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Preparation method for supported metal catalysts using w/o microemulsion: Study on immobilization conditions of metal particles by hydrolysis of alkoxide

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Abstract

It was previously found that the silica-supported rhodium catalyst prepared using water-in-oil microemulsion had rhodium particles partly, or wholly, embedded in silica. In this work, consequently, we investigated the effect of hydrolysis conditions of tetraethylorthosilicate, employed as the source of silica, on the atomic ratio of surface rhodium in contact with the gas phase, to total surface rhodium of nanoparticles. This ratio is denoted as R in this paper. R became higher when the catalyst was prepared under the following hydrolysis conditions: a shorter hydrolysis time and a smaller amount of tetraethylorthosilicate. On the other hand, R showed the minimum value when the water content in the preparation solution was 33 vol%. From these results, it is demonstrated that it was important to form silica as early as possible in hydrolysis of TEOS in order to increase R values. In addition, the effect of R on the catalytic behavior in CO hydrogenation was investigated. At R values below 30%, the turnover frequencies increased with a decrease in R . © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst preparation method; Microemulsion; Immobilization of nanoparticles

1. Introduction

Recently, nanoparticle synthesis has been studied by many researchers, but it is difficult to immobilize the nanoparticles on catalyst supports without large aggregates. We have studied a novel method for the preparation of supported metal catalysts using nanoparticles in water-in-oil (w/o) microemulsion, and have succeeded in preparing the supported catalyst having monodispersed metal particles of nanometer

size [1,2]. The catalysts prepared by the microemulsion method have exhibited a high activity for CO and CO₂ hydrogenation [3,4]. However, there was a problem that some of the nanoparticles in the catalyst were embedded in the support [2,5], since the support was formed from metal alkoxide in the microemulsion containing the nanoparticles synthesized beforehand. It would be desirable, for catalyst use, to increase the nanoparticles exposed on the catalyst surface.

In this work, we prepared the supported metal catalysts by the microemulsion method, and investigated the effects of immobilization conditions on the atomic ratio of surface rhodium, in contact with the

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gas phase, to total surface rhodium. Furthermore, the effect of this ratio on the catalytic behavior in CO hydrogenation was investigated.

2. Experimental

The cetyltrimethylammonium bromide (CTAB)/1-hexanol/RhCl₃aq. microemulsion of water-in-oil (w/o) type was used in the catalyst preparation. The CTAB concentration in 1-hexanol and the RhCl₃·3H₂O concentration in an aqueous solution (water-pool of microemulsion) were 0.25 and 0.38 mol/dm³, respectively. Complex nanoparticles composed of RhCl₃ and N₂H₄ were synthesized in the w/o microemulsion by directly adding hydrazine hydrate. Then, tetraethylorthosilicate (TEOS) as the silica source and

The size of rhodium particles of the catalysts was determined by X-ray diffraction (Rigaku RINT-2500) and CO chemisorption measurements. For the catalysts prepared by the ME method, the rhodium particle size calculated from CO uptake was always larger than that determined by XRD broadening technique [2,5]. This result suggested that some of the rhodium particles of the catalyst were partly or wholly embedded in the support, as illustrated in Fig. 1. Thus, it became important to determine the atomic ratio of surface rhodium in contact with the gas phase, to total surface rhodium. This ratio will be denoted as *R*. Assuming that the true average size of the rhodium particle can be determined by XRD measurement and that one CO molecule adsorbs on one rhodium atom exposed to the gas phase, the *R* value was calculated by the following equation:

$$R = \frac{\text{mole of CO chemisorbed on rhodium}}{\text{mole of total surface rhodium calculated from the average rhodium size}} \quad (1)$$

a diluted ammonium solution were charged into the w/o microemulsion, and the hydrolysis and polycondensation of TEOS were performed at 5° or 50°C, and consequently, silica gel containing the Rh–N₂H₄ nanoparticles was precipitated. After being washed with ethanol and dried in a desiccator, the precipitate was calcined in flowing air at 500°C for 2 h to remove the surfactant. It was then reduced in flowing hydrogen at 450°C for 2 h. This catalyst preparation method will be denoted as ME method.

