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Investigation of the SMSI Phenomenon with $TiO_2/Ru/SiO_2$ Model-Dispersed Catalysts

JAS PAL S. BADYAL,*,[1] RICHARD M. LAMBERT,*,[2] KEVIN HARRISON,†
CHRISTOPHER C. A. RILEY,† AND JONATHAN C. FROST†

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England; and
†B.P. Research Centre, B.P. International plc, Sunbury-on-Thames, Middlesex TW16 7LN, England

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The response of ternary SiO_2-supported Ru/TiO_2 catalysts to a series of characteristic treatments has been examined in detail by chemisorption measurements, XPS, SIMS, and HREM observations, appropriate comparisons being made with binary Ru/SiO_2 and Ru/TiO_2 reference samples. The SMSI state is shown to be air-sensitive and the active highly dispersed phases on the ternary $TiO_2/Ru/SiO_2$ catalysts exhibit SMSI behavior even after low-temperature reduction. SIMS and XPS data indicate that the SMSI condition does not involve intermixing of the Ru and TiO_2 phases. Rather it is associated with highly dispersed metal entities whose XP spectra exhibit significant surface core-level binding energy shifts. Further aspects of the SMSI state are also discussed.

INTRODUCTION

The phenomenon of electronic interaction between metal catalyst particles and oxide supports has been extensively researched and reviewed over many years (see for example (*1–3*) and references therein) despite which the subject continues to be somewhat controversial (*4*). Electronic interaction between Ni and TiO_2 was proposed nearly 30 years ago by Szabó and Solymosi (*5*), widespread interest in the subject being stimulated by the work of Tauster and Fung (*6*) who introduced the term strong metal support interaction (SMSI). High-temperature reduction of Group VIII transition metal catalysts on certain types of support can lead variously to reduced chemisorption capacity, increased catalytic activity in CO/H_2 reactions, and marked retardation of structure-sensitive reactions (*6, 7*). In earlier work (*8–10*) we have made use of well-characterized macroscopic single-crystal model systems to investigate some aspects of the Ru/TiO_x system which may be relevant to an understanding of the strong metal support interaction. The present paper uses an approach which is intermediate between that represented by such model systems (where the metal is present in large excess) and the classical method of investigating Ru/TiO_2 catalysts (where a large amount of the reducible oxide is necessarily present). The object is to provide a link between the single-crystal data and systems of practical interest. We have attempted to do this by preparing Ru/SiO_2 catalysts loaded with a small quantity of TiO_2 which may be reversibly taken into or out of the SMSI condition. A similar, although not identical, approach has been followed by Lin *et al.* (*11*) in the case of Rh, $Pt–V_2O_3/SiO_2$ and by Bond *et al.* (*12*) in the case of $Ru–TiO_2/SiO_2$ and $Ru–TiO_2/Al_2O_3$. In the present case, we have carried out surface-sensitive physical measurements of changes occurring on those areas of the specimen that are likely to be of cata-

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[1] Permanent address: Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham DH1 3LE, UK.

[2] To whom correspondence should be addressed.

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lytic significance (i.e., the Ru/TiO_x interface) in the absence of overwhelming signals due to bulk TiO_2 support. This approach also avoids problems associated with the use of high metal loadings as a means of increasing experimental sensitivity (*13, 14*). The $TiO_x/Ru/SiO_2$ catalysts are therefore a highly dispersed analogue of the Ru(0001)/ TiO_x model system which we have already studied, and their behavior is compared with that of Ru/SiO_2 and Ru/TiO_2 standard samples. In particular, this strategy is aimed at elucidating whether SMSI involves alloy formation between the metal particles and the support (*15–19*) and whether ruthenium ions are present in a mixed oxide system (*20*).

