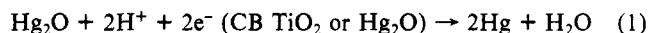
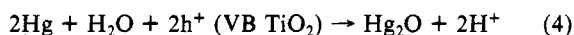
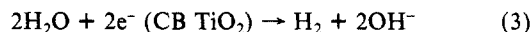


photosystem II



photosystem I



The redox levels of (1)–(4) with respect to the band positions of TiO_2 are shown in Figure 6. An increase in pH favors hole reactions, both energetically and from the number of charge transfers involved; the hole reaction (4) is a more probable process than the hole reaction (2). Again because of the shift of the flat-band potential of TiO_2 in the negative direction with an increase in pH,^{13,14} the electron reaction (3) becomes possible at

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higher pHs. Thus, one could expect that an increase in pH favors PS I suppressing PS II. In addition to the above scheme of electron and hole transfers, there could be photoreactions due to light absorption by the redox couple and direct photoelectrochemical effects in TiO_2 (as suggested by generation small quantities of H_2).

In practice, the efficiency gradually decreases with the repetition of cycles. The more serious problem is that reaction rates drastically slow down with the accumulation of photogenerated gases and visible bubbling of O_2 or H_2 is not observed at ordinary light intensities. Again the cycling of the system will use up acid and base, and practically only few cycles can be completed as the ionic strength would be intolerably high. Alternatively, the catalyst could be separated and transported between acid and alkaline solutions; this operation consumes some energy.

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EXAFS Evidence for Direct Rh–Fe Bonding In SiO_2 -Supported Rh–Fe Bimetallic Catalysts

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Rh K-edge and Fe K-edge EXAFS spectra were observed on Rh–Fe bimetallic catalysts supported on silica, by use of synchrotron radiation. By combining the EXAFS data with the results of Mössbauer spectroscopy, we obtained structural models for the catalysts. It is concluded that, in the catalyst of a low Fe/Rh ratio ($\text{Fe/Rh} = 0.3$), Fe atoms are mostly in the state of Fe^{3+} and are located in the metal–support interface forming bonds with Rh atoms and with oxygen atoms of the support. In the case of a higher Fe/Rh ratio, the excess Fe atoms are in the state of Fe^0 and are on the surface of metal particles. Discussion is given on the relation between the structures and the catalytic properties.

Introduction

Supported bimetallic catalysts exhibit catalytic activities and selectivities markedly different from those of the supported catalysts of the constituent metals, and their catalytic properties are strongly influenced by the metal dispersion as well as by the surface composition of dispersed metal particles.^{1,2} Sinfelt et al.^{3–6} investigated by EXAFS spectroscopy the surface compositions of the bimetallic Ru–Cu, Pt–Ir, and Rh–Ir (1:1) alloy particles dispersed on alumina and silica and reported that the composition near the surface of an alloy particle was generally different from that of the bulk region.

The Rh–Fe bimetallic catalyst exhibits a unique catalytic activity for producing a mixture of MeOH and EtOH with a high efficiency in the $\text{CO} + \text{H}_2$ conversion reaction, while the catalysts of the constituent metals, Rh and Fe, give a mixture of AcH and AcOH and that of hydrocarbons, respectively.^{7–9} Recently, from the study by Mössbauer spectroscopy, it was claimed that Fe atoms

in Rh–Fe/ SiO_2 catalysts were mostly in the state of Fe^{3+} even when the catalysts had been highly reduced with H_2 at 400–500 °C.^{10–13} In the present study, we have conducted an in situ

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EXAFS investigation on the Rh-Fe/SiO₂ catalysts to elucidate their surface structures. We report here the first EXAFS evidence which indicates that Fe atoms in these catalysts are highly dispersed in the metal-support interface forming Rh-Fe-O(support) bonding and on the surfaces of Rh metal particles. This fact seems to be important for understanding the role of Fe in these catalysts to enhance the MeOH and EtOH yields in the CO + H₂ conversion and to prevent the sintering of metal particles under the prevailing reaction conditions.

Experimental Section

Rh-Fe/SiO₂ catalysts were prepared by the impregnation of SiO₂ gel (Aerosil 300; surface area 280 g/cm²) with a methanol solution containing RhCl₃ and FeCl₃. Before the impregnation, SiO₂ gel was preheated at 320 °C for 2 h in vacuo. The impregnated samples were dried and pressed into thin disks (20-mm diameter, 70 mg) and then reduced by temperature-programmed heating to 400 °C for 2 h in flowing H₂ gas. The examination of the metal dispersion and the determination of metal particle size were done with a transmission electron microscope (TEM) and by the measurement of CO/H₂ chemisorption stoichiometry. The mean particle size was found to be 20–40 Å for all the Rh-Fe catalysts prepared in the present study, having an Fe/Rh atomic ratio of 0.3–1.0.