The CO hydrogenation was carried out in a fixed-bed reactor at 4 MPa using 1 g of catalysts. The catalyst was also reduced in situ in flowing hydrogen at 450°C for 2 h prior to reaction. The H₂/CO/Ar mixture gas of the composition of 60/30/10 was passed over the catalyst, and the products were analyzed with on-line gas chromatographs (Shimadzu GC-4BPT, GC-7BPT, GC-8A). Ar, CH₄, CO and CO₂ were separated in a 3-m packed column containing active carbon. Hydrocarbons and oxygenated compounds

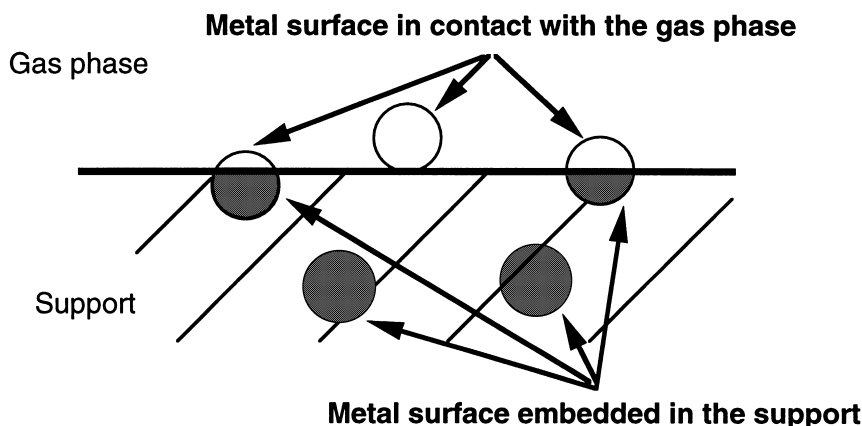


Fig. 1. Schematic illustration of metal particles in the support.

were separated in a 3 m packed column (VZ-10) and in a 6 m packed column (PEG1500), respectively.

3. Results and discussion

In this work, the nanoparticles of Rh–N₂H₄ complex synthesized in the microemulsion were immobilized in-situ onto the silica support formed by hydrolysis and polycondensation of TEOS. The location of the immobilized nanoparticles in the support was considered to be dependent on hydrolysis conditions of TEOS. Thus, the effects of hydrolysis conditions of TEOS on *R* were investigated. The average size of rhodium particles synthesized was always kept within the range of 4.5 to 6.7 to neglect the size effects.

3.1. Effect of hydrolysis time

Fig. 2 shows the changes in *R* and silica yield from TEOS when hydrolysis time was varied. Here, the silica yield means the ratio of the weight of silica actually obtained to the weight corresponding to the amount of TEOS charged. The water content and the amount of TEOS charged were 30% and 50 g, respectively. As can be seen from Fig. 2, the *R* value decreased as the hydrolysis time increased to 30 min and, thereafter, showed a constant value. On

the contrary, the silica yield increased with the hydrolysis time up to 30 min, after which it attained a constant value, ≈90%, for hydrolysis times >30 min. By inductive coupled plasma spectroscopy, a small amount of rhodium (<0.1% initial amount of rhodium) was detected in a filtrate even after hydrolysis time as short as 10 min, which means that the immobilization of the nanoparticles was completed over a short time.

These results indicate that the Rh–N₂H₄ nanoparticles were almost immobilized onto silica in hydrolysis time <10 min and that the surface of immobilized nanoparticles was covered with silica formed after the immobilization was over, as illustrated in Fig. 3. Thus, it can be seen that the decrease of *R* values continued until the silica formation was completed.

The shortening of the hydrolysis time for improving *R*, as can be seen from Fig. 2, resulted in the increase in rhodium contents in the catalyst since silica yield was reduced. Thus, it also became important to improve *R* at a constant rhodium content, that is, at a constant silica yield. The *R* value will become higher when less silica is formed after the immobilization of the nanoparticles was over. Accordingly, it is important for increasing *R* value at a constant silica yield to form silica as early as possible in hydrolysis of TEOS.

3.2. Effect of water content

The rate of silica formation from TEOS usually depends on water content and TEOS concentration in hydrolysis. Thus, the effect of water content and TEOS concentration on *R* was investigated. The *R* value and silica yield of the catalysts prepared at various water contents were plotted against the water content in Fig. 4. Here, the hydrolysis temperature, hydrolysis time and amount of TEOS were 50°C, 5 min, and 50 g, respectively. As can be seen from Fig. 4, the silica yield increased monotonously with increasing water content, while the *R* value showed the minimum value at the water content of 33%. The decrease in *R* with water contents in the range below 33% can be elucidated in terms of the increase in the silica yield, as can be seen from the *R* change at hydrolysis time in Fig. 3. On the other hand, the increase in *R* at water contents >33% is attributed to the increase in the amount of silica formed at the initial stage of hydrolysis, because the increase in

