Synergy of Ru and Ir electrocatalysts supported on Ketjenblack for Selective Electrohydrogenation of Toluene to Methylcyclohexane

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Abstract: Electrohydrogenation of toluene (TL) to methylcyclohexane (MCH) has been proposed for the hydrogenation process in the organic hydride technology. In this study, we found that Ketjenblack (KB)-supported Ru and Ir cathode was effective for the selective hydrogenation. Characterization studies by TEM-EDS indicated that Ru and Ir formed Ru-Ir alloy. A model of synergy mechanism by Ru and Ir for the electrohydrogenation was proposed.

Keywords: Electrohydrogenation, organic hydride, Ru-Ir alloy

1. Introduction

The conversion of renewable energy, such as solar power and wind power, to hydrogen energy by water electrolysis is proposed for the efficient utilization in society, because hydrogen is clean energy and essential in the industry. Serious problem of hydrogen energy is storage and transportation. Organic hydride compounds, which is applied organic redox coupe such as toluene (TL)/methylcyclohexane (MCH), are expected as a hydrogen storage and transportation materials.[1,2] At energy supply area, MCH is produced by catalytic hydrogenation of TL with H_2 produced by water-electrolysis, MCH is transported to energy demanding area and stored. H_2 is reproduced by catalytic dehydrogenation of MCH to TL.

If TL can be directly hydrogenated to MCH with water, efficiency of energy conversion would increase. Therefore, a direct electrohydrogenation of TL to MCH has been proposed using proton exchange membrane electrolyzer (Fig. 1).[3] In the system, water is oxidized at the anode, and TL is electrochemically reduced to MCH at the cathode. H_2 evolution is a side reaction at the cathode. For the efficient hydrogenation of TL to MCH, it is essential that how to suppress the H_2 evolution.

It was reported that the 50 wt% Pt/Ketjenblack (KB) electrocatalysts is active for the electrohydrogenation of TL[3]; however, the high loading of Pt is disadvantage. Recently, we have reported that 1 wt% Ru/KB electrocatalysts was active for the hydrogenation and showed a higher faradic efficiency for MCH formation (FE(MCH)).[4,5] Moreover, we have found the synergy of Ru and Ir electrocatalysts on the electrohydrogenation.[5] In this study, we investigated the synergy mechanism for the electrohydrogenation of TL to MCH by the Ru-Ir/KB electrocatalysts.

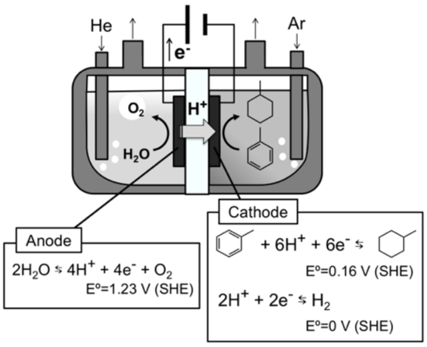

Figure 1. Schematic diagram of electrolysis cell for the electrohydrogenation of TL to MCH.

2. Experimental

A KB support, $RuCl_3 \bullet nH_2O$ and $IrCl_3 \bullet nH_2O$ aq. were added to deionized-water and warmed to 353 K. Subsequently, NaOH aq. was added to the solution to adjust pH=12, and $NaBH_4$ (10 eq. against metals) aq. was slowly dropped. After stirring the mixture overnight, the suspension solution was filtrated and the residual substrate was washed with water and dried under vacuum. This material was denoted as Ru(x)-Ir(y)/KB electrocatalysts (x as Ru and y as Ir loadings (wt%))

An electrocatalyst ink was prepared from the electrocatalyst, Nafion solution and acetone solvent. The ink was casted on carbon paper (Sigracet® GDL-25BC, 2 cm^2) to prepare electrode. A membrane electrode assembly was fabricated by the hot-press method and set in an electrolysis cell. TL was added to the cathode compartment and H_2 was flowed to the anode one. Galvanostatic electrolysis at 0.2 A cm^{-2} was conducted at

298 K for 2 h. The standard redox potential of the hydrogenation of TL to MCH is +0.16 V (SHE). Electrocatalytic activities were evaluated by a FE(MCH) and an overpotential for the electrohydrogenation.

