Promoting Effects of Se on the Activity and Selectivity of Rh–ZrO_2 Catalyst for Ethene Hydroformylation

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Se-Modified Rh–ZrO_2 catalysts, prepared by treatment of Rh–ZrO_2 with Me_2Se or by a co-impregnation method using SeO_2, exhibit high activities and selectivities for ethene hydroformylation, having an optimum ratio of Se : Rh.

While chalcogens such as S and Se are known to have strong poisoning effects on metal catalysis,[1] Se has been found to act as a good catalyst for liquid phase carbonylations[2] suggesting that the Se atom can interact with and activate carbon monoxide. We now report Se-promoted Rh–ZrO_2 catalysts which exhibit high activities and selectivities for ethene hydroformylation.

Two types of catalysts, (**1**) and (**2**), were prepared as follows. ZrO_2 (surface area 12 m^2 g^{-1}, Soekawa Co., Ltd.) was impregnated with $Rh(NO_3)_3$ (Soekawa Co., Ltd.) in aqueous solution, followed by calcination in air at 673 K and reduction with H_2 at 673 K for 1 h. CO was preadsorbed onto the Rh–ZrO_2, reaching full coverage[3] at 295 K, and the catalyst was treated with Me_2Se (0.025—0.12 kPa) (Toyo Stauffer Chemical Co.) at 373 K for 30 min. The Se-modified catalyst was further treated with H_2 at 373 K for 30 min to remove weakly physisorbed Me_2Se without reaction with surface Rh atoms. The Se-promoted Rh–ZrO_2 catalyst thus obtained was denoted as catalyst (**1**). Se-modified catalysts (**2**) were prepared by co-impregnation of ZrO_2 with $Rh(NO_3)_3$ and SeO_2 (Tri Chemical Co., Ltd.) in aqueous solution, followed by calcination in air at 673 K and reduction with H_2 at 673 K for 1 h. Rh loadings were fixed at 1 or 3 wt%, the Se content was varied in the range Se : Rh 0.01 to 0.17 by changing the amount of Me_2Se or SeO_2. The Se contents of the catalysts were determined by means of *X*-ray fluorescence. Very little Se was lost from either catalyst (**1**) or (**2**) during the calcination, reduction, and hydroformylation reactions.

Ethene hydroformylation was carried out in the temperature range 393—473 K in a closed circulating system (dead volume 119 cm^3) using a dry ice–acetone trap (179 K) to isolate propanal and propanol. The activities for the hydroformylation as a function of Se content for catalyst (**1**) are shown in Figure 1. As the Se : Rh ratio increased, propanol formation was considerably enhanced, reaching a maximum at Se : Rh 0.066, while ethene hydrogenation was suppressed. As a result, the selectivity toward oxo-compounds also changed markedly with increasing Se content, having a maximum at Se : Rh 0.066 as shown in Figure 2. The selectivity was four times that of the unmodified Rh–ZrO_2 catalyst.

Figure 2 shows the selectivities to oxo-products in ethene hydroformylation on catalysts (**2**) with Rh loadings of 1 and 3 wt% plotted against the Se : Rh ratio. Similarly to catalyst (**1**), propanol formation was enhanced by Se addition, while ethene hydrogenation and propanal formation were reduced. The selectivity for oxo-compounds was maximised at Se : Rh 0.019 for 1 wt% Rh–ZrO_2 and at Se : Rh 0.032 for 3 wt% Rh–ZrO_2.

The activation energies (E_a) for the formation of ethane, propanal, and propanol on 1 wt% Rh–ZrO_2 catalyst were 60, 22, and 30 kJ mol^{-1}, respectively. On Se-modified catalyst (**2**) (Rh 1 wt%, Se : Rh 0.012), which gave almost maximum hydroformylation selectivity, E_a's were found to be 53, 0.9, and 36 kJ mol^{-1}, respectively. While a decrease in E_a for propanal formation was observed, the E_a for propanol increased slightly, contrary to the observation that propanol formation was promoted by Se addition. Temperature programmed desorption (t.p.d.) spectra for catalyst (**2**) (Rh 1 wt%, Se : Rh 0.01—0.07),[4] in the presence of H_2 in the temperature range 300—773 K, immediately after ethene hydroformylation at 453 K showed desorbed products pro-