The self-supporting wafers of the prepared catalysts were set into a specially designed Pyrex-made sample cell having a Kapton window (500 μm thick) for EXAFS measurements. The cell allows to make in situ treatments of the catalysts with H₂ and/or CO at an elevated temperature. EXAFS measurements were carried out at the BL 10-B in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF).¹⁴ The spectrum around the Rh K-edge (23.2 keV) and that around the Fe K-edge (7.11 keV) were measured on each catalyst sample, and the EXAFS oscillations were extracted from the observed spectra by the procedures which we have described elsewhere in detail.¹⁶ First, the Fourier transform of k^3 weighted EXAFS oscillation $k^3\chi(k)$ was calculated, and then the curve-fitting analysis was carried out on the inverse Fourier transform of the selected region by using the theoretical amplitude and phase-shift functions given by Teo et al.¹⁵ The coordination numbers were determined by using the EXAFS data of the standard materials, Fe foil and Rh powder. All the present analyses were performed by use of the EXAFS-1 program system.¹⁶

Mössbauer spectra were obtained at 293 K with an Austin Science S-600 spectrometer, and the data were treated by the computer-processing analysis in a way similar to the one done in our previous studies.^{10,11}

Results and Discussion

Figure 1, a and b, shows the k^3 weighted oscillation $k^3\chi(k)$ of the Fe K-edge EXAFS obtained for the Rh-Fe catalyst with an Fe/Rh atomic ratio of 0.3 and its Fourier transform, respectively. The relatively high amplitude in the high k region of the observed Fe K-edge EXAFS indicates that the Fe atom is surrounded by Rh atoms. In fact, the Fourier transform shown in Figure 1b exhibits a strong peak attributable to Fe-Rh at about 2.5 Å, the small peak in the low k side of the main peak (at about 2 Å in Figure 1a) being the one arising from the splitting of the Fe-Rh peak by the nonlinearity of the Fe-Rh phase-shift function. The curve-fitting analysis of the inverse Fourier transform of the Fe-Rh peak gave the Fe-Rh coordination number of 4.7 and the interatomic distance of 2.63 Å. The shoulder peak at 1.5 Å in Figure 1b can be attributed to Fe-O, the interatomic distance being 2.05

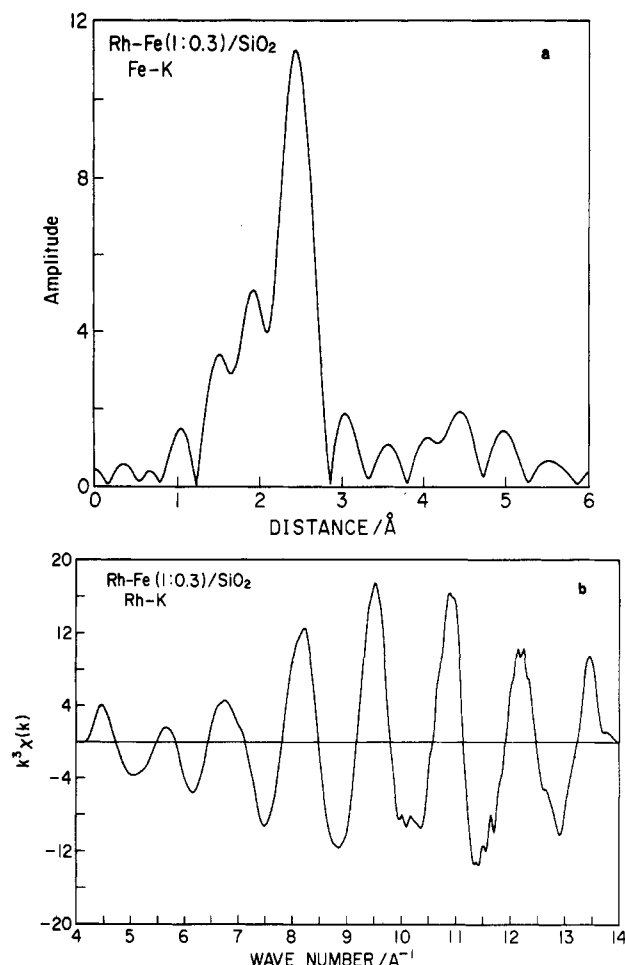


Figure 1. Fe K-edge EXAFS oscillation $k^3\chi(k)$ (a) and its Fourier transform (b) of the Rh-Fe catalyst (Fe/Rh = 0.3, total metal 4.0 wt %) after H₂ reduction at 400 °C.

