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SYNERGISTIC EFFECT IN ALUMINA SUPPORTED Pt-Ru BIMETALLIC CLUSTER CATALYSTS USED FOR DEHYDROGENATION OF CYCLOHEXANE

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The dehydrogenation of cyclohexane, accompanying hydrogenolysis, was studied over well characterized Pt-Ru/Al_2O_3 catalysts. For dehydrogenation synergistic effect was clearly observed, whereas for hydrogenolysis simple dilution effect was observed.

Alloy of Pt and Ru is often used as an electrode material. It has also excellent catalytic properties for hydrogenation and isomerization reactions.1-3) In recent papers4-6) studies on the structure of supported Pt-Ru catalysts have been reported, showing the formation of Pt-Ru bimetallic clusters. However, very little attention has been focused on catalytic reaction studies over well characterized Pt-Ru bimetallic cluster catalysts. Miura and Gonzalez6) reported that the surface composition of silica supported Pt-Ru catalysts can be measured by means of O_2-CO titration, and that Pt is enriched on the surface. In this study we tried dehydrogenation of cyclohexane to form benzene over alumina supported Pt-Ru bimetallic cluster catalysts in the light of surface characterization by the O_2-CO titration method.

Methods of catalyst preparation, pretreatment and O_2-CO titration are described in detail in the previous paper,6) except that alumina (Al_2O_3-C, supplied by Japan Aerosil Co.) was used as a support instead of silica. Amount of metal loading was fixed to 0.3 mmol(Pt+Ru) per g-support. In Table 1, results of the surface composition measurements are shown. From Table 1 surface enrichment of Pt is clearly suggested, in agreement with the previous results on SiO_2 supported catalysts. In addition dispersion increased by adding 25-38% Ru on Pt.

Dehydrogenation of cyclohexane, accompanying hydrogenolysis to C_1-C_6 hydrocarbons, was carried out with a conventional flow reactor. 0.1 g of catalyst was kept at 570K, and 100 ml/min of H_2 flow together with 1/5 molar ratio of cyclohexane was passed through the catalyst. Pt/Al_2O_3 had higher activity for dehydrogenation than Ru/Al_2O_3, without forming any hydrogenolysis products. On Ru/Al_2O_3 actalyst, dehydrogenation and hydrogenolysis occurred simultaneously at comparable rates. Pt-Ru/Al_2O_3 had an intermediate charactor of the former two catalysts. Figure 1 illustrates the change in turnover frequency (reaction rate/number of surface metal atoms, Pt+Ru) of dehydrogenation and hydrogenolysis against the surface composition. For hydrogenolysis, the rate of reaction

Table 1. Surface composition and dispersion of Pt-Ru/Al_2O_3 catalysts.

catalyst composition Pt/Ru, %	dispersion %	surface composition Pt/Ru, %
0/100	14.7	0 /100
10/90	17.2	34.8/65.2
25/75	22.7	55.7/44.3
38/62	32.4	69.8/30.2
51/49	27.5	80.9/19.2
62/38	39.9	85.9/14.1
75/25	45.5	94.3/ 5.7
100/0	39.1	100 / 0

was estimated on the basis of moles of cyclohexane reacted.

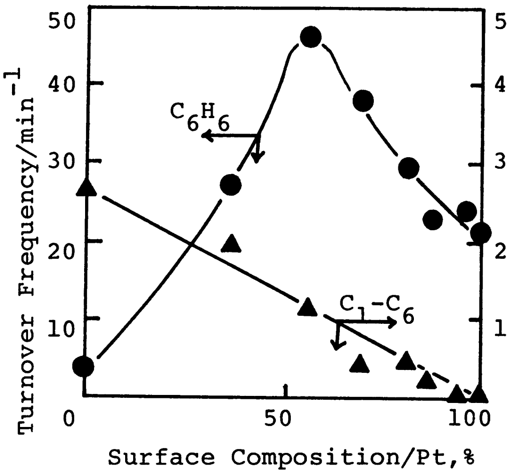

Fig.1. Turnover frequency of cyclohexane dehydrogenation and hydrogenolysis over Pt-Ru/Al_2O_3 catalyst.
● ; dehydrogenation to C_6H_6.
▲ ; hydrogenolysis to C_1-C_6.

The dehydrogenation activities of Pt-Ru/Al_2O_3 catalysts were higher than either Pt/Al_2O_3 or Ru/Al_2O_3, suggesting the existence of synergistic effect. Highest turnover frequency was observed on the catalyst Pt/Ru=25/75, on which the rate of benzene formation was 5 times higher than Pt/Al_2O_3 based on the weight of Pt in the catalyst. In contrast, the turnover frequency of hydrogenolysis reaction decreased linearly from Ru/Al_2O_3 to Pt/Al_2O_3, showing a simple dilution effect of Pt in the Pt-Ru/Al_2O_3 catalysts. It is clear that the turnover frequency per surface Ru atoms does not change by diluting with Pt.

The synergistic effect in the dehydrogenation of cyclohexane is very remarkable, although its mechanism is unknown. One possible mechanism is that an electronic interaction of Pt and Ru increases the intrinsic activity of Pt (ligand effect). Another possibility is that a combination of Pt and Ru forms a new site such as Pt-Ru site which is more active than a Pt atom site. We cannot determine yet which mechanism is working in this case.

References

1) A. Amano and G. Parravanno, Advan. Catal., 9, 733 (1957).
2) P. N. Rylander and G. Cohn, Int. Congr. Catal. 2nd, Paris, 1-997 (1960).
3) T. J. Gray, N. G. Masse and H. G. Oswin, *ibid,* 2-1687 (1960).
4) P. Ramamoorthy and R. D. Gonzalez, J. Catal., 59, 130 (1979).
5) G. Blanchard, H. Charcosset, *et al.,* J. Catal., 70, 168 (1981); Surf. Sci., 106, 509 (1981).
6) H. Miura and R. D. Gonzalez, J. Catal., 74, 216 (1982).

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