EXPERIMENTAL PROCEDURE

Techniques

X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) were performed in a VG ESCALAB system at BP Research Centre (Sunbury), operating at a typical pressure of 1×10^{-9} Torr. The system was equipped with an *in situ* treatment cell, allowing reduced samples to be characterized without prior exposure to air. All the samples were examined in copper boats (volume about 0.25 cm^3) except the pure TiO_2 which was pressed into indium foil. XPS was carried out using Mg$K\alpha$ radiation; spectra were acquired in constant analyzer energy mode at a pass energy of 50 eV. Because of sample charging, the Si(2*p*) signal from the SiO_2 support was used as an internal standard (BE = 103.4 eV). SIMS observations were carried out using a 4-keV Ar^+ beam at current density of 360 nA cm^{-2}. The analyzed area was ~4 mm^2 (i.e., covering many pellets) and a depth of ~30 Å of material was sputtered from the pellet surfaces during a single experiment.

Catalyst Preparation

Catalysts were made by an impregnation technique. The Ru/SiO_2 and Ru/TiO_2 samples were made using an aqueous ruthenium nitrosyl nitrate solution and the appropriate support:

Silica: Grace type 432, BET surface area 320 m^2g^{-1}

Titania: Degussa P-25 TiO_2, 76% anatase, 24% rutile, BET surface area 55 m^2g^{-1}

Excess solvent was removed under vacuum at 363 K, followed by drying in a vacuum oven (383 K, 10 h); the samples were then reduced in flowing hydrogen at 473 K for 2 h. The ruthenium content (determined by XRF) and measured total surface areas (determined by BET) of the catalysts were as follows. Ru/SiO_2: Ru = 1.4 wt%, surface area 282 ± 6 m^2g^{-1}; Ru/TiO_2: Ru = 1.5 wt%, surface area 53 ± 1 m^2g^{-1}. Ruthenium nitrosyl nitrate was used as precursor instead of the more usual $RuCl_3$ in order to eliminate any possibility of contamination by residual chlorine; such contamination can lead to problems associated with incomplete reduction of the impregnated ruthenium salt (*21, 22*); for both catalysts, the chlorine content was measured to be less than 0.01 wt% by XRF and EDAX analysis.

Half of the Ru/SiO_2 catalyst was used as a precursor for preparation of the $TiO_x/Ru/SiO_2$ catalyst. TiO_x was impregnated into the Ru/SiO_2 from aqueous solution by hydrolysis of $TiCl_4$ (Aldrich 4N pure): a calibrated volume of $TiCl_4$ was added to an agitated 1 : 1 methanol/water solution containing the Ru/SiO_2 catalyst in suspension. Next, the catalyst was brought to dryness under vacuum, baked overnight in a vacuum oven at 383 K, and finally reduced in flowing hydrogen at 473 K for 2 h. From XRF analysis, the titanium content was 1.1 wt% and the level of chlorine was less than 0.1 wt%, in agreement with EDAX analysis of the catalyst. Total BET sample area was 295 ± 11 m^2g^{-1}. The catalyst was prepared in this manner (i.e., leaving the impregnation of TiO_x until last) to hinder possible solid solution formation between TiO_x and the SiO_2 support (*23*). Prior to characterization, the various pretreatments used on the catalysts were as follows:

TABLE 1

Atomic H/Ru Ratios for Hydrogen Chemisorbed at STP (H/Ru)

Treatment	Ru/SiO_2	Ru/TiO_2	$TiO_x/Ru/SiO_2$
LTR	0.45	0.18	<0.05
HTR	0.26	<0.05	<0.05
Air/LTR	0.20	0.24	<0.05

Low-temperature reduction (LTR): Reduction in flowing hydrogen at 523 K for 2 h.

High-temperature reduction (HTR): Reduction in flowing hydrogen at 773 K for 2 h.

Low-temperature oxidation (LTO): Oxidation in flowing 20% oxygen/helium at 573 K for 2 h.

Air: Air exposure at room temperature.

