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Novel Effects of K-Addition to Ru/SiO_2 on Conversion of Cyclohexane

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The effects of the addition of alkalis to a Ru/SiO_2 catalyst upon the conversion (hydrogenolysis and dehydrogenation) of cyclohexane, hydrogenolysis of butane, and hydrogenations of benzene and CO were studied. The addition of K or Cs slightly enhanced the catalytic activity for the hydrogenolysis of cyclohexane, whereas dehydrogenation to benzene was markedly suppressed. This result is contrary to the effect of the addition of Cu or Au to group-VIII metals, as reported in the literature. Changes in the activities became less significant as the atomic number of the added alkali decreased. From a systematic examination by varying the alkali content, it was revealed that dehydrogenation and CO hydrogenation were very sensitively suppressed by an electronic effect imposed by the alkalis, whereas changes in the activities of hydrogenolysis and benzene hydrogenation were not great.

Practically important heterogeneous catalysts are often modified by alkali metals.1,2) K_2O in doubly promoted Fe catalysts for ammonia synthesis and Cs in a Ag catalyst for the epoxidation of ethylene are typical examples.2) There have been many fundamental studies on the enhancement of the activities and selectivities by the addition of alkali. Regarding activity, K to Ru in ammonia synthesis,3) Na or K to $Ni/SiO_2-Al_2O_3$ in methanation reaction,4) and Li to Pd/SiO_2 in methanol synthesis5,6) were effective.

The selectivity is also improved by the addition of alkali. In a Fischer-Tropsch synthesis, the modification of Ru by alkali greatly increased the olefin/paraffin ratios in the product hydrocarbons.7,8) K to $Rh/TiO_2$9) or Mo/SiO_2 increased C_2-oxygenated products10) or higher alcohols11) from the $CO+H_2$ reaction.

Alloying also brings about changes in both the activity and selectivity. Sinfelt et al.12) reported that the addition of Cu to Ni markedly suppressed the hydrogenolysis of ethane, but did not change the rate of dehydrogenation of cyclohexane. Also, it has been shown by Ponec et al.13) that the hydrogenolysis reaction was sensitively affected by the Pt content of the $Pt-Au/SiO_2$ catalyst. SMSI (Strong Metal-Support Interaction) caused a change in the activities of hydrogenolysis and dehydrogenation. Resasco and Haller14) found that hydrogenolysis was suppressed by a high-temperature reduction, while dehydrogenation was only slightly influenced.

IR7,15) and XPS16) studies have shown that K (probably as K_2O) on Ru/Al_2O_3 or Ru/SiO_2 acts as a base capable of electron-donating to Ru. On the other hand, Li exhibited a different effect from K;17) the addition of Li to Ru/SiO_2 effectively suppressed methane formation in CO hydrogenation without any great decrease in activity, while K significantly decreased the activity while not suppressing methane formation. It was concluded that a Li compound on Ru particles brought about a geometrical effect similar to an ensemble effect, rather than an electronic effect.

Contrary to CO hydrogenation, so far there are very few reports about the effect of alkali on the conversion of hydrocarbons, such as hydrogenolysis and dehydrogenation. We have preliminarily reported that K to Ru/SiO_2 appreciably enhances the activity for the hydrogenolysis of cyclohexane, but completely suppresses dehydrogenation.18) Since it has been reported that the addition of Au to Pt,19) Ru to Pt,20) and Cu to Ru21) preferentially enhances the dehydrogenation of cyclohexane, the effect of K observed here is novel. In order to elucidate this novel effect, we systematically examined the effects of various alkalis added to a Ru/SiO_2 catalyst on several reactions such as the conversion of cyclohexane, the hydrogenolysis of butane, and hydrogenations of benzene and CO.

Experimental

Materials. Silica (Aerosil 200, 160 $m^2 \cdot g^{-1}$) was used as a support after being calcined at 773 K in air for 20 h. The Ru/SiO_2 catalyst, which contained 2.5 wt% of Ru, was prepared by incipient-wetness impregnation with an aqueous solution of $RuCl_3$. It was then dried at 373 K for 10 h and reduced at 723 K in flowing H_2 for 2 h. Alkali-promoted Ru/SiO_2 catalysts were prepared in two different ways, as described previously.17) The first catalysts were obtained as follows. SiO_2 was impregnated with an aqueous solution of an alkali carbonate. It was then calcined at 773 K for 10 h in air, and was again impregnated with an aqueous solution of $RuCl_3$. The product was dried at 373 K and reduced at 723 K in flowing H_2 for 2 h. The loading amount of Ru was fixed to 2.5 wt%, and the alkali content (defined as M/(M+Ru) in atom basis, M=alkali) was changed from 0.20 to 0.82. Hereafter, these catalysts will be designated as, e.g., Ru-Li(0.20)/SiO_2, where the figure in the parenthesis is the alkali content. The second catalysts were obtained by impregnating the reduced Ru/SiO_2 with an aqueous solution of alkali carbonate. These were dried at 373 K and reduced at 723 K in flowing H_2. These will be

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designated as, e.g., K(0.2)-Ru/SiO_2. As references, 1 wt% K/SiO_2 and 0.18 wt% Li/SiO_2 were prepared from K_2CO_3 and Li_2CO_3, respectively.