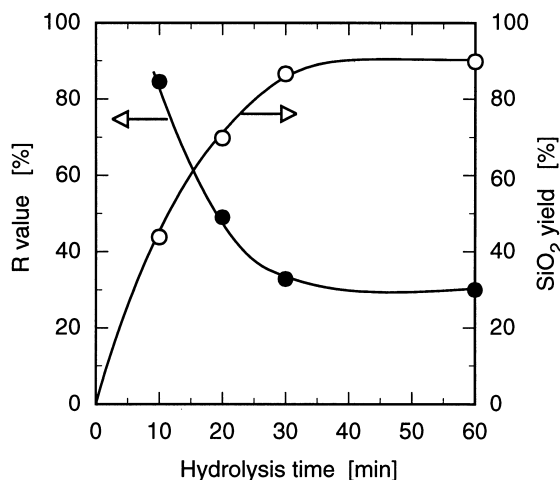


Fig. 2. Change in *R* with hydrolysis time. Hydrolysis conditions: temperature 50°C; water content 40%; and the amount of TEOS charged 50 g.

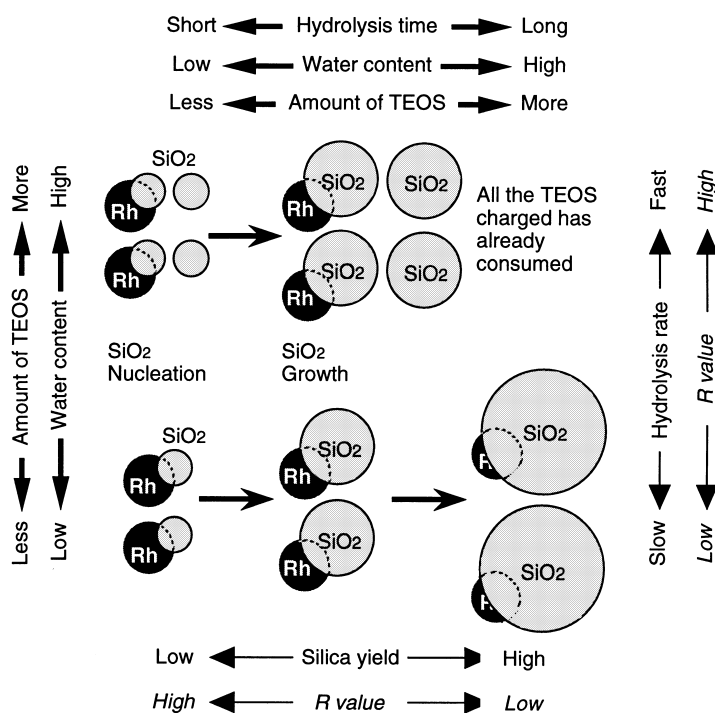


Fig. 3. Illustrated scheme for the change in R value with silica formation.

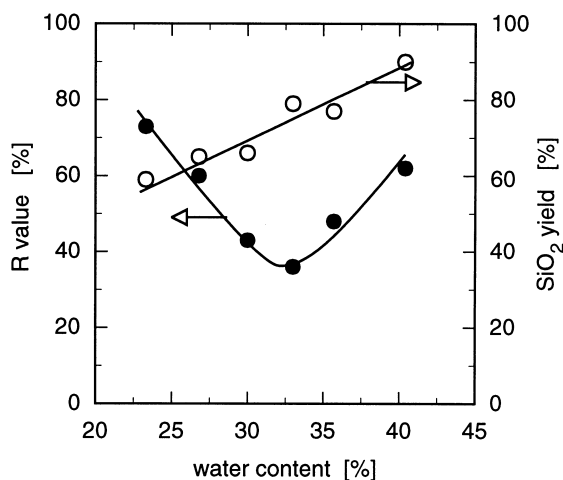


Fig. 4. Change in R with water content during the hydrolysis of TEOS. Hydrolysis conditions: temperature 50°C; hydrolysis time 5 min; and the amount of TEOS charged 50 g.

water content promotes hydrolysis of TEOS and, furthermore, promotes the nucleation of silica particles [6–8], as illustrated in Fig. 3.

Table 1

Effect of the amount of TEOS charged on the R value CTAB/1-hexanol microemulsion system. Hydrolysis conditions: temperature 5°C; hydrolysis time 30 min; and water content 40%

TEOS ^a (g)	Silica ^b (g)	Rh particle size (nm)	R (%)
20	5.1	5.8	41
30	7.4	5.5	33
40	9.3	6.7	36
50	10.8	5.5	29

^a Weight to TEOS charged into emulsion solution of 80 cm³.

^b Weight of silica formed by hydrolysis of TEOS.

