

Effects of Removing Residual Chlorine on the Hydrogenation of Aromatic Hydrocarbons over Supported Ru Catalysts

Takashi Nakamura, Masa-aki Ohshima, Hideki Kurokawa, and Hiroshi Miura*

Graduate School of Science and Engineering, Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570

(Received September 17, 2009; CL-090841; E-mail: hmiura@mail.saitama-u.ac.jp)

Hydrogenation activity of aromatic hydrocarbons was remarkably increased when the residual chlorine on Ru/Al₂O₃ and Ru/SiO₂ was removed by washing. On the basis of FT-IR spectra in the CO region, a site active for hydrogenation reactions was created by removal of the residual chlorine.

Supported Ru catalysts have been widely studied because they can be used in a variety of practical applications.¹ The effect of residual chlorine has been reported. For instance, Narita et al.^{2,3} have reported that the adsorption of CO and H₂ was inhibited by residual Cl, and Mazziari et al.⁴ have reported that residual Cl inhibits the reduction of Ru in Ru/Al₂O₃. In this study, we tried to completely remove Cl from Ru/Al₂O₃ and Ru/SiO₂ and found a remarkable enhancement in the hydrogenation activity of naphthalene and toluene.

The catalysts 2 wt % Ru/Al₂O₃ and 2 wt % Ru/SiO₂ were prepared by using an impregnation method with RuCl₃·*n*H₂O (*n* = 2.2, Wako Pure Chem.). Al₂O₃ (Neobead GB-45, Mizusawa Industrial Chem.) and SiO₂ (Silbead, Mizusawa Industrial Chem.) were used as supports. The support granules (<100 mesh) were immersed in a solution of RuCl₃ and water was removed under vacuum. The granules were then kept at 403 K in air overnight. The catalysts were reduced in flowing hydrogen at 673 K for 5 h and then washed with hot deionized water or aqueous ammonia (0.01 mol L⁻¹) using a volume of 500 mL g-cat⁻¹.

Hydrogenation of naphthalene and toluene was performed in a 100-mL stainless steel autoclave equipped with a stirrer. Because the naphthalene (Kanto Chem.) contained a considerable amount of benzothiophene as an impurity, it was purified using a Ni catalyst (C-28, Süd Chemie Catalyst) in 0.1 MPa of hydrogen at 373 K. The purified naphthalene (1.00 g, 7.8 mmol) or toluene (0.719 g, 7.8 mmol) was dissolved in *n*-tridecane (40 mL) as a solvent. The catalyst (0.1–0.2 g) was reduced at 673 K for 1 h in a Pyrex tube and then transferred to the autoclave for the hydrogenation reaction. Hydrogenation reactions were carried out in the temperature range of 273–303 K for 1 h with an initial H₂ pressure of 0.98 MPa and agitation at 1000 rpm. The reaction products were analyzed using FID gas chromatography. The amount of metal atoms exposed was estimated by analyzing the amount of adsorbed CO using a pulse adsorption apparatus (BP-1, Ohkura Riken). The amounts of Ru loading and remaining Cl were determined by using X-ray fluorescence (XRF). FT-IR spectra were acquired on a Jasco FT-IR-350 at room temperature after exposing the catalysts to CO (20 Torr) at room temperature for 20 min and then evacuating at room temperature for 30 min.

The amounts of Ru loading, remaining Cl, and adsorbed CO before and after washing are listed in Table 1. Before washing, Ru/Al₂O₃ contained about five times more Cl than Ru/SiO₂ did,

Table 1. Effect of catalyst washing on the content of Ru and Cl and the amount of adsorbed CO on Ru/Al₂O₃ and Ru/SiO₂

Catalyst	Washed with	Ru /wt %	Cl /wt %	CO adsorption /μmol g-cat ⁻¹
Ru/Al ₂ O ₃	—	2.3	1.4	42
Ru/Al ₂ O ₃	Pure water (1) ^a	1.9	0.6	46
Ru/Al ₂ O ₃	Pure water (2)	1.9	0.3	35
Ru/Al ₂ O ₃	Pure water (3)	1.9	0.2	29
Ru/Al ₂ O ₃	Aqueous ammonia	2.2	0.02	40
Ru/SiO ₂	—	2.3	0.3	49
Ru/SiO ₂	Aqueous ammonia	2.6	<0.01	83

^aThe number of treatment times.

