Short Articles
Bull. Chem. Soc. Jpn. Vol. 82, No. 5, 627–629 (2009) 627

Bimetallic Effect of Silica-Supported Pt–Ru Catalyst for Hydrogenation of Aromatic Hydrocarbons

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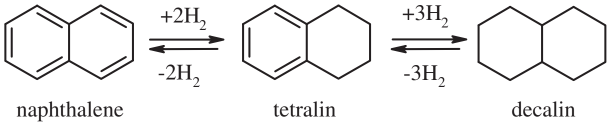
A drastic synergistic effect has been found for the liquid-phase hydrogenation of aromatic hydrocarbons by the combination of Pt and Ru. The surface composition of Pt–Ru/SiO_2 was estimated using O_2–CO titration, and it was found that Pt was enriched on the surface of the bimetallic particles. The surface composition of the most active catalyst was nearly 50% Pt, suggesting that the Pt–Ru ensemble of a 1-to-1 ratio was active for the hydrogenation reaction.

The organic chemical hydride method is expected to be an effective method for the storage and transportation of hydrogen using the hydrogenation–dehydrogenation reactions of cyclic hydrocarbons (Scheme 1).[1–6] This method is advantageous because of its high storage density as well as safety in handling. Okada et al.[1] reported a Pt-based dehydrogenation catalyst having high and stable activity.

The hydrogenation of aromatic hydrocarbons has been studied for a long time. It is reported that Rh is the most active metallic catalyst for the hydrogenation.[5–7] However, Rh is one of the most expensive noble metals and highly active catalysts using different elements are required. In this paper, we report supported Pt–Ru bimetallic catalysts which show a much higher activity than Rh, and discuss the catalyst structure and mechanism of the synergistic effects.

Experimental

The Pt–Ru/SiO_2 catalyst was prepared by the co-impregnation of silica (Silbead, Mizusawa Chem. Co., $S_{(BET)} = 330\,m^2\,g^{-1}$) with a mixed solution of metal precursors. $H_2PtCl_6 \cdot 6H_2O$ (Kanto Chem. Co.) was used as the Pt precursor, and $RuCl_3 \cdot nH_2O$ (Wako Pure Chem. Co.) was used as the Ru precursor. The slurry was dried and kept at 130 °C overnight. It was then reduced in flowing hydrogen at 573 K for 5 h. While changing the atomic ratio of Pt/Ru, the amount of total metal loading (Pt + Ru) was kept constant; i.e., 0.2 mmol (g-SiO_2)$^{-1}$.



Scheme 1.

The number of metal atoms exposed to the surface was determined by O_2–CO titration at room temperature using a pulse adsorption apparatus. The average surface composition of the metal particles was obtained by means of this technique. The sample was prereduced in H_2 at 300 °C for 1 h, and then evacuated at 300 °C for 1 h. The details of the O_2–CO titration have been previously reported in the literature.[8–10] The internal composition was calculated by the difference of total composition and surface composition.

The liquid-phase hydrogenation of naphthalene and tetralin was carried out using a stainless steel autoclave equipped with a mechanical stirrer and thermocouple. Because naphthalene (Merck Ltd.) contained benzothiophene, it was purified before use by hydrogen treatment using a Ni catalyst. 7.8 mmol of naphthalene was dissolved in 40 mL (164 mmol) of tridecane. Tetralin (7.2–21.6 mmol) was dissolved in 40 mL of tridecane. Then, 0.05–0.5 g of the catalyst was prereduced in flowing H_2 at 300 °C for 1 h. The reaction was carried out at 0 or 30 °C for 30–180 min at the initial H_2 pressure of 0.5–1.5 MPa with agitation at 1000 rpm. The reaction products were analyzed by gas chromatography (Shimadzu GC-18A, DB-17 capillary column). In the case of the naphthalene hydrogenation, only tetralin and decalin were found as the products, with the tetralin selectivity higher than 95%. In the case of tetralin, the hydrogenation produced only decalin. The rate of reaction was obtained by initial rate, keeping the conversion low enough to use this approximation.

Results and Discussion

The surface composition of 0.2Pt–Ru/SiO_2 was studied by O_2–CO titration. The results are shown in Table 1. The catalyst of the composition Pt/Ru = 20/80 suggested a nearly equal surface composition to the total ratio, indicating neither Pt nor Ru was enriched on the surface of the bimetallic particles. On the other hand, catalysts containing a 40% or higher amount of Pt suggested a higher concentration of Pt on the surface, indicating the surface enrichment of Pt.