RESULTS

H_2 Chemisorption

Hydrogen chemisorption data were obtained by a pulsed-flow method which measured the amount of irreversible adsorption. Results for the three types of catalyst, pretreated as above, are summarized in Table 1. It can be seen that the Ru/TiO_2 catalyst exhibited characteristic SMSI behavior which appeared even under mild LTR conditions. Air exposure at room temperature was sufficient to reverse the effect of HTR treatment. Ru/SiO_2 does not generally exhibit SMSI characteristics and the H_2 chemisorption behavior observed here is in accord with this. The effect of HTR can be attributed to sintering, since oxidation followed by LTR does not restore the original chemisorption behavior. Negligible hydrogen uptake is exhibited by the $TiO_x/Ru/SiO_2$ catalyst regardless of the pretreatments employed. Oxidation at 573 K for 2 h (in order to remove any trace amount of chlorine) followed by LTR gave rise to no change in these results. It thus appears that this catalyst exhibits SMSI behavior *much more readily* than the Ru/TiO_2 catalyst.

XPS

Quantification of the XPS data was performed using the empirical sensitivity factors of Wagner *et al.* (*24*). The [Ti(2*p*) + Ru(3*p*)] and [Ru(3*d*) + C(1*s*)] spectral regions were computer synthesized in order to resolve out the individual components. TiO_2 and Ru/SiO_2 (LTR) were used as calibration samples. The two Gaussian peaks fitted to the Ti(2*p*) region of the TiO_2 spectrum were not quite in the theoretical ratio of 2 : 1, but they gave much better and more consistent fits to the $TiO_x/Ru/SiO_2$ catalyst spectra (in conjunction with a third Gaussian peak representing the overlapping $Ru(3p_{3/2})$). The binding energy of the $Ti(2p_{3/2})$ peak in the XP spectrum of the TiO_2 sample corresponds to the reported value in the literature for TiO_2 of 458.5 eV (*25*).

In the [C(1*s*) + Ru(3*d*)] region, the ruthenium signal was defined in terms of a doublet of Gaussians, separation 4.1 eV, peak heights in the ratio 3 : 2 in accordance with theory and published data (*26*); the C(1*s*) signal was assigned to carbonaceous species (285 eV). The $Ru(3d_{5/2})$ binding energy of the Ru/SiO_2 (LTR) catalyst is in agreement with the reported value (280.2 eV) for bulk ruthenium (*27*), which is reasonable, given the metal particle size of ~50 Å as determined by electron microscopy.

The results of XPS measurements on the various samples are summarized in Tables 2 and 3. No significant variations in Ti(2*p*) binding energy are evident, indicating that

TABLE 2

XPS Binding Energies (eV) Referenced with Respect to Si(2*p*) at 103.4 eV

Sample/treatment	$Ru(3d_{5/2})$	$Ti(2p_{3/2})$	$Ru(3p_{3/2})$
TiO_2	—	458.4	—
1. $TiO_x/Ru/SiO_2$ as prepared	279.9	458.4	461.2
2. $TiO_x/Ru/SiO_2$ LTR	279.5	458.3	460.7
3. $TiO_x/Ru/SiO_2$ HTR	279.2	458.3	460.6
4. $TiO_x/Ru/SiO_2$ HTR/Air	279.6	458.3	460.9
5. $TiO_x/Ru/SiO_2$ HTR/LTO	280.2	458.3	462.1
6. $TiO_x/Ru/SiO_2$ HTR/LTO/LTR	279.2	458.6	460.8
7. Ru/SiO_2 LTR	280.2	—	461.3

TABLE 3

Atomic Ratios with Respect to Si(2*p*) at 103.4 eV

Sample/treatment	Ru($3d_{5/2}$)	Ti($2p_{3/2}$)	Ru($3p_{3/2}$)
1. $TiO_x/Ru/SiO_2$ as prepared	0.010	0.010	0.010
2. $TiO_x/Ru/SiO_2$ LTR	0.035	0.019	0.025
3. $TiO_x/Ru/SiO_2$ HTR	0.028	0.020	0.020
4. $TiO_x/Ru/SiO_2$ HTR/Air	0.028	0.017	0.022
5. $TiO_x/Ru/SiO_2$ HTR/LTO	0.001	0.006	0.002
6. $TiO_x/Ru/SiO_2$ HTR/LTO/LTR	0.038	0.026	0.024
7. Ru/SiO_2 LTR	0.017	—	0.013

titanium ions in the detected volume remained in the 4+ oxidation state throughout. Possible contamination due to chloride ions can be ruled out because the reported binding energy for Ti($2p_{3/2}$) in $TiCl_3$ is 459.4 eV (*14*), much larger than any of the values we observe. Absence of chloride contamination is confirmed by the Ru binding energies; such contamination would lead to an increase in Ru binding energy, whereas a decrease below the value associated with the chlorine-free Ru/SiO_2 catalyst is actually observed on reduction of the $TiO_2/Ru/SiO_2$ sample.