suggesting that the alumina support had an affinity toward Cl, which is in agreement with the literature.^{3,5} Washing with deionized water gradually lowered the amount of Cl. However, a considerable amount of Cl remained after washing three times, and the amount of adsorbed CO decreased. In contrast, the amount of Cl decreased dramatically by washing with aqueous ammonia without any reduction in the Ru loading and adsorbed CO. After washing with aqueous ammonia, both Ru/Al₂O₃ and Ru/SiO₂ had almost no Cl. In the case of Ru/SiO₂, the amount of adsorbed CO increased significantly after washing with aqueous ammonia because the residual Cl in Ru/SiO₂ effectively covered the Ru surface, which is in agreement with previously reported results.² As described later, the adsorbed CO on Ru/Al₂O₃ contained multiple bonded CO, such as Ru^{*m*+}(CO)_{*x*}, and this adsorbed species disappeared after washing with aqueous ammonia. Since the adsorption stoichiometry changed after removing the residual Cl, the amount of adsorbed CO did not increase after washing the Ru/Al₂O₃ catalyst with aqueous ammonia. However Ru particle growth should be also considered.

Catalytic activities for naphthalene and toluene hydrogenations were determined, and the results are shown in Table 2. Before washing, Ru/Al₂O₃ showed poor activity for hydrogenation, but the activity increased remarkably as Cl was washed away. Cl-free Ru/Al₂O₃ washed with aqueous ammonia showed the highest activity. A similar increase in the naphthalene hydrogenation activity was observed when Ru/SiO₂ was washed with aqueous ammonia. Toluene hydrogenation was also tried over Ru/Al₂O₃ and Ru/SiO₂. A remarkable increase in the toluene hydrogenation activity was observed after removing the residual Cl from both supported Ru catalysts.

The effects of removing the residual Cl were studied by analyzing the spectra of adsorbed CO using FT-IR at room temperature. As shown in Figure 1, three peaks were observed at around 2140 cm⁻¹ (HF1), 2080 cm⁻¹ (HF2), and 2040–2020 cm⁻¹ (LF). Peaks HF1 and HF2 were attributed to Ru^{*m*+}(CO)_{*x*} (*x* = 2 and 3), and peak LF was attributed to linear CO on a surface Ru⁰ site.⁶ LF was deconvoluted into peaks at

Table 2. Hydrogenation of aromatic hydrocarbons over Ru/Al₂O₃ and Ru/SiO₂ after washing

Catalys	Washed with	Conversion/%
Naphthalene hydrogenation ^a		
Ru/Al ₂ O ₃	—	0.9
Ru/Al ₂ O ₃	Pure water (1)	11.5
Ru/Al ₂ O ₃	Pure water (2)	25.4
Ru/Al ₂ O ₃	Pure water (3)	31.3
Ru/Al ₂ O ₃	Aqueous ammonia	72.6
Ru/SiO ₂	—	2.1
Ru/SiO ₂	Aqueous ammonia	64.8
Toluene hydrogenation ^b		
Ru/Al ₂ O ₃	—	0.0
Ru/Al ₂ O ₃	Aqueous ammonia	39.7
Ru/SiO ₂	—	0.5
Ru/SiO ₂	Aqueous ammonia	50.2

^aReaction conditions: catalyst weight 0.1 g, initial H₂ pressure 0.98 MPa, reaction temperature 303 K, reaction time 1 h.

^bMass of the catalyst 0.2 g, initial H₂ pressure 0.98 MPa, reaction temperature 273 K, reaction time 1 h.

