared to ~ 800 m^2/g of TiO_2 prepared by the gel route).

In order to understand the importance of the nature as well as the thermal treatment of the oxide support in the metal-support interaction, we have carried out Mössbauer studies on the Fe/Al_2O_3 catalysts I and II prepared with γ-alumina calcined at 570 K and 770 K respectively. These two calcined samples show similar Mössbauer spectra, both characteristic of Fe^{3+} (fig. 5a and b). Fe/Al_2O_3(I) undergoes reduction to the Fe^{2+} state leading to the formation of $FeAl_2O_4$ after ~ 20 h at 770 K. The Mössbauer spectrum in fig. 5c is similar to that of $FeAl_2O_4$ reported by Rossiter [15]. We do not see the formation of any Fe^0 in this catalyst even when the catalyst is reduced at 770 K for long periods. Unlike the Fe/Al_2O_3(I) catalyst, Fe/Al_2O_3(II) prepared from Al_2O_3 calcined at

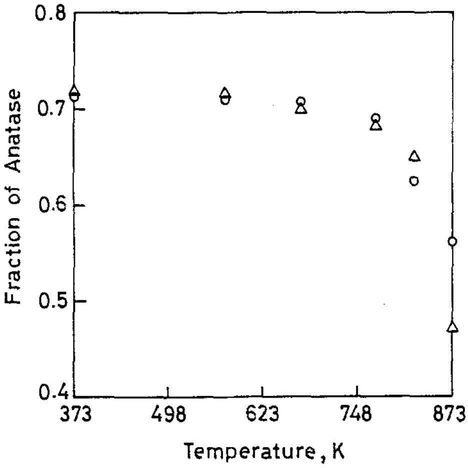

Fig. 6. Fraction of anatase plotted as a function of calcination temperature in different TiO$_2$-supported catalysts: open circles, Rh/TiO$_2$ (wet-impregnation method); triangles, Cu/TiO$_2$ (wet-impregnation method).

773 K shows partial reduction to Fe^0 when the catalyst is reduced at 770 K for 20 hrs (fig. 5d). These results are somewhat similar to those found with the Fe/TiO$_2$ catalysts, suggesting that the nature of the metal-support interaction in the catalyst could depend on the extent to which the active transition metal ion (iron in the present case) interacts initially with the oxide support.

The anatase-rutile transformation in the Cu/TiO$_2$ and Rh/TiO$_2$ samples prepared by the wet-impregnation method occurs when they are calcined in air. The fraction of anatase is plotted against the calcination temperature in fig. 6. We see that the transformation from anatase to rutile becomes significant above 770 K. The transformation is more marked in the Cu/TiO$_2$ catalyst than in the Rh/TiO$_2$ catalyst. The behaviour of the Rh/TiO$_2$ and Cu/TiO$_2$ catalysts prepared by the wet-impregnation method is somewhat similar to that of Ni/TiO$_2$, although there is no evidence for the formation of a ternary oxide intermediate in the first two systems.

In all the TiO$_2$-supported catalyst systems studied, what is significant is that the anatase-rutile transformation occurs at much lower temperatures compared to pure anatase [16] because of the catalytic effect of the transition metal ions [17–19]. Furthermore, the anatase-rutile transformation seems to be necessary for SMSI to occur since in Fe/TiO$_2$, Rh/TiO$_2$ and Cu/TiO$_2$ catalysts the effect is evidenced around or above the temperature of the anatase-rutile transformation (Note that most catalysts showing SMSI are reduced around 770 K). If the anatase-rutile transformation occurs at a considerably higher temperature than 770 K, as in some of the catalysts prepared by the ion-exchange method, there is no SMSI [10]. The catalytic effect of the transition metal ions may involve the formation of a well-characterized solid state intermediate such as NiTiO$_3$ [10] or a surface intermediate, the reactivity of the solid being enhanced in the phase transition regime [19]. It is possible that during the high temperature-reduction the active transition metal particles get embedded in the rutile support to form a favourable composite structure leading to the metal-support interaction. There is some evidence in the literature for an inward diffusion of the transition metals into rutile [3,20]. The occurrence of the anatase-rutile phase transformation in the various TiO_2 supported catalysts could be of significance in metal-support interaction in another way. It has been reported that in Ni/TiO_2 and other such catalysts, TiO_2 itself undergoes reduction to lower oxides in the SMSI state [2,3]. Lower oxides such as Ti_3O_5 are related to the rutile form of TiO_2 [18], making it possible only for the rutile form of TiO_2 to give rise to SMSI on reduction.

It is interesting to speculate whether catalysts with the Al_2O_3 support reduced at high temperatures ($>$ 1200 K) would show SMSI characteristics. This would probably involve the reduction of the aluminate (e.g. $FeAl_2O_4$, formed initially by the interaction of the impregnated transition metal ions with the γ-Al_2O_3 support) to give the reduced transition metal and α-Al_2O_3. The occurrence of such a γ-α transformation of Al_2O_3 could be of some significance just as the anatase-rutile transformation of TiO_2.

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