Butane and CO in a glass cylinder were obtained from Takachiho Chem. Co., Ltd. The butane was purified by a freeze-thaw cycle prior to the reaction. The cyclohexane and benzene were purchased from Nakarai Chemicals, Co. and used without any treatment.

Apparatus and Procedure. The adsorption of H_2 was volumetrically measured after the catalysts were reduced with H_2 at 723 K for 2 h, as in the previous work.[22] A chemisorption measurement was carried out at room temperature in a static system (60 cm^3). The total uptakes of hydrogen were measured after the H_2 pressure became constant (in about 1.5 h). The equilibrium H_2 pressure was adjusted to about 60 Torr (1 Torr=133.3 Pa). Hydrogenations of benzene and the conversion of cyclohexane (hydrogenolysis and dehydrogenation) were carried out in a conventional flow reactor under 1 atm. In the case of benzene hydrogenation, a mixture of benzene and hydrogen (1 : 6 in molar ratio) was supplied at 358 K just after the catalysts were reduced at 723 K for 2 h in flowing H_2. The benzene and cyclohexane produced were analyzed by using a Methoxy PEG column (4 m, 4 mm of inside diameter, 473 K).

In the case of the conversion of cyclohexane, a mixture of cyclohexane and hydrogen (1 : 5) was introduced to the catalysts at 573 K. Benzene was analyzed by a Methoxy PEG column; the C_1—C_6 hydrocarbons produced were analyzed by an FID gas chromatograph (Yanagimoto GC 2800) using a Porapak R column (1.5 m, 2 mm of inside diameter), the temperature of which was increased from 323 to 473 K at a rate of 2 $K s^{-1}$.

The hydrogenolysis of butane was carried out in a closed circulation system (volume; 250 cm^3). Prior to the reaction, the catalysts were reduced at 723 K in H_2 (300 Torr) for 2 h. A mixture of butane (50 Torr) and H_2 (100 Torr) was introduced to the catalysts at 373 K. The product hydrocarbons were analyzed by a gas chromatograph with a VZ-10 column. Hydrogenation of CO was performed in a flow reactor under 1 atm pressure at 533 K, as described previously.[17]

Results

Adsorption of H_2. Data regarding H_2 adsorption are given in Table 1. No H_2 was adsorbed on SiO_2, K/SiO_2, and Li/SiO_2. Here, the dispersion of Ru is expressed by H/Ru (the amount of hydrogen atom adsorbed divided by the amount of Ru atom in the catalyst), assuming that one H atom is adsorbed on one exposed Ru atom. It was observed that the dispersion decreased as the content of alkali increased for the Ru-M/SiO_2 systems (M=alkali).[17] For example, the dispersion of Ru on Ru-Li(0.82)/SiO_2 was one-third that of Ru/SiO_2. K-addition caused greater decreases in the dispersion than Li-addition.

Table 1. H_2 Adsorption on Ru-M/SiO_2 (M=alkali)

Alkali content[a]	Dispersion[b]			
	Li	Na	K	Cs
0	0.17	0.17	0.17	0.17
0.20	0.12	0.09	0.08	0.10
0.60	0.12	—	0.06	—
0.82	0.06	—	0.04	—
1.0	—	0	0	—

a) M/(M+Ru) in atom basis (M=alkali). b) H/Ru; the amount of hydrogen atom adsorbed divided by the amount of Ru in the catalyst.

Hydrogenolysis of Butane. The hydrogenolysis of butane was carried out over Ru/SiO_2 and Ru-Li/SiO_2. The product composition was independent of the conversion levels (<80%) over these catalysts, showing that the distributions of the carbon number of the products are of the primary products. The influence of the Li content on the activity and selectivity are given in Table 2. The catalytic activity per unit weight of Ru was almost independent of the Li content, although H/Ru decreased as the Li content increased (Table 1). For all the catalysts given in Table 2, the main product was ethane, which constituted about 50 mol% of the products; the mole fraction of methane slightly increased as the Li content increased.

Hydrogenation of Benzene. The product was only cyclohexane at 358 K for all catalysts. The conversion of benzene gradually decreased with the reaction time and reached stationary values after 1.5 h, which were about one half of the initial conversions. The catalytic activities were calculated from the stationary conversions. The conversions were adjusted to be less than 40% by controlling the flow rate and the catalyst weight. Table 3 shows the effects of Li, Na, and K on the activity. The reaction rate decreased as the contents of alkali increased. The effect of K was

Table 2. Effect of Li-Addition on Hydrogenolysis of Butane

Li/(Li+Ru)	Activity[a]	Selectivity/mol%		
		CH_4	C_2H_6	C_3H_8
0	22.3	31.7	52.7	15.6
0.60	17.6	38.2	50.8	11.0
0.82	20.0	40.1	49.4	10.5

a) 10^{-2} mol g-Ru^{-1} h^{-1}. The reaction was carried out at 373 K and 150 Torr (H_2/C_4H_{10}=2).