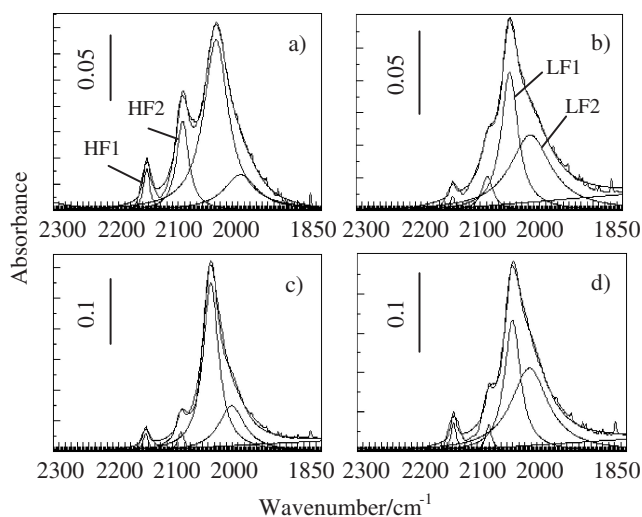


Figure 1. FT-IR spectra of adsorbed CO on supported Ru catalysts at room temperature. a) Unwashed Ru/Al₂O₃ containing 1.4 wt % of Cl, b) Ru/Al₂O₃ containing 0.02 wt % of Cl after washing with aqueous ammonia, c) unwashed Ru/SiO₂ containing 0.3 wt % of Cl, and d) Ru/SiO₂ containing less than 0.01 wt % of Cl after washing with aqueous ammonia.

2020 cm⁻¹ (LF1) and 1990 cm⁻¹ (LF2). LF1 and LF2 seemed to be related to linear CO adsorbed on Ru⁰ at differently coordinatively unsaturated sites.⁷ LF2 was related to CO on the site of higher degree of coordinative unsaturation.^{7,8}

On unwashed Ru/Al₂O₃, HF1 and HF2 were clearly observed, suggesting that the residual Cl retarded the reduction of surface Ru atoms. After washing with aqueous ammonia, the

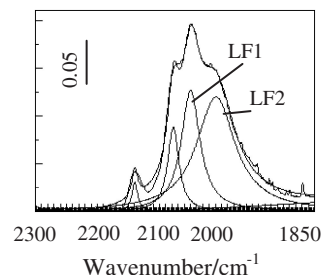


Figure 2. FT-IR spectrum of adsorbed CO on a supported Ru catalyst prepared from Ru(C₅H₇O₂)₃.

intensities of HF1 and HF2 decreased significantly. On the other hand, LF2 significantly increased in intensity after washing, indicating that the residual Cl blocked the adsorption of CO on the sites corresponding to LF2.

In the spectra of Ru/SiO₂, HF1 and HF2 were small even before washing the catalyst. This is because Ru/SiO₂ contained a smaller amount of Cl as compared with that of Ru/Al₂O₃. However, the intensity of LF2 was different between unwashed and washed samples. Removal of Cl increased LF2 significantly.

Cl-free Ru/Al₂O₃ was prepared using Ru(C₅H₇O₂)₃ as a precursor. The Ru catalyst was highly dispersed on the support (amount of CO adsorption, 232 μmol g-cat⁻¹). This catalyst showed high activity for naphthalene hydrogenation, which was comparable with that of Ru/Al₂O₃ washed with aqueous ammonia. In the CO region of the FT-IR spectrum, four peaks, i.e., HF1, HF2, LF1, and LF2, were observed, as shown in Figure 2. It was clear that the sites corresponding to LF2 were prevalent on this catalyst. Since the Cl-free Ru catalysts showed intense LF2 peaks, the residual Cl in the Ru catalysts preferentially block the formation of the sites corresponding to LF2.

Residual Cl blocked the LF2 site. By washing the catalyst, we were able to remove all of residual Cl, and the catalytic activities for hydrogenation of naphthalene and toluene increased remarkably. In other words, the site corresponding to LF2 seems to be active for the hydrogenation reaction of aromatic hydrocarbons. However, only qualitative relation was found between hydrogenation activity and the LF2 peak area.

References

- Z. You, K. Inazu, K. Aika, T. Baba, *J. Catal.* **2007**, *251*, 321.
- T. Narita, H. Miura, K. Sugiyama, T. Matsuda, R. D. Gonzalez, *J. Catal.* **1987**, *103*, 492.
- T. Narita, H. Miura, M. Ohira, H. Hondou, K. Sugiyama, T. Matsuda, R. D. Gonzalez, *Appl. Catal.* **1987**, *32*, 185.
- V. Mazzieri, F. C. Pascual, A. Arcoya, P. C. L'Argentière, N. S. Fígoli, *Appl. Surf. Sci.* **2003**, *210*, 222.
- A. Bossi, F. Garbassi, G. Petrini, L. Zanderighi, *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1029.
- K. Hadjiivanov, J.-C. Lavalley, J. Lamotte, F. Maugé, J. Saint-Just, M. Che, *J. Catal.* **1998**, *176*, 415.
- R. D. Gonzalez, H. Miura, *J. Catal.* **1982**, *77*, 338.
- M. Kantcheva, S. Sayan, *Catal. Lett.* **1999**, *60*, 27.