

Identification of catalytic active sites for the dehydrogenation on Pt/C with XAFS

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Introduction

As a catalyst for the dehydrogenation of decalin, Pt/C has been suggested as one of the candidates. It has been noticed that active carbon pretreated with NaOH affords great activities after the impregnation of K_2PtCl_4 while lower activities are obtained on the catalysts, which support is not pretreated with NaOH [1]. Although direct contribution of NaOH-pretreatment to the enhancement of the activities is suggested [1], structural information on platinum in the catalysts treated with and without NaOH is not clear. In the present study, Pt/C catalysts prepared from various procedures were analyzed with XAFS to reveal the information on fine structure changes around Pt species in the catalysts.

Experimental

The preparation procedure of 5wt% Pt/C catalysts was essentially identical to that described earlier [1]. Pt/C catalysts obtained with the support with and without NaOH-pretreatment were identified as "catalyst A" and "catalyst B", respectively. In order to investigate the effects of the reduction on the nature of Pt on the support pretreated with NaOH, H_2 reduction at 523 K for 3 h was employed for the $NaBH_4$ reduction, which was employed for the preparation of catalysts A and B, and the catalyst thus obtained was identified as "catalyst C". Batch-wise catalytic dehydrogenation of decalin (1 ml) was investigated with Pt/C catalysts (0.3 g) at 483 K under reactive distillation conditions [1]. X-ray absorption fine structure (XAFS) near Pt L_3 -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 the BL-7C and 10B stations, respectively, and the absorption spectra were observed using ionization chambers in a transmission mode.

Results and Discussion

The order of the activities for the catalytic hydrogen evolution from decalin (1 ml) on 5% Pt/C (0.3 g, catalysts A, B and C) under the conditions of boiling at 483 K and refluxing at 278 K is $A > C > B$ (hydrogen evolution of 6, 4 and 2.5 ml for 2.5 h, respectively) while that of surface areas of the catalysts A-C is $B (2343 \text{ m}^2/\text{g}) > C (2116 \text{ m}^2/\text{g}) > A (1952 \text{ m}^2/\text{g})$. Therefore the activities appear to be independent of the surface area but dependent on the nature of platinum on those catalysts.

XAFS analyses have been employed to characterize platinum species in those Pt/C catalysts. The enlargement

for the absorption edge (XANES) showed that the increasing order of the absorption position from Pt L_3 -edge was catalysts $B < A < C$, indicating that the local structure around Pt species is strongly influenced by the preparation procedure. The shapes after the Fourier transformation of the EXAFS oscillation of Pt L_3 -edge of the corresponding catalysts reveal that the signal with the lowest intensity was observed at a rather long distance from the catalyst B. It should be noted that the catalyst B was prepared from the active carbon not-pretreated with the NaOH solution and showed the lowest activities among those three catalysts. However, the signals from the catalysts A and C, which were prepared from the support pretreated with NaOH and showed rather greater activities than the catalyst B, were observed at rather shorter distances. At least two Pt species were thus evident in the catalysts A and C. The results from the curve-fitting analyses of those three catalysts revealed that the increasing order of the nearest neighbour distance around the Pt, which afforded the greatest intensity in the Fourier transform, was catalysts $C (2.51 \text{ \AA}) < A (2.65 \text{ \AA}) < B (2.80 \text{ \AA})$. The nearest neighbour distances of Pt^0 , Pt^{2+} and Pt^{4+} , which were estimated with Pt foil, K_2PtCl_4 and PtO_4 , respectively, in the present study, were 2.80, 2.34 and 2.08 \AA , indicating that the distance of cationic Pt was shorter than that of metallic Pt. Based on those valence states, it is reasonable that Pt species in the catalyst B, in which the distance was 2.80 \AA , is metallic. However, based on the reaction mechanism, it is rather strange to suggest that cationic Pt species are present in the active catalysts A and C due to the observation of the shorter distance of 2.65 and 2.51 \AA , respectively. Pt species formed on the active catalysts A and C can be explained as the formation of Pt species with covalent nature while the formation of Pt species with metallic nature in the catalyst B, due to the employment of the support not-pretreated with NaOH, results in the lowest activities for the evolution of hydrogen from decalin. The nearest neighbour distance of the catalyst C was shorter than that of the catalyst A, indicating that the employment of $NaBH_4$ reduction rather than H_2 reduction seems to be favourable, since the cationic nature is still present in the catalyst C.

References

[1] S. Hodoshima et al., *Stud. Surf. Sci. Catal.*, **132**, 323 (2001).

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