

Effects of the supports in Pt-catalysts on dehydrogenation of decalin

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Introduction

As a key technology for hydrogen supply to fuel cell vehicles, the combination of decalin/naphthalene system has been proposed as an effective hydrogen carrier. In our previous paper [1], it has been revealed that catalytic active sites on Pt/C, which was prepared with the active carbon support treated with NaOH and showed great activities for the dehydrogenation of decalin to naphthalene, are non-metallic Pt species. In the present report, the dehydrogenation of decalin to naphthalene has been investigated on Pt/C, Pt/Al₂O₃ and Pt/Al(OH)O in order to examine the effects of the supports on the catalytic activities and active sites over those catalysts.

Experimental

Commercially available 5 wt.% Pt/C (Aldrich) and 1 wt.% Pt/Al₂O₃ (Aldrich) were employed. The preparation procedure of 1.46 wt.% Pt/Al(OH)O is as follows. Boehmite (Al(OH)O) was prepared from sol-gel method with aluminum iso-propoxide. Precursor of Pt species (K₂PtCl₄ (Wako)) was impregnated on Al(OH)O, followed by the reduction with aqueous solution of NaBH₄ (Wako) at 363 K. The surface areas of 5 wt.% Pt/C, 1 wt.% Pt/Al₂O₃ and 1.46 wt.% Pt/Al(OH)O were 1445, 286 and 170 m²/g, respectively. X-ray absorption fine structure (XAFS) near Pt L₃-edge was measured (2.5 GeV) with a storage ring current of 340 mA at the High Energy Research Organization. The X-rays were monochromatized with Si(111) and Si(311) crystals at BL-7C and BL-10B station, respectively. And the absorption spectra were observed using ionization chambers in a transmission mode. Batch-wise catalytic dehydrogenation of decalin (1 or 1.25 ml) was examined with 0.3 g of Pt/C or 1.0 g of Pt/Al₂O₃ and Pt/Al(OH)O, respectively, at 483 K under reactive distillation conditions. Under those conditions, 0.015, 0.010 and 0.0146 g of Pt species were contained in the systems with Pt/C, Pt/Al₂O₃ and Pt/Al(OH)O, respectively.

Results and Discussion

The dehydrogenation behaviors on the commercially available Pt/C, Pt/Al₂O₃ and Pt/Al(OH)O were described in Fig. 1. Although the rather similar contents of Pt species in those systems and the dissimilar surface areas of those three catalysts are evident, it is of interest to note that hydrogen evolution from decalin after 150 min are rather identical. Therefore the nature of Pt species is strongly influenced by the supports.

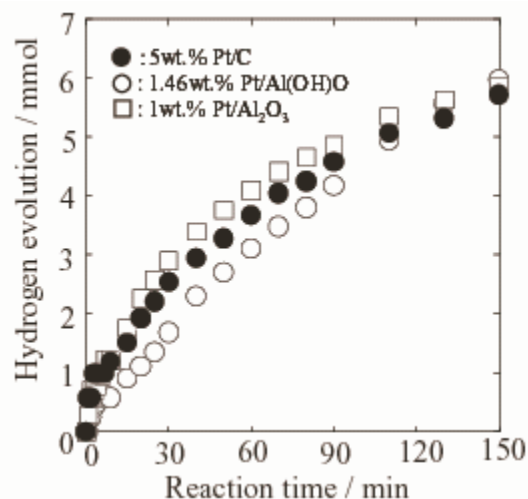


Fig. 1: Dehydrogenation of decalin at 483 K.

From XAFS analyses, the nearest-neighbor distances of Pt-Pt in Pt/Al₂O₃ and Pt/Al(OH)O were 0.283 and 0.279 nm, which were corresponding to that (0.280 nm) in Pt foil, indicating that the nature of Pt species in those catalysts is essentially identical to that of metallic Pt. However the rather shorter Pt-Pt distance (0.259 nm) was obtained from the commercially available Pt/C. As shown in our previous study [1], the nearest-neighbor distance of Pt-Pt in active Pt/C prepared with active carbon treated with NaOH solution was 0.265 nm while that in non-active Pt/C prepared with the support not-treated with NaOH was 0.280 nm. Those results from the active Pt/C indicate that the high dispersion of Pt affords a more covalent species, resulting in the great activities for the dehydrogenation of decalin. Based on those previous results, present XAFS analyses of the commercially available Pt/C reveal that Pt species with covalent nature are also present on the commercial Pt/C catalysts. It should be noted that metallic Pt species in Pt/Al₂O₃ and Pt/Al(OH)O afforded the corresponding activities to those of Pt/C catalysts, indicating that the interaction of Pt species and the support contributes to the activities together with the nature of the catalytic active species.

References

- [1] C. Shinohara et al., Appl. Catal. A: Gen., 266, 251 (2004).

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