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Promoting Effects of Se on Rh/SiO_2 Catalysis for Ethene Hydroformylation

Promoting effects of the added second components on metal catalysis have extensively been studied from industrial points of view as well as from chemical interests (*1–4*). The promoting phenomenon may also be related to the genesis of activity and selectivity for metal catalysis. Electropositive additives are generally interpreted to donate electrons to surface metal atoms, resulting in promotion of catalytic activities or improvement of the reaction selectivities (*5*).

It is possible for electronegative additives to have a direct electronic interaction with the metal surface through chemical bonds. The poisoning effects of S have been examined experimentally and theoretically. Sulfur poisons methanation and the Boudouard reaction on Ni catalysts in a non-linear manner (*6*). MacLaren *et al.* (*7*) calculated the local density of states (LDOS) at the Fermi level (E_f) of Rh(100) and Ni(100) surfaces by a MS–Xα method. They showed that S adatoms reduced the LDOS at E_f, resulting in poisoning to CO adsorption. They also estimated the area of the ligand (electronic) effect of S to be <5 Å laterally at the surfaces. Feibelman and Hamann (*8*) have also reported similar results by surface-linearized-augmented-plane-wave (SLAPW) calculations. Carbon monoxide adsorption sites on S-modified Rh(111) and Ni(111) can be classified by the distance from a threefold S adatom; nearest sites M_A, far sites M_B, and remote sites M_c (*9*). The MS–Xα calculation suggests that M_B sites can promote CO adsorption to a small extent. This allows us to predict that Se, which has an electronegativity of 2.4 similar to 2.5 for S, will give a positive effect on CO adsorption and hence CO insertion at the Rh surface. Furthermore, Se has been found to act as a good catalyst for liquid-phase carbonylations, suggesting that the Se atom can interact with CO to activate it (*10, 11*).

We have recently reported the promoting effect of Se on Rh/ZrO_2 catalysis for ethene hydroformylation (*12, 13*). The addition of Se electronically modified Rh metal sites around the Se atom to be relatively positive, judging from XPS data which revealed that the oxidation state of Se on Rh particles is -2. This mechanism for the creation of positive metal sites is different from the mechanism induced by site segregation of cationic additives (*14*). From IR, isotope effects and TPD studies, Se was suggested to interact with CO and propanoyl intermediate. This interaction should not only be electronic but also geometric by the appropriate distance between Se and adsorbates on Rh sites. For hydroformylation or CO/H_2 reaction on Rh, it has been reported that the activity and selectivity depend on the kind of supports (*15–17*). Support effects can be classified as follows: (i) change of metal particle size, (ii) modification of the electronic structure of surface metal site, (iii) SMSI effect, and (iv) surface groups (for example, OH groups) which directly react or interact with reaction intermediates. Rh on SiO_2 may have a different electronic structure near its Fermi level, and Se would have a different interaction with the Rh to play a different role as promoter as compared to the Rh/ZrO_2 system.

In the present paper we report the promoting effects of Se on Rh/SiO_2 catalysis for ethene hydroformylation and the interaction of Se and Rh atoms by kinetics, FT-IR, XPS, and EXAFS in comparison with the case of $Se/Rh/ZrO_2$.

Se-modified Rh/SiO_2 catalysts were prepared in two different ways. Silica (surface area: 50 m^2g^{-1}, Japan Aerosil Co.) was co-

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impregnated with aqueous solution of $Rh(NO_3)_3$ (Soekawa Co.) and SeO_2 (Tri Chemical Co.), followed by drying at 393 K and calcination at 673 K in air. The sample was treated by H_2 at 673 K for 1 h *in situ* before use as a catalyst. The Se-promoted catalyst thus obtained is denoted as catalyst **(1)**. Se content in the catalysts**(1)** was varied in the range of Se/Rh from 0.001 to 0.05. $Rh_6(CO)_{16}$-derived Rh/SiO_2 was prepared by using a $CHCl_3$ solution of $Rh_6(CO)_{16}$ (Aldrich Chem. Co.) in Ar atmosphere at room temperature. After $CHCl_3$ was evacuated, sample was interacted with $(CH_3)_2Se$ (Toyo Stauffer Chemical Co.) at 428 K for 30 min. The Se-modified $Rh_6(CO)_{16}$-derived catalysts thus obtained are denoted as catalyst**(2)**. Selenium content in the catalysts**(2)** was varied in the range of Se/Rh from 0.03 to 0.6. Rh loadings were always 1 wt% as Rh/SiO_2.

Ethene hydroformylation was carried out in the temperature range 393–473 K in a closed circulating system (dead volume: 119 cm^3) with a U-shaped liquid N_2/acetone trap (179 K). The reaction products were analyzed by a gas chromatograph, using a 2-m column of VZ-10 at 353 K for ethene and ethane, and a 4-m column of DOS at 353 K for propanal and propanol. IR and XPS spectra were taken on a JASCO FT/IR-7000 spectrometer and a Shimadzu ESCA750 spectrometer as previously reported (*12*, *13*). EXAFS spectra for the $Se/Rh/SiO_2$ catalysts were measured at BL–10B of the Photon Factory in the National Laboratory for High Energy Physics (Proposal No. 87013). The samples were transferred into an EXAFS cell after they were given treatments without contacting air. The EXAFS analysis was performed by using theoretical phase shifts and amplitude functions.