3. Results and discussion

Table 1 shows electrohydrogenation activities of (Ru(x)-Ir(y)/KB)/GDL cathodes under the galvanostatic electrolysis at 0.2 A cm^{-2}. At the (Ru(10)/KB)/GDL cathode (entry 1), a high FE(MCH) of 94% was observed, but a working potential was very negative at -0.330 V, corresponding to an overpotential as 0.490 V. At the (Ir(10)/KB)/GDL cathode (entry 2), H_2 evolution mainly proceeded, but a working potential was more positive than that of the Ru(10)/KB. At the (Ru(5)-Ir(5)/KB)/GDL cathode (entry 3), a cathode potential was positive at -0.183 V with keeping a high FE(MCH) of 86% nevertheless total metal loadings were the same as Ru(10)/KB. This result indicates that synergy of Ru and Ir catalysis on the electrohydrogenation of TL to MCH. To compare with a result of (Pt(50)/KB)/GDL cathode (entry 4), which is known as an active cathode,[3] the FE(MCH) of the Ru(5)-Ir(5)/KB was high though the working potential was slightly negative. This indicated that the Ru(5)-Ir(5)/KB was effective for the electrohydrogenation of TL.

The electrocatalysts were characterized by using TEM-EDS. From the TEM images, average metal particle sizes on the Ru(10)/KB, Ir(10)/KB and Ru(5)-Ir(5)/KB electrocatalysts were 2.3 nm, 2.3 nm and 2.5 nm, respectively. There are no significant differences in particle sizes and no relation to the electrocatalytic activities. At EDS analysis of Ru(5)-Ir(5)/KB electrocatalyst, Ru and Ir were uniformly detected from each particles, indicating that Ru and Ir formed uniform Ru-Ir alloy.

In our previous work,[4,5] we proposed the reaction scheme of the electrohydrogenation of TL as below; adsorbed H species formed by the electrochemical reduction of H^+ ($H^+ + e^- \rightarrow H_{ad}$) reacted with adsorbed TL ($TL_{ad} + 6H_{ad} \rightarrow MCH$). H_2 evolution proceeds by a coupling of H_{ad} ($2H_{ad} \rightarrow H_2$). Based on the scheme, synergy of Ru and Ir electrocatalysts are discussed. Though Ru showed a large overpotential for the formation of H_{ad}, a high FE(MCH) was observed (Table 1, entry 1). In contrast, Ir showed a small overpotential for the formation of H_{ad} but a low FE(MCH) (Table 1, entry 2). Our synergy model is (i) Ir-H_{ad} species electrochemically form with a small overpotential, (ii) H_{ad} on Ir spillover to Ru surface, and (iii) H_{ad}-Ru reacts with TL_{ad}-Ru to form MCH. This is the reason why Ru(5)-Ir(5)/KB shows a high FE(MCH) with a small overpotential.

Table 1. Galvanostatic hydrogenation of TL on the (Ru-Ir/KB)/GDL and (Pt/KB)/GDL cathodes.

Entry	Electrocatalyst	Cathode Pot. / V (SHE)	FE / %		
			MCH	MCH-1-ene$^{b)}$	H_2
1	Ru(10)/KB	-0.330	94	4	2
2	Ir(10)/KB	-0.171	24	0.2	76
3	Ru(5)-Ir(5)/KB	-0.183	86	0.8	12
4	Pt(50)/KB$^{a)}$	-0.071	72	0.06	26

T = 298 K, j = 0.2 A cm^{-2}. Cathode: Ru(x)-Ir(y)/KB (2.0 mg cm^{-2})/GDL, a sum loading of Ru and Ir as 10 wt%, TL 25 mL. Anode: 50 wt% Pt/KB (5.0 mg cm^{-2})/GDL, p(H_2) = 1 atm.
a) TEC10E50E, made by Tanaka Precious Metal Co., b) 1-methyl-1-cyclohxene.

4. Conclusions

The KB-supported Ru-Ir cathode was active for the electrohydrogenation of TL to MCH, as same as the Pt/KB. Characterization studies indicated formation of Ru-Ir alloy. The synergy model of Ru and Ir electrocatalysts which contribute spillover of electrochemically formed H species on Ir to Ru was proposed.

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