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Selective Acceleration Effects of K-Addition in Hydrogenolysis of Cyclohexane over Ruthenium Supported on Silica

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By addition of K to Ru/SiO_2 catalyst ($K/(K+Ru)=0.2$), catalytic activity for hydrogenolysis of cyclohexane was enhanced, whereas those for dehydrogenation of cyclohexane and hydrogenation of CO were markedly suppressed.

The effects of additives to metal catalysts on conversion of hydrocarbons have already been investigated extensively. Among them, the important examples are bimetallic catalysts between Ib and VIII metals, in which the addition of Cu to Ni, Os, and Ru improved markedly the selectivity to benzene in conversion of cyclohexane.1,2) In these cases, the hydrogenolysis was always suppressed by the addition of Cu. These findings played a role in the development of reforming catalysts.1) Recently, Miura et al. have found that when Pt was added to Ru/Al_2O_3, the activity for dehydrogenation of cyclohexane increased. Also in this case, the hydrogenolysis was suppressed.3)

The authors wish to report here that the addition of K to Ru/SiO_2 accelerated, in contrast, the hydrogenolysis of cyclohexane, suppressing completely the dehydrogenation to benzene. As far as we know, there has been no report, in which selective enhancement of activity for hydrogenolysis reaction by additives was observed.

Preparation and pretreatment of the catalysts are described in the previous paper.4) The amount of Ru was 2.5wt% in all catalysts. Conversion of cyclohexane (hydrogenolysis and dehydrogenation) was carried out in a conventional flow system under 1 atm. A mixture of H_2 and cyclohexane (H_2/cyclohexane = 5) was supplied to the catalysts at 300 °C. The hydrogenation of CO was performed at 260 °C and 1 atm ($H_2/CO = 2$) in a flow reactor.4)

The %-conversions of these reactions decreased to about one half during the initial stage of the reaction (1 h) and the steady-state conversions were obtained after about 2 h. Figure 1 shows the effects of the addition of K to Ru/SiO_2 on the rates of cyclohexane hydrogenolysis, dehydrogenation, and CO hydrogenation. It was found that for the hydrogenolysis of cyclohexane, the activity of $Ru-K/SiO_2$ having $K/(K+Ru)$ ratio of 0.2 (in atomic ratio) was higher than that of Ru/SiO_2. As the K content ($K/(Ru+K)$) increased from 0.2, the activity decreased monotonically. K/SiO_2 showed no catalytic activity. In all cases, the product of the hydrogenolysis was mainly methane, which was consistent with the results of Ru-Cu.[1)] In contrast with this reaction, dehydrogenation to benzene was completely suppressed by the addition of K. Furthermore, the activity of the CO hydrogenation was markedly decreased by the addition of K (Fig. 1) as described previously.[4)] The dispersion of Ru obtained from hydrogen adsorption decreased as the K content increased;[4)] H/Ru values are 0.17, 0.08, 0.06, and 0.04 for 0, 0.2, 0.6, and 0.82 of K content (open marks in Fig. 1). Accordingly, turnover frequency (TOF) of hydrogenolysis for Ru-K/SiO_2(K/(Ru+K)=0.2) was about 7 times higher than that for Ru/SiO_2.

Table 1 shows the effect of addition of various kinds of alkali metals on the rate and TOF of the conversion of cyclohexane. It is clear that the ratio of the two reaction rates as well as TOF of hydrogenolysis increased as the atomic number of alkali metal increased. K and Cs-added Ru/SiO_2 showed 100% selectivity for the hydrogenolysis of cyclohexane.

In hydrogenolysis reactions over metals, there are two types of reactions such as "single hydrogenolysis" and "multiple hydrogenolysis".[5)] In the latter case (Ni or Ru), reactant hydrocarbons convert to hydrogen deficient species, then undergo the rupture of C-C bond.[6)] Since the rupture of C-C bond seems to be the rate determining step,[6)] K probably on Ru may accelerate this step to form the C_1 fragment which is hydrogenated to methane.

Table 1. Effect of Alkali Metals on the Conversion of Cyclohexane

Alkali[a)]	H/Ru[b)]	Rate[c)]		TOF[d)]		H/D[e)]
		H	D	H	D	
None	0.17	0.75	0.35	7.4	3.5	2.1
Li	0.12	0.67	0.20	9.4	2.8	3.4
Na	0.09	0.59	0.16	11.1	3.0	3.7
K	0.08	2.38	0	49.9	0	∞
Cs	0.10	2.97	0	49.8	0	∞

a)Ru was added to M/SiO_2 (M = alkali). M/(Ru+M) = 0.2. b)Dispersion. c)10^{-2}mol(g-Ru)$^{-1}$min^{-1}, H;hydrogenolysis D;dehydrogenation. d)10^{-2}s^{-1}. e)Ratio of the reaction rate of hydrogenolysis to dehydrogenation.

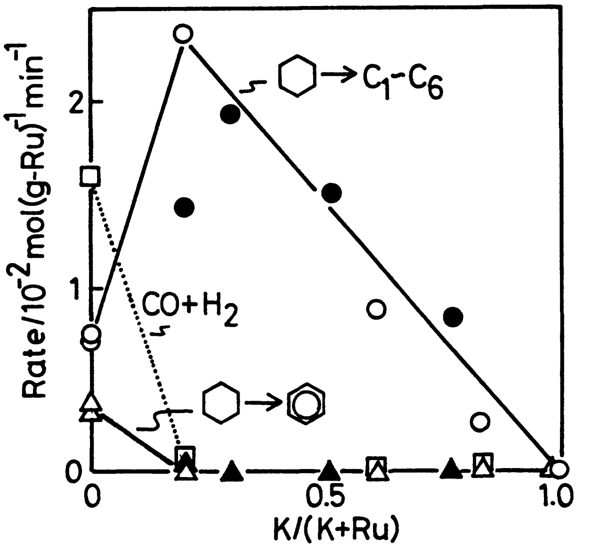

Fig. 1. Effect of K content on rates of cyclohexane + H_2 (300 °C) and CO + H_2 (260 °C) over Ru-K/SiO_2
○△□:Ru was added to K/SiO_2.
●▲:K was added to reduced Ru/SiO_2.

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