Such results are in good agreement with the literature data.[8–10] Because Pt has a larger atomic size and lower surface energy than Ru, it is natural that Pt is enriched on the surface of Pt–Ru particles.

The hydrogenation of naphthalene was examined over Pt–Ru/SiO_2 catalysts. The results are shown in Figure 1. At the stated reaction conditions, Ru/SiO_2 was almost inactive and Pt/SiO_2 was mildly active. The mechanical mixture of Pt/SiO_2

Table 1. The Surface Composition and Internal Composition of Pt–Ru/SiO_2 Catalysts

Catalyst comp. Pt/Ru	Dispersion /%	Number of surface atoms/μmol g^{-1}			Surface comp. Pt/Ru (%/%)	Internal comp. Pt/Ru (%/%)
		Pt	Ru	Total		
100/0	35.0	67.4	0	67.4	100/0	100/0
80/20	39.5	73.5	2.7	76.3	96.4/3.6	69.3/30.7
60/40	34.7	56.4	10.8	67.2	84.0/16.0	47.3/52.7
40/60	31.9	36.0	26.1	62.1	57.9/42.1	31.6/68.4
20/80	21.6	7.5	34.6	42.1	17.8/82.2	20.6/79.4
0/100	16.1	0	31.6	31.6	0/100	0/100

Published on the web May 13, 2009; doi:10.1246/bcsj.82.627

and Ru/SiO_2 produced intermediate activity. In clear contrast, all the bimetallic catalysts suggested a much higher activity than Pt/SiO_2. The optimal surface composition was nearly 50% Pt, and this catalyst suggested a 25-fold higher activity than the mechanically mixed catalyst. The TOF (based on $Pt_{(s)} + Ru_{(s)}$) of the hydrogenation was also significantly improved. Thus we concluded that Pt and Ru had a clear synergistic effect by forming an ensemble of Pt–Ru.

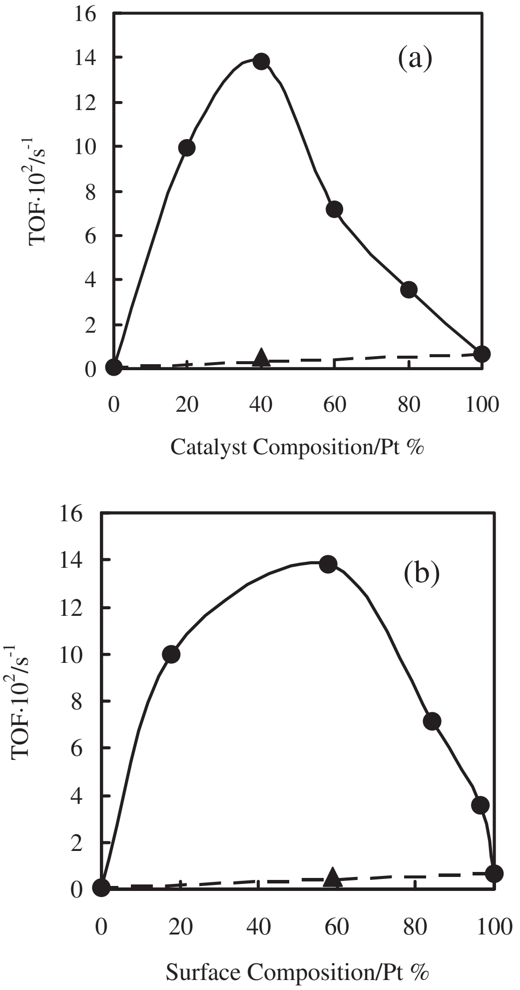


Figure 1. Hydrogenation of naphthalene over $Pt–Ru/SiO_2$ catalysts. (a) TOF vs. catalyst composition, (b) TOF vs. surface composition. ●: $Pt–Ru/SiO_2$, ▲: mechanical mixture of Pt/SiO_2 and Ru/SiO_2. Reaction temperature: 0 °C, reaction time: 1–3 h, $P_{H_2} = 1.0$ MPa, catalyst weight: 0.05–0.4 g.