The TEM photographs of Rh/SiO_2 **(1)** showed the averaged particle sizes of 40 Å, which are compatible with the H/Rh value (0.33) by H_2 adsorption. The TEM images of the Se-doped catalysts did not show any distinguishable changes as compared with those of the undoped catalyst. Figure 1 shows that the amount of H_2 adsorbed on $Se/Rh/SiO_2$ **(1)** at 293 K monotonously decreased eventually to almost zero as the Se quantity increased up to Se/Rh = 0.03. The initial slope of the amount of H_2 adsorbed as a function of the amount of added Se indicates that 1 Se blocks 12 Rh sites. The poisoning effect is larger than that in the case of $Se/Rh/ZrO_2$, where one Se atom blocked 8 sites (*13*). The acidic SiO_2 may be hard to offer electrons to Rh particles and hence is more easily deactivated by the electronegative additive. In contrast to H_2 adsorption, CO adsorption did not decrease until Se/Rh = 0.01. With larger amounts of Se the CO adsorption decreased, but it was possible to adsorb CO even at the Se/Rh > 0.03, where the H_2 adsorption was nearly zero. These results suggest that Se atoms at the Rh surface can interact with adsorbed CO.

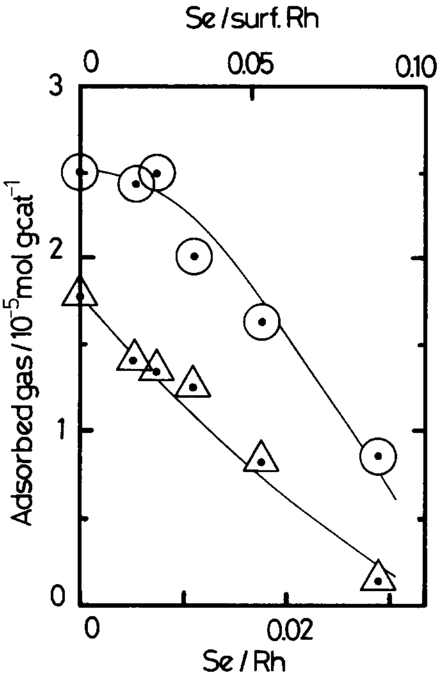

FIG. 1. The variation of the amounts of H_2 and CO adsorbed at 293 K with the amount of Se contained in the catalysts **(1)**: ⊙, CO; △, H_2.

Linear (2062 cm^{-1}), bridged (1856 cm^{-1}), and twin (2092 and 2022 cm^{-1}) CO peaks were definitely observed with Rh/SiO_2, whereas no twin CO peak was observed on the Se-modified surfaces, and the intensities of the linear and bridged CO peaks decreased in a similar ratio with an increase of Se content, suggesting that Se preferentially blocked the twin sites on the Rh metal surface. On the contrary, it has been claimed that S selectively poisons bridging-CO adsorption site, while the twin CO site (corner or edge sites) is less effected by S (*18*). The behavior of IR peaks for our $Se/Rh/SiO_2$ is similar to the result of H_2S dissociative adsorption on the Ru(1,1,10) stepped surface (*19*). Hydrogen sulfide selectively poisons the step sites initially, and after the completion of adsorption on the step sites, it becomes possible to adsorb on the terrace sites.

The Se $3d_{5/2}$ binding energies for the catalysts**(1)** with Se/Rh = 0.001–0.05 and for the catalyst**(2)** with Se/Rh_6 = 1.21 before the reaction were determined to be 54.7 ± 0.1 eV and 55.2 ± 0.1 eV, respectively. The same values were observed for the samples after the hydroformylation reaction. These results reveal that the oxidation states of Se correspond to be $-1 - -0.5$ for the $Se/Rh/SiO_2$ catalysts employed in the present study. The XPS peaks for Rh $3d_{3/2}$ and $3d_{5/2}$ in the $Se/Rh/SiO_2$ catalysts were always observed at 311.9 ± 0.1 and 307.3 ± 0.1 eV, respectively, showing neither a definite peak nor a shoulder on the higher binding side. The values are almost the same as those for undoped Rh/SiO_2, referred to metallic Rh. Cationic charge might be delocalized to more than several Rh atoms around Se. As Se dispersed on the SiO_2 surface should have a cationic oxidation state, most of the Se anions must be distributed on Rh surfaces.

In fact the direct bonding between Rh and Se atoms was observed by EXAFS. Figure 2 shows the Se *K*-edge EXAFS oscillation and its associated Fourier transformation for the $Se/Rh/SiO_2$ catalysts**(2)**. The Fourier transform spectrum had only one peak (Fig. 2(b)) and the curve-fitting analysis for the inversely-Fourier transformed oscillation by using theoretical parameters for the Se–Rh bond in Fig. 2(c) showed the existence of an Rh–Se bond at 2.41 Å.