Å according to the result of the curve-fitting analysis. This is attributable to the bonding with the oxygen atoms of the support. There is little contribution of Fe-Fe bonding.

The Rh K-edge EXAFS of the same catalyst and its Fourier transform are shown in Figure 2, a and b, respectively. The major peak in the Fourier transform is attributable to Rh-Rh. According to the curve-fitting analysis, the Rh-Rh coordination number is as large as 11 and the Rh-Rh distance is 2.66 Å, which are almost the same as the coordination number and the interatomic distance in the bulk Rh metal. These facts indicate that Rh atoms are forming relatively large Rh metal particles. This is consistent with the TEM observation of the catalyst, where the average size of metal particles was found to be about 25 Å. Although Fe-Rh bonding was the major contribution in the Fe K-edge EXAFS, the contribution of Rh-Fe bonding was not detectable in the Rh K-edge EXAFS. The contribution of Rh-Fe becomes detectable when the Fe/Rh atomic ratio is increased to 1.0. As shown in Table I, the Rh-Fe coordination number is 2.1 in this catalyst, and the Rh-Rh coordination number is reduced to 6.3.

The oxidation states and the abundance ratios of the Fe species were studied by Mössbauer spectroscopy on the reduced Rh-Fe/SiO₂ catalysts.¹¹ The observed Mössbauer spectra were reasonably interpreted as those due to Fe³⁺ and Fe⁰. No contribution of Fe²⁺ could be detected. These Mössbauer results are basically consistent with the results previously reported by Niemantsverdriet et al.¹² They claimed from the comparison of the Mössbauer spectra obtained at 300 and 4 K that the recoilless fractions of Fe³⁺ and Fe⁰ as measured from the areas of the resonant absorptions are lower at room temperature than the corresponding values at low temperature because of the low effective Debye temperatures¹³ (Fe³⁺: $\theta_D = 175 \pm 25$ K; Fe⁰: $\theta_D = 450 \pm 50$ K). Thus, we have corrected for the difference in the recoilless fraction to determine the ratio of Fe³⁺ to Fe⁰. The

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TABLE I: Results of the Curve-Fitting Analysis of EXAFS Data and Mössbauer for the Rh-Fe Bimetallic Catalyst Supported on Silica

catalyst	fraction of Fe ³⁺ , ^a %	Fe K-edge EXAFS ^b				Rh K-edge EXAFS ^b					
		Fe-O		Fe-Rh		Rh-Rh		Rh-Fe		Rh-O	
		CN	R	CN	R	CN	R	CN	R	CN	R
Fe/Rh = 0.3											
H ₂ red. (400 °C)	91	1.5	2.05	4.7	2.63	11.4	2.66				
O ₂ ox. (25 °C)	97	5.2	1.94			4.9	2.66			3.3	2.01
Fe/Rh = 0.5											
H ₂ red. (400 °C)	86	0.9	1.99	4.0	2.62	9.5	2.66				
Fe/Rh = 1											
H ₂ red. (400 °C)	75	1.1	2.02	3.4	2.61	6.3	2.65	2.1	2.58		

^a Estimated from the Mössbauer data obtained at room temperature. ^b CN = coordination number; R = interatomic distance (in Å). Total metal 4.0 wt %.

