CHEMISTRY LETTERS, pp. 1643-1644, 1990. 

# Crucial Effects of Residual Chlorine on the Dependency of the Selectivity of Cyclohexane Conversion on the Ru Dispersion of $Ru/Al_2O_3$

Ayumi KYOMASU, Toshio OKUHARA,* and Makoto MISONO
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The selectivity of cyclohexane conversion over $Ru/Al_2O_3$ oppositely depended on the Ru dispersion between Cl-free $Ru/Al_2O_3$ and Cl-containing $Ru/Al_2O_3$, indicating that the residual Cl and the dispersion are the crucial factors controlling the selectivity.

Supported metal catalysts are usually prepared from metal chlorides and thus contained more or less the residual Cl.[1] However, the effects of Cl have long been controversial.[1,2] Here, we wish to report great effects of the residual Cl on the selectivity, and the "real" dependency of the selectivity on the dispersion, in which the effect of Cl is excluded.

$Ru/Al_2O_3$ catalysts were prepared from $Ru_3(CO)_{12}$ and $RuCl_3$ by the same methods as in the previous paper,[3] and were denoted as $Ru/Al_2O_3$(A)(Cl-free) and $Ru/Al_2O_3$(B)(Cl-containing), respectively. The catalysts were reduced with $H_2$ (1 atm) at 723 K for 2 h (this treatment is abbreviated as **R**). Some of them were subsequently oxidized at 773 K and again reduced (abbreviated as **R-O-R**).[3a] Conversion of cyclohexane was carried out in a conventional flow reactor at 573 K ($H_2$/cyclohexane = 5).[3b]

Figure 1 shows the dependencies of the turnover frequencies (TOF) of dehydrogenation and hydrogenolysis of cyclohexane on the Ru dispersion measured by $H_2$ adsorption.[3] The TOF was calculated on the basis of the $H_2$ adsorption. Over $Ru/Al_2O_3$(A)(Cl-free), TOF of dehydrogenation was almost independent of the dispersion, and that of the hydrogenolysis increased as the dispersion increased (Fig. 1b-c). That is, the selectivity to benzene (Fig. 1a) varied from 89 to 43% as the dispersion increased. On the other hand, the dependencies for $Ru/Al_2O_3$(B) (Fig. 1d-f) were in contrast with those for the Cl-free $Ru/Al_2O_3$(A). It is remarkable that the dependencies for $Ru/Al_2O_3$(B) were similar to those of $Ru/SiO_2$ prepared from $RuCl_3$.[4] Since both $Ru/Al_2O_3$(B) and $Ru/SiO_2$ were prepared from $RuCl_3$ and therefore contained Cl,[1] the different dependency between $Ru/Al_2O_3$(A) and (B) may be induced by the residual Cl.

In order to confirm the effect of the Cl, 5wt%Ru/$Al_2O_3$(A)(both **R** and **R-O-R**) were treated with HCl (100 - 300 Torr) at 573 K in a closed circulation system and were used for the reaction. The Cl contents of these HCl-treated catalysts measured by XPS were similar to those of Ru/$Al_2O_3$(B); the atomic ratios of Cl to Al estimated from the XPS peak intensities were 0.052 - 0.122. In Fig. 1d-f, the TOF's and the selectivity obtained over the Cl-treated Ru/$Al_2O_3$(A)(○ and ●) are included. It may be noted that these data are consistent with those for Ru/$Al_2O_3$(B). Therefore, it is concluded that the residual Cl is an essential factor changing the dependencies of the selectivity on the dispersion.

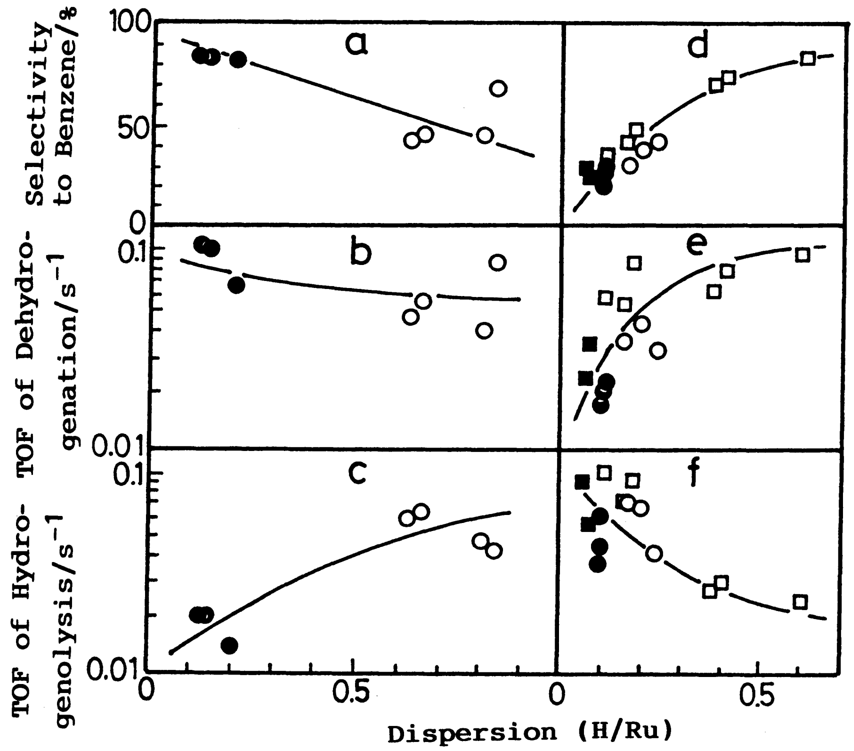


Fig. 1. Changes of the TOF's and selectivity to benzene of cyclohexane conversion over Ru/$Al_2O_3$ as a function of the Ru dispersion.
(a-c): Ru/$Al_2O_3$(A), (d-f): Ru/$Al_2O_3$(B) and HCl-treated Ru/$Al_2O_3$(A);
○: Ru/$Al_2O_3$(A)-**R**, ●:Ru/$Al_2O_3$(A)-**R-O-R** (Cl-free in a-c; HCl-treated in d-f), □: Ru/$Al_2O_3$(B)-**R**, ■:Ru/$Al_2O_3$(B)-**R-O-R**.

References

1) T. Narita, H. Miura, K. Sugiyama, and T. Matsuda, J. Catal., 103, 492 (1987); H. Miura, T. Narita, K. Sugiyama, and T. Matsuda, Shokubai, 26, 396 (1984); H. Miura, H. Hondou, K. Sugiyama, T. Matsuda, and R. D. Gonzalez, Proc. 9th Intern. Congr. Catal., 1988, p. 1307.
2) K. Lu and B. J. Tatarchuk, J. Catal., 106, 166 (1987); 106, 176 (1987).
3) a) Z. Lin, T. Okuhara, and M. Misono, J. Phys. Chem., 92, 723 (1988); b) Z. Lin, T. Okuhara, and M. Misono, Bull. Chem. Soc. Jpn., 62, 1740(1989).
4) Y. L. Lam and J. H. Sinfelt, J. Catal., 42, 319 (1976).

(Received June 4, 1990)