The activities and selectivities of the catalysts**(1)** as a function of Se/Rh atomic ratio or Se/surface Rh ratio are shown in Fig. 3. The turnover frequency (TOF) for propanal formation had a curve with a maximum at Se/Rh = 0.008, where TOF is defined as the amount of propanal formed per unit time per surface unblocked Rh atoms (estimated by H_2 adsorption in Fig. 1). Figure 3 shows that propanal formation was enhanced by Se addition. On the contrary, ethane formation was suppressed monotonously by the addition of Se. Propanol was not produced under the present conditions. As for the hydroformylation selectivity, we also observed a maximum selectivity (64.8%) at Se/surf. Rh = 0.042 (Fig. 3). For the catalysts**(2)**, the maximum selectivity was observed at Se/Rh = 0.20, but the TOF's for the formation of ethane and propanal monotonously decreased with an increase of Se content. The difference between the two catalysts may be derived from the different coordination structures of Rh (*20*) and electron densities of Se. Konishi *et al.* (*18*) reported the promotion effect of S in ethene hydroformylation on Rh/SiO_2 showing a similar result to ours. TOF for propanal formation increased 1.8 times at an optimum amount of S added, and the selectivity of hydroformylation at the optimum amount of S was 25.3%. The $Se/Rh/SiO_2$ catalyst showed a much higher selectivity (64.8%). This difference in selectivity should be derived partly from the drastic suppression of ethane formation by the larger Se anion relative to the S anion and partly from the interaction of adsorbed CO and Se anions on the Rh surface.

The interaction between CO or propanoyl intermediate and the Se–Rh ensemble in the $Se/Rh/SiO_2$ catalysts seems to be similar to that in $Se/Rh/ZrO_2$ catalysts (*12,*

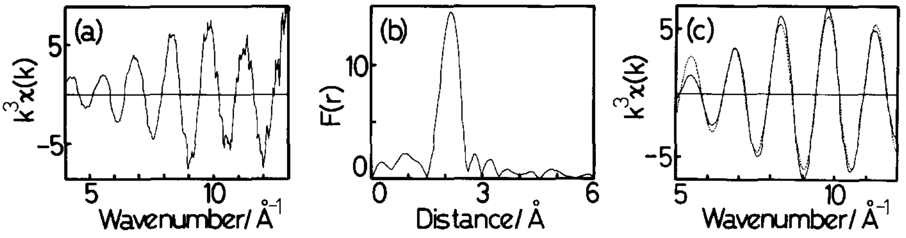

FIG. 2. Se K-edge EXAFS spectra for the catalyst (2) (Se/Rh = 0.19): (a) k^3-weighted EXAFS oscillation, (b) its associated Fourier transform, and (c) curve fitting analysis (______, observed; - - - - calculated).

13), but Rh/SiO_2 (**1**) was more active by a factor of 5.2 than Rh/ZrO_2 for ethene hydroformylation. The difference of the two catalysts in activity and selectivity may be explained by different microscopic electronic charges of Se or Rh. The oxidation state of Se in $Se/Rh/ZrO_2$ was -2, in contrast to -0.5– -1 for $Se/Rh/SiO_2$. The Rh–Se bond on SiO_2 surface may be more covalent and a more efficient electronic ensemble composed of Rh and Se for hydroformylation may be formed, as compared to the ZrO_2 surface. It is suggested, based on the decrease in the activation energy for propanal formation from 89 to 67 kJ mol^{-1} by the addition of Se, that $Se^{\delta-}$ (δ: 0.5–1) electronically modifies the Rh catalysis.

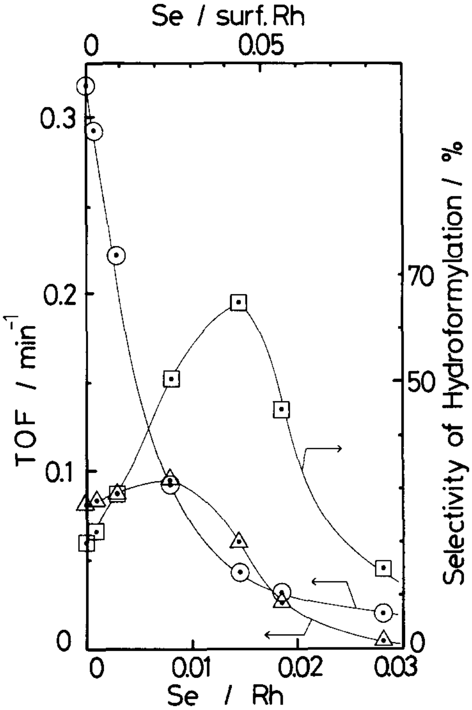

FIG. 3. Turnover frequencies (TOF) and selectivities of ethene hydroformylation on the Se-modified Rh/SiO_2 catalysts (**1**) as a function of Se content: react. temp., 453 K; total pressure, 40.0 kPa; C_2H_4 : CO : H_2 = 1 : 1 : 1; ⊙, ethane; △, propanal; ⊡, selectivity.

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