The experimental results of the tetralin hydrogenation are shown in Table 2. The synergistic effect of Pt and Ru was also found in the case of the tetralin hydrogenation. The most active catalyst was $0.2Pt_{40}–Ru_{60}/SiO_2$. Because the surface composition of this catalyst is 58% Pt, the ensemble of Pt–Ru has a high hydrogenation activity. The reaction product, decalin, contained cis and trans isomers. Although the trans isomer is thermodynamically advantageous, the cis isomer prevailed in the reaction products. Ru/SiO_2 had a higher selectivity toward the *cis*-decalin than Pt/SiO_2, as reported in the literature.[6] The bimetallic Pt–Ru catalysts suggested a selectivity similar to Pt/SiO_2.

It is reported[5,6,11,12] that *cis*-decalin is formed when $\Delta^{9,10}$-octalin is formed as an intermediate and the intermediate is strongly adsorbed on the catalyst surface. On the other hand, *trans*-decalin is formed when $\Delta^{1,9}$-octalin is formed as an intermediate and the intermediate rolls over on the surface due to weak adsorption. In case of our Pt–Ru bimetallic catalysts, $\Delta^{1,9}$-octalin is formed and it is weakly adsorbed on the surface, similar to Pt/SiO_2.

The reaction rate of tetralin hydrogenation was measured using the initial rate, and the reaction orders of tetralin and hydrogen were determined. As shown in Figure 2, the reaction rate was almost independent of the tetralin concentration over Pt, Ru, and the Pt–Ru bimetallic catalyst. Figure 3 shows that the reaction was positively dependent on the H_2 pressure. However, the reaction order with respect to H_2 of the bimetallic Pt–Ru catalyst was an intermediate value between those of Pt and Ru. Thus we could not find any drastic changes in the parameters of the Langmuir–Hinshelwood mechanism caused by the formation of the Pt–Ru pair. It seems that the presence of Ru significantly accelerated the activity of Pt sites.

The activity of Rh/SiO_2 was measured and compared to $Pt–Ru/SiO_2$ using naphthalene and tetralin as the reactants, because Rh was the most active supported metal catalyst for the naphthalene hydrogenation.[7] As shown in Figure 4, the $Pt–Ru/SiO_2$ catalyst suggested a 5-fold higher activity than Rh/SiO_2 for the hydrogenation of naphthalene. The activity of the $Pt–Ru/SiO_2$ catalyst was 2.5-times higher than that of the Rh/SiO_2 catalyst for the tetralin hydrogenation.

In this way, the combination of Pt and Ru suggested an excellent hydrogenation activity, superior to Rh which is an expensive metal. The surface ensemble of Pt–Ru seems to remarkably increase the activity of Pt. In the field of fuel cell

Table 2. Hydrogenation Rate of Tetralin ($r_{tetralin}$) and Selectivity of Decalin over $Pt–Ru/SiO_2$ Catalysts[a)]

Catalyst	$r_{tetralin}$ /mmol h^{-1} g^{-1}	TOF·10^2 /s^{-1}	Selectivity/%		cis/trans
			cis-Decalin	*trans*-Decalin	
$0.2Pt/SiO_2$	3.4	1.31	79.9	20.1	4.0
$0.2Pt_{80}–Ru_{20}/SiO_2$	12.7	4.63	77.6	22.4	3.5
$0.2Pt_{60}–Ru_{40}/SiO_2$	19.3	7.96	79.1	20.9	3.8
$0.2Pt_{40}–Ru_{60}/SiO_2$	21.1	9.83	81.2	18.8	4.3
$0.2Pt_{20}–Ru_{80}/SiO_2$	8.2	5.45	85.7	14.3	6.0
$0.2Ru/SiO_2$	1.1	0.91	96.5	3.5	27.6

a) Reaction conditions: temperature, 30 °C; reaction time, 30–60 min; catalyst weight, 0.05–0.4 g; $P_{H_2} = 1.0$ MPa.