Variations in the ruthenium XPS binding energies and in the estimated atomic concentrations for the various catalysts are presented in diagrammatic form in Figs. 1a and 1b; it can be seen that the two properties are strongly correlated. The prediction of core-level binding energy shifts of supported metal clusters remains an area of intensive study (*28*). In general, the observed deviations in binding energy from those of the bulk metal can reflect changes in both the initial and final states of the photoemitting system. The physical basis for binding energy shifts in supported metal clusters has been described by Mason (*29*) and DiCenzo and Wertheim (*30*). The shift in ruthenium binding energies to lower values than those reported for bulk ruthenium could arise from one of the following possibilities:

(i) Formation of a dilute alloy of TiO_x in Ru (*8*).

(ii) Significant negative charge transfer from TiO_x/SiO_2 to the ruthenium metal particles (*31*).

(iii) An increase in dispersion of the ruthenium particles due to either cluster formation or raft formation, leading to an increase in the number of surface ruthenium atoms. Shifts toward lower binding energies have been reported for surface metal atoms (*32, 33*): such surface core-level shifts reflect the excess charge at the surface layer of metal atoms due to the reduced coordination (*34–37*). The shift in binding energy depends on the degree of reduction of neighboring

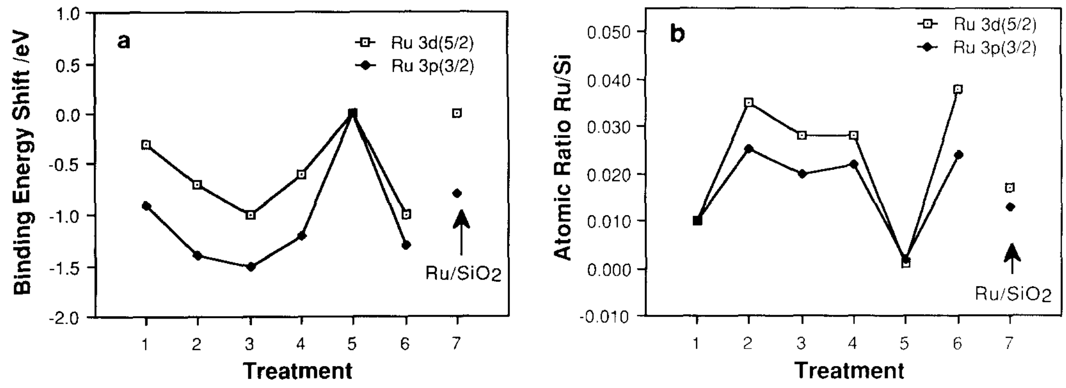

FIG. 1. (a) Variation of Ru XPS binding energy shifts with respect to treatment: $TiO_x/Ru/SiO_2$ (1–6): 1, as prepared; 2, LTR; 3, HTR; 4, HTR/Air; 5, HTR/LTO; 6, HTR/LTO/LTR; and 7, Ru/SiO_2 LTR. (b) Variation of estimated Ru/Si atomic ratios with respect to treatment: $TiO_x/Ru/SiO_2$ (1–6): 1, as prepared; 2, LTR; 3, HTR; 4, HTR/Air; 5, HTR/LTO; 6, HTR/LTO/LTR; and 7, Ru/SiO_2 LTR.

atoms in the surface layer; the shift is to smaller binding energy for a more than half-filled *d* band and to larger binding energy for a less than half-filled *d* band. The observed downward shift is consistent with the above initial state effects arising from charge transfer from reduced titania species, alloying, and/or an increase in the dispersion of the ruthenium. It may represent a minimum, due to changes in the final state relaxation effect arising from changes in the cluster size. Note that high-temperature reduction of Pt/TiO_2 and Rh/TiO_2 is also known to yield negative chemical shifts of the Pt and Rh core levels (*31*).