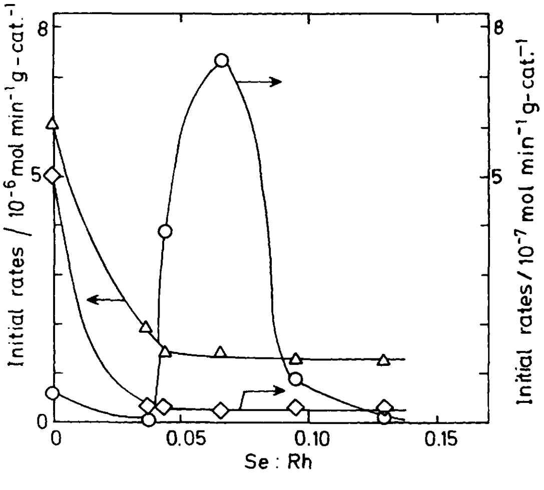

Figure 1. Catalytic activities of Se-modified catalysts (**1**) for ethene hydroformylation as a function of Se content; reaction temp. 453 K, total pressure 4.0 × 10^4 Pa; C_2H_4 : CO : H_2 1 : 1 : 1, Rh–ZrO_2 1 wt%; △ ethane, ◇ propanal, ○ propanol. Scales on the left and right vertical axes refer to the formation of ethane and of propanol and propanal, respectively, as indicated by arrows.

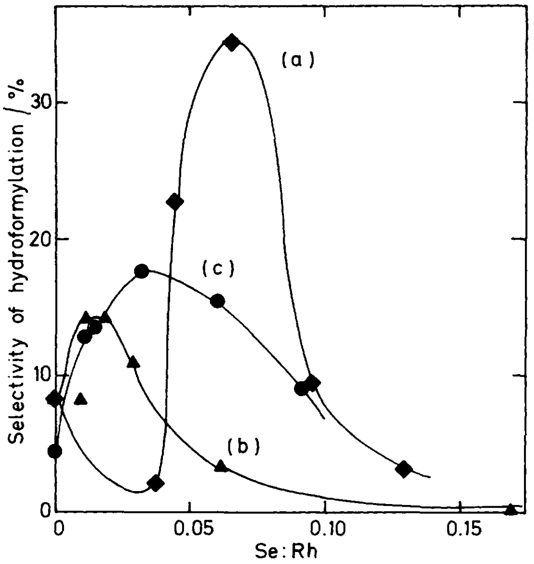

Figure 2. Selectivities of ethene hydroformylation on Se/Rh–ZrO_2 catalysts (**1**) and (**2**) as a function of Se content; (a) catalyst (**1**) (Rh 1 wt%), (◆), (b) catalyst (**2**) (Rh 1 wt%) (▲), (c) catalyst (**2**) (Rh 3 wt%) (●), reaction temp. 453 K; total pressure 4.0 × 10^4 Pa; C_2H_4 : CO : H_2 1 : 1 : 1.

panol, ethene, ethane, and CO. The desorption peak temperature and the peak area, which varied with Se : Rh ratio, suggested that intermediate propanoyl species (EtCO) were more stabilized on Se-modified Rh catalysts than on unpromoted Rh/ZrO_2, enabling them to evolve long enough for further hydrogenation to occur to produce propanol. The amount of the intermediate species was markedly reduced on the catalyst modified with more Se.

X-Ray photoelectron spectra (x.p.s.) showed that the binding energy of Se $3d_{5/2}$ is modified by increasing amounts of Se. It had a value of 53.2 eV for catalyst (**1**) and 53.1 eV for catalyst (**2**), indicating that the oxidation state of Se was 2−, independent of Se content in the range of Se : Rh 0.01—0.13, while Rh had 3d peaks corresponding to the metallic state[5] for both catalysts (**1**) and (**2**). H_2 adsorption decreased steadily as Se quantity increased,[6] eventually to almost zero. However, for CO adsorption the decrease was less marked and the more Se-modified surface still adsorbed CO, suggesting that CO molecules are adsorbed on or around Se–Rh ensembles more easily than H_2.[7]

The marked promoting effects of Se on the activity and selectivity of Rh–ZrO_2 catalysts for ethene hydroformylation may thus be ascribed to the preferable interaction of CO with Se^{2-} on Rh, the resulting promotion of CO insertion to C_2H_5, and the stabilization of intermediate propanoyl species leading to the formation of propanol by Se–Rh ensembles.

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