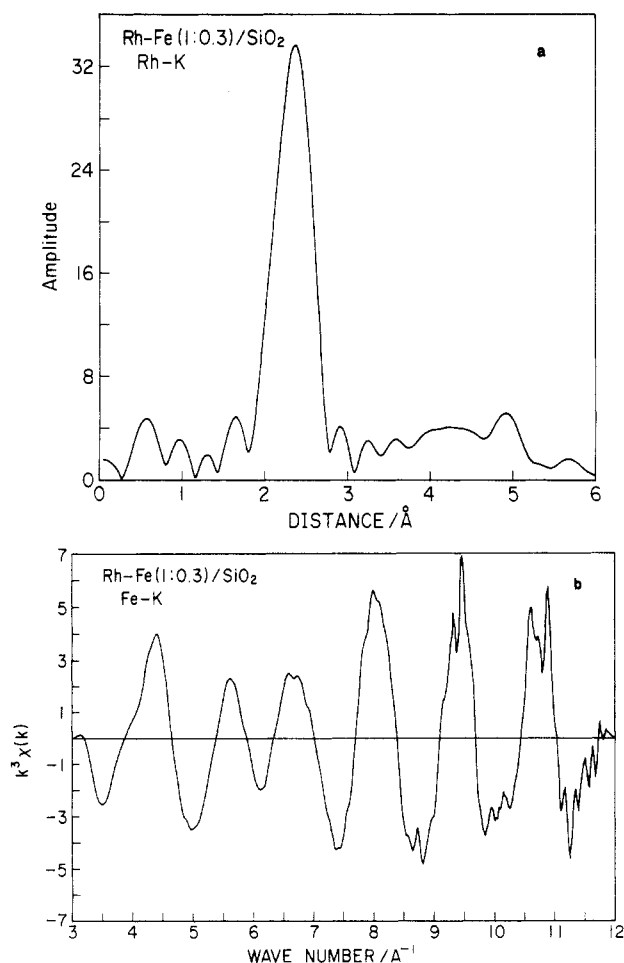


Figure 2. Rh K-edge EXFAS oscillation $k^3\chi(k)$ (a) and its Fourier transform (b) of the Rh-Fe catalyst (Fe/Rh = 0.3, total metal 4.0 wt %) after H₂ reduction at 400 °C.

results thus obtained are given in Table I. In the case of the catalyst with an Fe/Rh ratio of 0.3, only about 10% of Fe atoms are in the state of Fe⁰ and the remaining 90% of Fe atoms are in the state of Fe³⁺. The fraction of Fe⁰ increases with the increase of the Fe/Rh ratio, but it is still only 25% even when Fe/Rh = 1.

Combining the above-mentioned results of Mössbauer spectroscopy with those of the analyses of EXAFS data, we can derive the following structural model for the Rh-Fe/SiO₂ catalysts. In the case of the catalyst with an Fe/Rh ratio of 0.3, Fe atoms which are mostly in the state of Fe³⁺ are located in the metal-support interface forming chemical bonds with the oxygen atoms of the

surface of SiO₂. Since the contribution of Fe-Fe is negligible in the observed EXAFS oscillation, Fe atoms should be highly dispersed without forming an aggregate by themselves. Thus, Fe³⁺ ions forming Fe-O(support) bonding in the metal-support interface have the role to anchor Rh particles onto the support. This structural model is consistent with the fact that Fe atoms in this catalyst remain in the high oxidation state even under a severe reducing condition (in 1 atm of H₂, at 400 °C). Yermakov¹⁷ and Huizinaga and Prins¹⁸ have suggested a similar anchoring effect by metal ions, such as Re²⁺ in the Pt-Re/Al₂O₃ catalyst and Pt²⁺ in the Pt/Al₂O₃ catalyst. Seemingly, it is the above-mentioned anchoring effect through Rh-Fe-O(support) bonding that prevents the agglomeration of metal particles during a catalytic reaction at a high temperature. When the Fe/Rh atomic ratio is increased, the fraction of Fe⁰ relative to Fe³⁺ increases, but still the majority of Fe atoms are in the state of Fe³⁺. In this case also, Fe³⁺ ions should be in the metal-support interface forming the Fe-O(support) bond as in the case of low Fe/Rh ratio. Judging from the results obtained from EXAFS data, the excess Fe atoms, which are in the state of Fe⁰, are likely to be on the surface of a Rh metal particle.

As we previously reported from the IR spectroscopic study on the CO chemisorbed states of Rh-Fe/SiO₂ catalysts,¹⁹ the amount of bridged CO bound to Rh was strongly reduced on increasing the Fe/Rh ratio, suggesting the formation of a Rh-Fe⁰ bimetallic ensemble on the particle surface. This is well reflected in the depression of the CO dissociation and in that of the methanation with the increase of Fe/Rh ratio in Rh-Fe/SiO₂ catalysts, and also in the enhancement of the MeOH and EtOH production in the CO + H₂ conversion catalyzed by these catalysts. These phenomena are consistent with the structural model derived from the present study.

Conclusion

The structures of the Rh-Fe bimetallic catalysts supported on silica have been discussed by combining the structural data derived from in situ EXAFS spectroscopy with the results of Mössbauer spectroscopy. In the catalysts of low Fe/Rh ratio, most Fe atoms are in the state of Fe³⁺ and located in the region of metal-support interface forming Rh-Fe-O(support) bonding. In the catalyst of higher Fe/Rh ratio, the majority of Fe atoms are in the metal-support interface as in the case of low Fe/Rh ratio, but excess Fe atoms are dispersed on the surfaces of Rh metal particles taking the valence state of Fe⁰. The structural models of the Rh-Fe catalysts proposed in the present study will explain the catalytic properties of these catalysts as well as the role of Fe to anchor metal particles on the support.

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