Electron Microscopy

Electron micrographs of the as-prepared (reduced at 473 K, air exposed) Ru/SiO_2 and $TiO_2/Ru/SiO_2$ samples show obvious differences (Fig. 2). Whereas metal particles are evident for the Ru/SiO_2 catalyst, the $TiO_2/Ru/SiO_2$ catalyst shows a significant reduction in the number of observable ruthenium metal particles, due presumably to the presence of TiO_2; several regions of the sample were examined to ensure that the data were representative. This is an indication that at least some of the ruthenium metal is redistributed under very mild reducing conditions (473 K) during the preparation procedure. In addition, no *discernible* TiO_2 regions are apparent in the ternary catalyst, indicating that the TiO_2 is highly dispersed. Finally, electron diffraction gave no evidence for the presence of any crystalline phases in the Ru/SiO_2 and $TiO_2/Ru/SiO_2$ catalysts.

SIMS Observations

The nature of the reaction occurring between ruthenium and TiO_2 on the silica surface was further investigated by SIMS. Positive SIMS data from the bulk TiO_2 support were taken as reference spectra, and Fig. 3 provides a graphical summary of the spectral data obtained with the $TiO_2/Ru/SiO_2$ catalysts: once again, a clear pattern emerges which correlates with the XPS and H_2 chemisorption results. Two important conclusions can be drawn from these SIMS data: first, there is no evidence for any Ru–Ti alloy formation under SMSI conditions (no Ru–Ti ions); second, under a reducing environment, the Ru and TiO_x species appear to be markedly spread out over the SiO_2 support, yielding high SIMS intensities.

DISCUSSION

In the present case, XPS data for the $TiO_2/Ru/SiO_2$ samples show that induction of the SMSI condition led to no increase in Ru binding energy, suggesting that the presence of Ru ions can be ruled out as a possible cause of the SMSI effect. Alloy formation in the SMSI state also seems improbable, since no changes in the titanium binding energies were observed and no Ru–Ti fragments were detected in the SIMS experiments. The reported XPS and SIMS results can however be explained on the basis of changes in dispersion of the ruthenium metal and/or the formation of a modified titania overlayer encapsulating the Ru. As already noted, the rationalization of XPS binding energy shifts in terms of metal dispersion is not free from ambiguity, although such arguments have often been used previously (*32–37*). In the present case, our conclusions about changes in dispersion are further supported by recent EXAFS results obtained with these same catalysts (*38*).

The formation of metal atom clusters after high-temperature reduction has previously been offered as a possible explanation for EXAFS data obtained with SMSI catalysts (*39–41*), a 13-atom cluster being postulated as the most probable active species. In this connection, it is interesting to note that recent *in situ* EXAFS observations on alloy-derived Ru/CeO_2 catalysts (*42*) indicate that the active material contains a form of highly dispersed Ru.

The formation of very highly dispersed ruthenium may be more evident than in previously reported studies on Ru/TiO_2 catalysts, due to the use of a non-chlorine-based ruthenium precursor. The use of an inert

FIG. 2. Electron micrographs of Ru/SiO_2, Ru/TiO_2 and $TiO_2/Ru/SiO_2$ catalysts (as prepared).