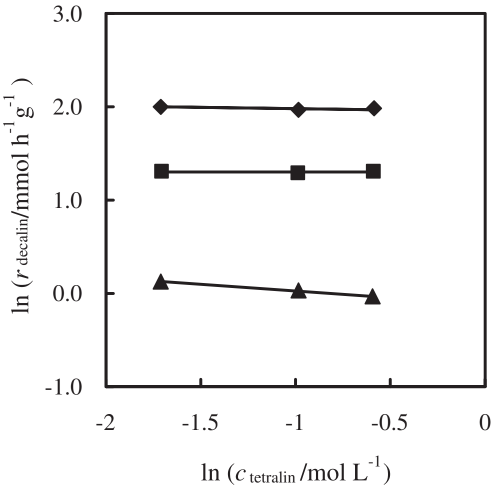


Figure 2. Effect of the initial reactant concentration (c_{tetralin}) on hydrogenation of tetralin over Pt, Ru, and Pt–Ru/SiO$_2$ catalysts. Reaction temperature: 30 °C, reaction time: 1 h, $P_{H_2} = 1.0$ MPa, catalyst weight: 0.1–0.4 g. ◆: 0.1Pt$_{40}$–Ru$_{60}$/SiO$_2$; $y = -0.03x - 1.95$, ■: 0.2Pt/SiO$_2$; $y = 0.00x + 1.29$, ▲: 0.2Ru/SiO$_2$; $y = -0.14x - 0.11$.

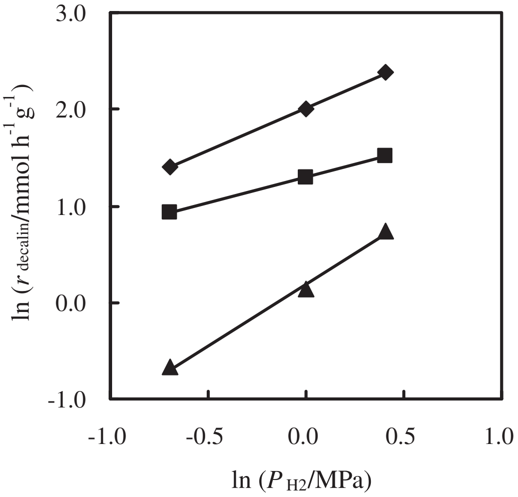


Figure 3. Effect of initial hydrogen pressure (P_{H_2}) on hydrogenation of tetralin over Pt, Ru, and Pt–Ru/SiO$_2$ catalysts. Reaction temperature: 30 °C, reaction time: 1 h, catalyst weight: 0.1–0.4 g, initial tetralin concentration: 0.18 mol L^{-1}, $P_{H_2} = 0.5$, 1.0, and 1.5 MPa. ◆: 0.1Pt$_{40}$–Ru$_{60}$/SiO$_2$; $y = 0.88x + 2.02$, ■: 0.2Pt/SiO$_2$; $y = 0.53x + 1.30$, ▲: 0.2Ru/SiO$_2$; $y = 1.27x + 0.19$.

electrodes, Watanabe and Motoo[13] found that the bifunctional mechanism improved the activity of the Pt–Ru bimetallic electrode. In our case however, the reaction circumstance is quite different from the fuel cell electrode and a similar effect is not expected. Therefore, our results suggest another kind of bimetallic effect between Pt and Ru.

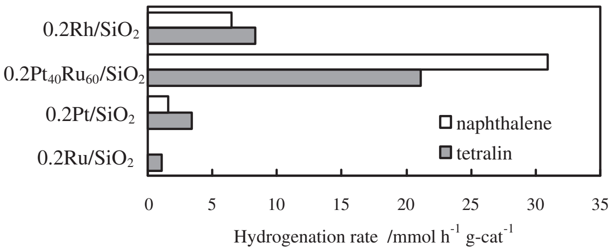


Figure 4. Reaction rate for hydrogenation of naphthalene and tetralin over Rh/SiO$_2$, Pt–Ru/SiO$_2$, Pt/SiO$_2$, and Ru/SiO$_2$ catalysts. Reaction temperature: 30 °C, reaction time: 1 h, $P_{H_2} = 1.0$ MPa, catalyst weight: 0.05–0.1 g.

Conclusion

Silica-supported Pt–Ru catalysts formed bimetallic particles in which Pt was enriched on the surface. A remarkable improvement in the activity was found for the hydrogenation of aromatic hydrocarbons as a result of a bimetallic effect. Because the surface composition of the most active catalyst was 50% Pt, the 1/1 ratio ensemble of Pt–Ru seemed effective for the reaction. The activity of Pt–Ru/SiO$_2$ was much higher than Rh/SiO$_2$ which has been believed to be the most active metal. We are expecting this catalyst to be available for the organic hydride method.

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