3.3. Effect of the amount of TEOS charged

The effect of the amount of TEOS charged on R was also investigated. Table 1 shows the R value of the catalysts prepared from various amounts of TEOS charged. Here, the hydrolysis was performed at a water content of 40% at 5°C for 30 min. The R value gradually decreased with increasing amounts of TEOS. Hydrolysis of TEOS was promoted by

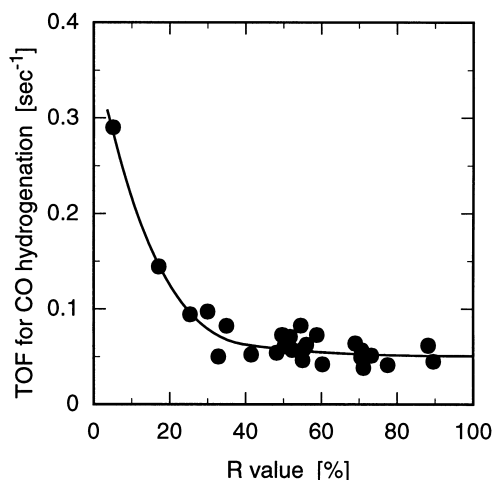


Fig. 5. Effect of R on turnover frequency in CO hydrogenation at 260°C.

increasing the concentration of TEOS as well as the water content. However, the effect of the amount of TEOS on R was not the same as that of the water content. This might be due to the increase in the amount of silica formed after the immobilization of the nanoparticles, although the amount of silica formed at the initial stage of hydrolysis increased as the hydrolysis rate was raised by increasing the amount of TEOS (see Fig. 3).

3.4. Effect of R on catalytic behavior in CO hydrogenation

The effect of R on the catalytic behavior in CO hydrogenation was examined using silica-supported rhodium catalysts with different R values. The catalysts had rhodium particles within the size range of 4.5 to 6.0 nm, because it has been found that the change within this range of rhodium particle size did not greatly affect the catalytic behavior in CO hydrogenation [9,10]. Figs. 5 and 6 show the effect of R on the turnover frequency (TOF) and product selectivity in CO hydrogenation at 260°C, respectively. TOF was determined on the basis of the amount of CO uptake. The products detected were oxygenated compounds (C_1 – C_3 alcohols, C_2 – C_3 aldehydes, methylacetate and ethylacetate), C_1 – C_4 hydrocarbons and CO_2 . As can be seen from Figs. 5 and 6, R did not affect both the TOF and product selectivity at R values >30%. This

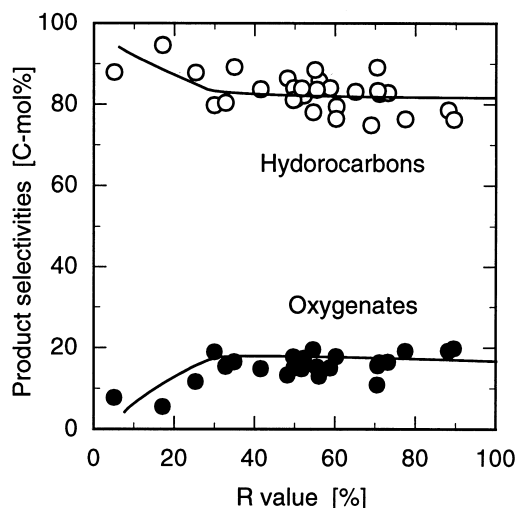


Fig. 6. Effect of R on product selectivity in CO hydrogenation at 260°C.

result indicates that the numbers of the active sites for the formation reactions of hydrocarbons and oxygenated compounds increased in proportion to R , which might be due to the random orientation of the rhodium particles in the catalyst. At R values <30%, however, the TOF and selectivity to hydrocarbons increased with a decrease in R , while the selectivity to oxygenated compounds decreased. These results might be due to the specificity of the rhodium surface in contact with the gas phase, which means that the specific rhodium surface was little covered by silica even at a low R value.

4. Conclusion

The silica-supported rhodium catalyst prepared using water-in-oil microemulsion had rhodium particles partly or wholly embedded in the silica support. In this work, the atomic ratio ($=R$) of surface rhodium in contact with the gas phase to total surface rhodium was investigated under various conditions for the catalyst preparation.

1. The R value became higher when the catalyst was prepared in a shorter hydrolysis time. At a constant hydrolysis time, the R value showed the minimum when the catalyst was prepared at a water content of 33 vol%, and the R value

increased with decreasing amounts of TEOS. From these results, it was found that it was important, in order to increase R values, to form silica as early as possible in hydrolysis of TEOS.

2. At R values <30%, the turnover frequencies increased with a decrease in R . However, the TOFs and product selectivities were not affected by R values >30%.

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