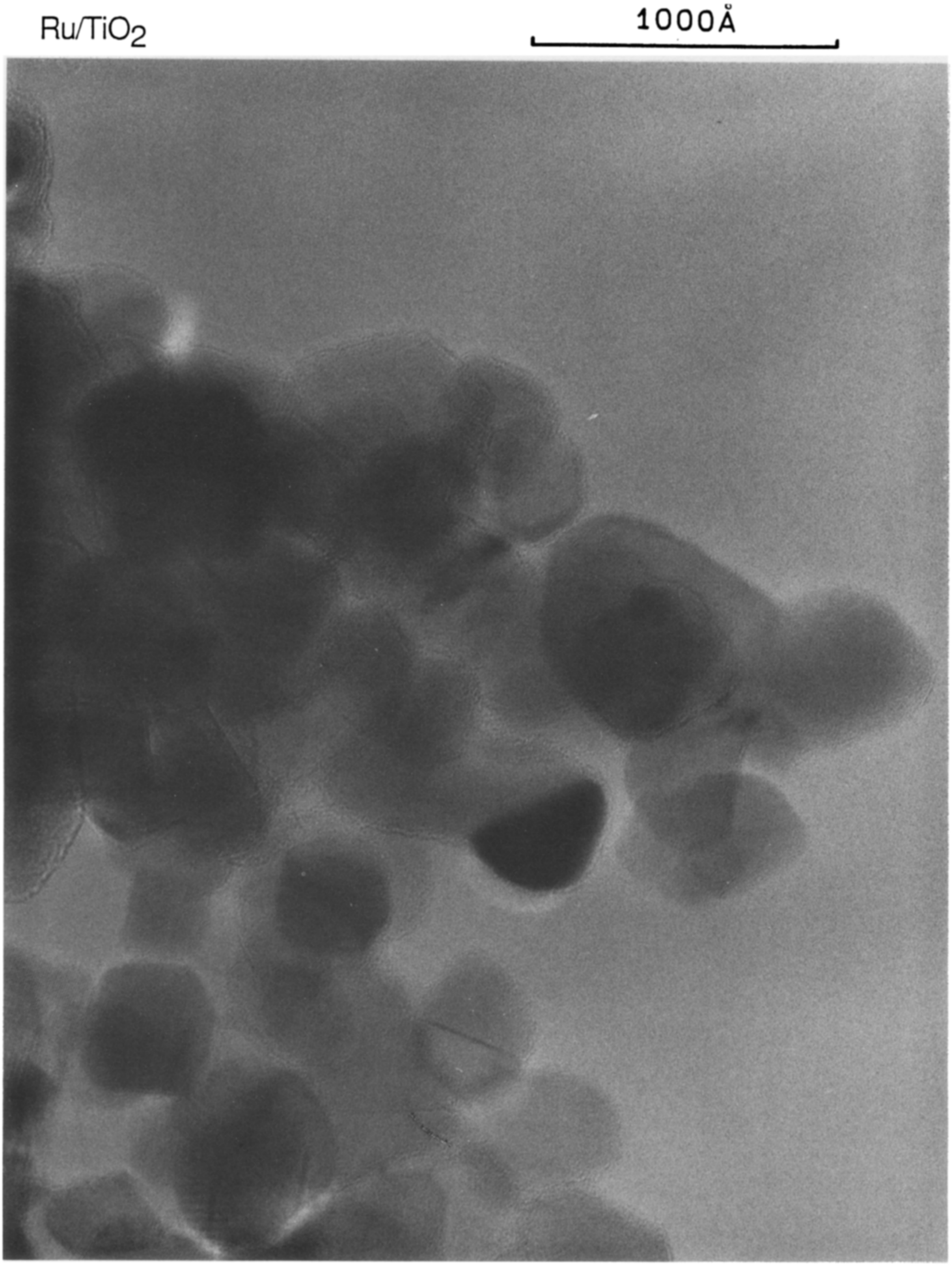

FIG. 2—*Continued*

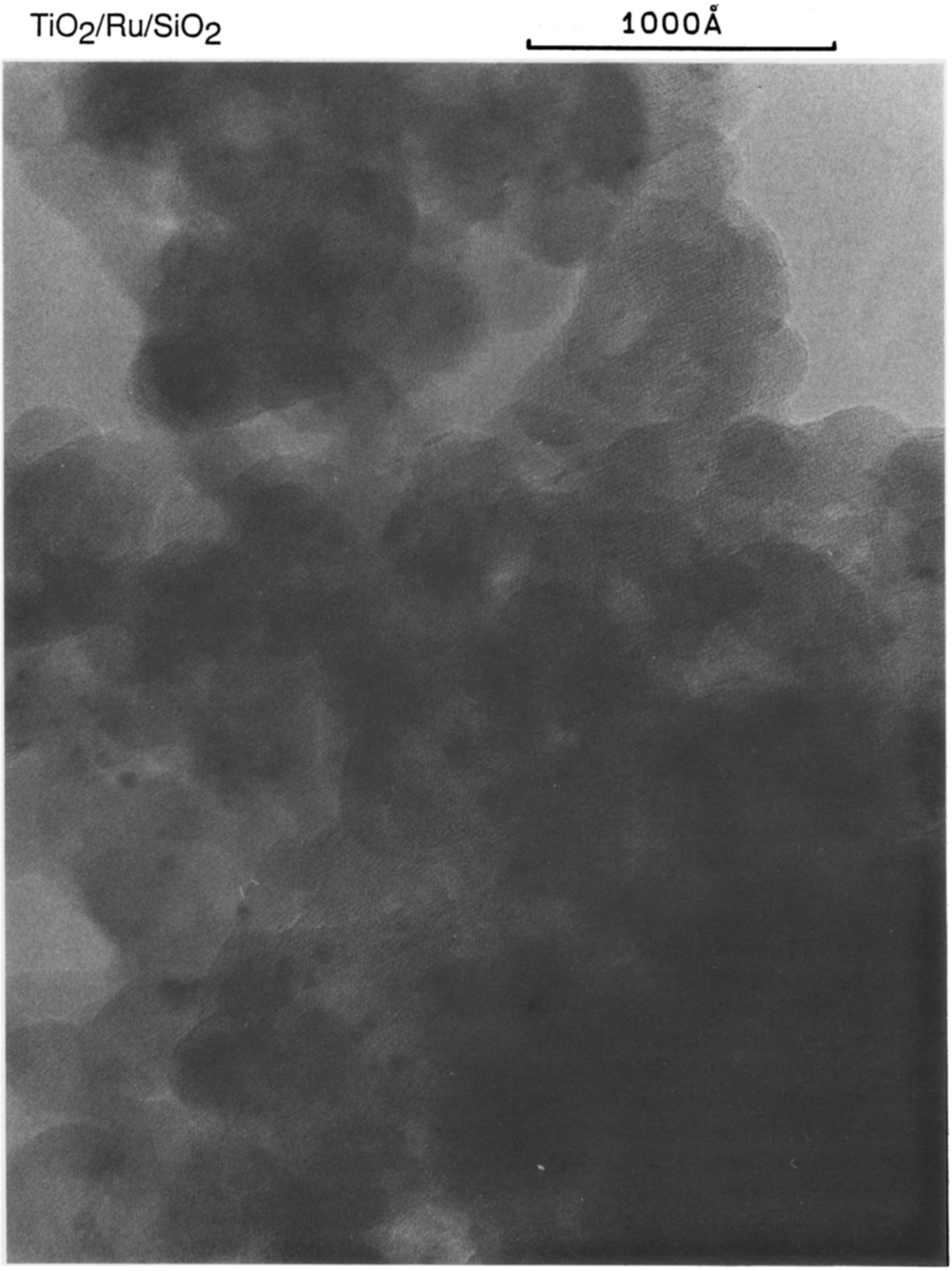

FIG. 2—*Continued*

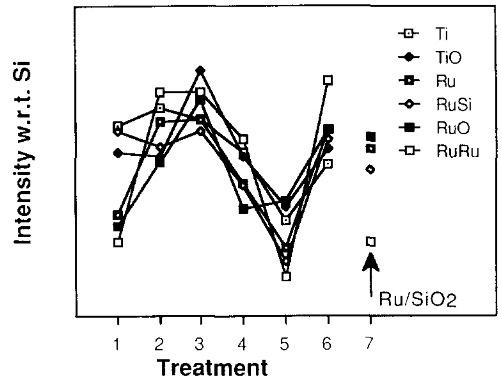

FIG. 3. SIMS fragment intensities (different scales) for the various treatments: $TiO_x/Ru/SiO_2$ (1–6): 1, as prepared; 2, LTR; 3, HTR; 4, HTR/Air; 5, HTR/LTO; 6, HTR/LTO/LTR; and 7, Ru/SiO_2 LTR.

