

Effect of Rh Dispersion on Vapor Phase and Pressurized Hydroformylation of Ethylene over Rh/SiO₂ Catalyst

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A significant Rh dispersion effect was observed on vapor phase and pressurized hydroformylation of ethylene over Rh/SiO₂ catalyst. Hydroformylation proceeds favorably over a high dispersed Rh/SiO₂ having Rh particle size below approximately 30 Å. This remarkable dispersion effect is attributed to the change of both surface Rh atom composition and electronic state of Rh particle on SiO₂. In addition, a striking structure sensitivity was also observed on the hydrogenation of ethylene to ethane as a by-product.

In the present paper, vapor phase and pressurized hydroformylation of ethylene over Rh/SiO₂ catalyst, as a model reaction of CO insertion step in C₂-oxygenates synthesis from synthesis gas, was studied to clarify the controlling factor of CO insertion reaction in terms of Rh dispersion.

All catalysts were prepared by impregnation method. Silica gel (Davison #57) was evacuated at 200 °C for 2 h. Then, it was impregnated with an aqueous solution of RhCl₃·3H₂O and was dried following H₂ reduction at 400 °C for 4 h. Hydroformylation reaction was conducted using a fix-bed flow micro reactor. After in situ reduction of catalyst with H₂ at 400 °C, mixed gas (C₂H₄:CO:H₂:Ar=30:40:20:10) was introduced at room temperature and then reaction was initiated. Products were analyzed by an on-line gas chromatograph. To determine the Rh dispersion of catalyst, H₂ and CO chemisorption and XRD measurement were applied.

Table 1. Reaction behavior of vapor phase hydroformylation over Rh/SiO₂

Catalyst	H ₂ adsorbed μmol (g-cat) ⁻¹	Rh particle ¹⁾ size Å	Yield/ μmol (min·g-cat) ⁻¹			(TOF)/ 10 ⁻² min ⁻¹	Oxo ³⁾ selec. %
			C ₂ H ₅ CHO	n-C ₃ H ₇ OH	C ₅ H ₉ CHO		
1wt%Rh/SiO ₂	25.0	(21) ²⁾	22.4(44.8)	0.2	2.6	42.9(85.8)	39
5wt%Rh/SiO ₂	102.7	30	55.4(26.9)	0.3	5.4	191.3(93.1)	26
5wt%Rh/SiO ₂	51.8 ⁴⁾	77	16.8(16.2)	0.1	0.9	56.5(54.5)	25
9wt%Rh/SiO ₂	138.8	39	33.0(11.9)	0.1	4.7	627.1(225.9)	6.4
10wt%Rh/SiO ₂	168.8	33	36.5(10.9)	0.1	4.4	629.6(186.6)	5.5
23wt%Rh/SiO ₂	50.0	154	7.2(7.2)	0.1	1.0	24.1(24.1)	28

Conditions; 180 °C, 20 kg/cm², 100 ml/min, C₂H₄:CO:H₂:Ar=30:40:20:10, Catalyst:1 g. Data were taken at 90 min later from initiation.

1): Estimated from XRD line broadening. 2): Estimated from H₂ chemisorption.

3): Oxo selectivity = (C₂H₅CHO + n-C₃H₇OH + C₅H₉CHO × 2) / (C₂H₆ + C₂H₅CHO + n-C₃H₇OH + C₅H₉CHO × 2).

4): CARIAC 50 (Fuji-Davison) was used as SiO₂ support.

Reaction behavior under the conditions of 180 °C, 20 kg/cm², 100 ml/min is shown in Table 1. Propionaldehyde, n-propanol, 2-methyl-2-pentene-1-al (C₅H₉CHO, aldol condensation product of propionaldehyde) and ethane were produced. It is obvious that oxo selectivity (see footnote of Table 1) as well as the yields of propionaldehyde and ethane formation is much dependent on Rh particle size of catalyst. Turnover frequencies of both propionaldehyde and ethane formation were plotted as a function of Rh particle size in Fig. 1. Turnover frequency of propionaldehyde formation increased abruptly at Rh particle size below 30 Å. On the other hand, turnover frequency of ethane formation has a maximum at Rh particle size around 40 Å. This structure sensitivity of ethylene hydrogenation is similar to that of cyclohexene hydrogenation over Ru/SiO₂ reported by Kitajima et al.¹⁾

It is well known that surface composition of metal particle changes with a decrease of Rh particle size. In the case of Rh particle composed of a fcc octahedron structure, the fraction of edge and corner Rh atom in total surface Rh atom increases dramatically at Rh particle size below 30 Å as shown in Fig. 2.²⁾ This trend is quite consistent with that of turnover frequency of propionaldehyde formation as shown in Fig. 1. This suggests that hydroformylation reaction proceeds favorably at the edge and corner Rh site. In addition, electronic state of Rh particle might be changed with decreasing Rh particle size. FT-IR observation showed a remarkable difference in wavenumber of adsorbed CO between a highly dispersed 1wt%-Rh/SiO₂ (Linear-CO=2065 cm⁻¹, Bridged-CO=1864 cm⁻¹) and a lowly dispersed 9wt%-Rh/SiO₂ (Linear-CO=2073 cm⁻¹, Bridged-CO=1916 cm⁻¹). This observation indicates indirectly that electronic state of Rh particle changes with decreasing Rh particle size. In conclusion, a marked dispersion effect was elucidated by the variation of surface structure and electronic state of Rh particle.

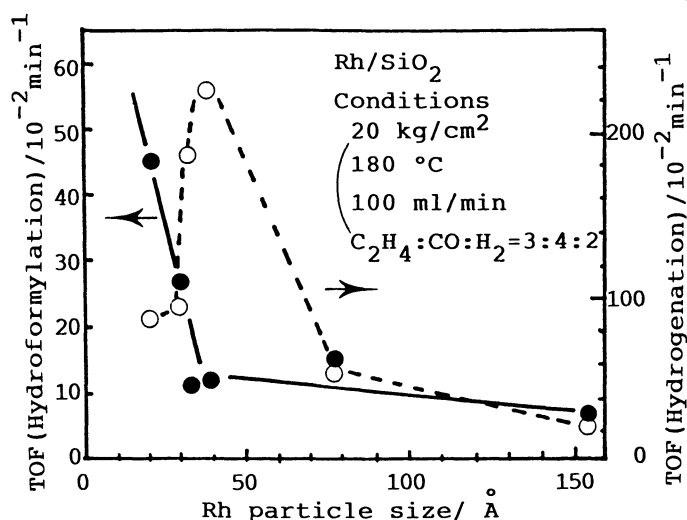


Fig. 1. Turnover frequencies as a function of Rh particle size.

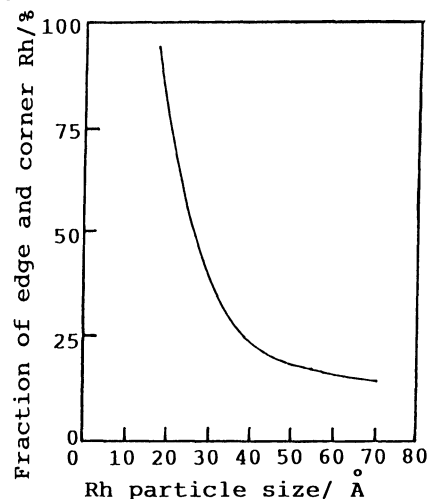


Fig. 2. Fraction of edge and corner Rh atom as a function of Rh particle size.²⁾

References

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(Received August 9, 1988)