support as a carrier for the active phases has been reported previously for Ru catalysts (*12*), although the authors of Ref. (*12*) used a preparative technique which differed significantly from that employed here. This approach has also been used with $La_2O_3/Pd/SiO_2$, $CeO_2/Pd/SiO_2$ (*43*), and $Nb_2O_5/Ni/SiO_2$ (*44*); such systems also exhibit SMSI behavior (*11, 45*), thus indicating that the phenomenon is not dependent upon the presence of bulk support but only on the support environment which is local to the metal particles.

H_2 chemisorption results for the $TiO_2/Ru/SiO_2$ catalyst show the presence of the SMSI state even after LTR; the system is evidently more susceptible to SMSI than Ru on bulk TiO_2. Furthermore, XPS and SIMS indicate that under the reducing conditions producing the SMSI state, enhanced wetting of the silica surface by TiO_2 and Ru occurs giving greater scope for any interaction between the two components. The silica-supported titania differs from the surface of bulk titania in that it is less strongly bound to the substrate and appears to be more mobile. Electron diffraction data also showed no evidence of bulk-like crystalline titania, indicating a highly dispersed TiO_2 phase. (Low coverages of titania deposited onto alumina are similarly known to exhibit a non-bulk-like form (*46*).) Consequently, encapsulation of Ru by mobile oxide may also contribute to formation of the SMSI state.

It is clear that the effects due to high-temperature treatment are complicated; site blocking by TiO_x, electron transfer effects, and the role of hydrides all need to be considered. Our results are also in agreement with the view that such metal support interactions result from the reduction of the TiO_2 surface (*47*). The interaction between oxide and metal can be described by junction effect theory (JET) (*48*). This treatment shows how the formation of Schottky junctions at the interface between metals and oxides enhances the population of oxide vacancies and implies significant charge transfer from the oxide to the metal and this could facilitate the dissociation of chemisorbed CO, for example. Such an effect has indeed been observed in studies with model $RuTiO_x$ catalysts (*10*). The creation of oxygen ion vacancies at the surface of the surrounding support could also lead to encapsulation of the metal by oxide and our earlier studies with model catalysts (*10*) indicate that in the absence of hydrogen such effects can be of significance. In the present case, incorporation of strongly bound hydrogen could occur at oxygen vacancy sites under high-temperature reduction, and NMR studies on these materials (*49*) show that the SMSI TiO_x phase is hydrogen rich. This is in agreement with the results of Sanz *et al.* (*49*). Air exposure leading to destruction of the dispersed $TiO_2/H/Ru$ phase with segregation and growth of Ru would account for our findings.

The loss of activity for structure-sensitive reactions (*51*) exhibited by catalysts in the SMSI state may be explained in terms of the increase in metal dispersion. Very small particles present different geometric surface environments compared to larger ones; such small metal particles may not have the correct ensemble of surface atoms for structurally demanding reactions. A change in character or size of the surface ensembles may also lead to the observed decrease in H_2 chemisorption. For example, we have shown that an ensemble of several atoms may be necessary for H_2 chemisorption on the basal plane of ruthenium (*52*). Alternatively, effects due to changes in electronic structure of Ru atoms (as evidenced by XPS BE shifts and described by JET) or oxide encapsulation of the Ru surface may contribute to this aspect of SMSI behavior.

CONCLUSIONS

The model catalyst $TiO_2/Ru/SiO_2$ has been found to be more vulnerable to the strong metal support interaction than the bulk Ru/TiO_2 catalyst. These experiments have shown that this behavior is associated with an increase in dispersion of the metal particles and the presence of modified TiO_2 species which may encapsulate the ruthenium.

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