Table 3. Effect of Alkali-Addition on Hydrogenation of Benzene

Alkali content[a]	Activity[b]		
	Li	Na	K
0	30	30	30
0.20	26	25	17
0.60	18	—	15
0.82	15	—	1.3

a) 10^{-2} mol g-Ru^{-1} min^{-1}. b) M/(M+Ru); M=alkali. The reaction was carried out at 358 K and 1 atm (H_2/benzene=6).

Table 4. Effect of Alkali-Addition on Conversion of Cyclohexane

Content of alkali	Activity$^{a)}$							
	Li		Na		K		Cs	
	H	D	H	D	H	D	H	D
0	0.70	0.30	0.70	0.30	0.70	0.30	0.70	0.30
0.20	0.65	0.20	0.60	0.15	2.70	0	3.00	0
0.60	0.70	0.15	—	—	0.80	0	—	—
0.82	0.70	0.05	—	—	0.35	0	—	—

a) 10^{-2} mol g-Ru^{-1} min^{-1} ; H: hydrogenolysis, D: dehydrogenation. The reaction was carried out at 573 K and 1 atm (H_2/cyclohexane=5).

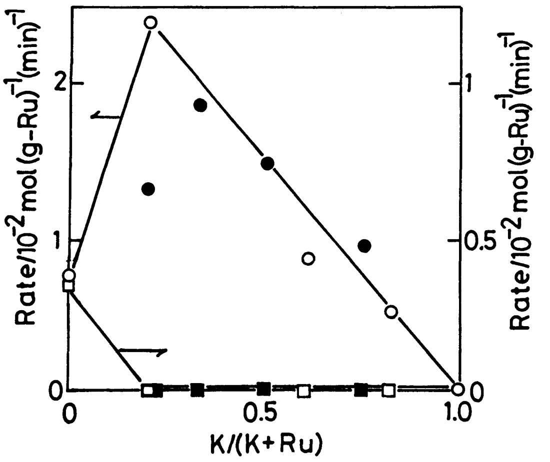

Fig. 1. Effect of K content on activity for conversion of cyclohexane at 573 K.
○: Hydrogenolysis, □: dehydrogenation over Ru-K/SiO_2 (Ru was added to K/SiO_2), ●: Hydrogenolysis, ■: deydrogenation over K-Ru/SiO_2 (K was added to reduced Ru/SiO_2).

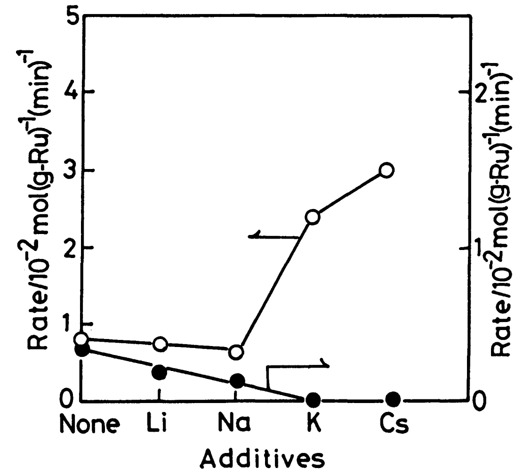

Fig. 2. Effect of kinds of alkali to Ru/SiO_2 on conversion of cyclohexane at 573 K. The content of alkali was 0.20.
○: Hydrogenolysis of cyclohexane, ●: dehydrogenation of cyclohexane.

not significant when the K content was less than 0.60. However, the activity decreased to 1/20 at a K content of 0.82. This decrease caused by Li was not significant, even at a Li content of 0.82.

Conversions of Cyclohexane. At 573 K, Ru/SiO_2 produced both benzene (dehydrogenation) and C_1—C_6 hydrocarbons (hydrogenolysis) in this reaction. The main product of the hydrogenolysis was methane (about 90%). The conversions of both reactions gradually decreased with the reaction time without marked changes in selectivity. Then, the conversions reached stationary values (about half that of the initial conversion) after about 1.5 h. Similar changes in the conversions were obtained for alkali-added catalysts.

Table 4 shows the activities and selectivities obtained at the stationary states. For all catalysts, the selectivity was measured at a conversion level of less than 30%. As shown in Table 4, the activities for hydrogenolysis were almost independent of the Li content, which is the same trend as was observed for the hydrogenolysis of butane (Table 2). On the other hand, dehydrogenation to benzene decreased significantly as the Li content increased. Contrary to this, the presence of K or Cs enhanced the hydrogenolysis. It is remarkable that the formation of benzene was completely suppressed by K or Cs.

In Fig. 1, the effects of K on the conversions of cyclohexane are given; the results of K-Ru/SiO_2 as well as Ru-K/SiO_2 are plotted. It is clear that hydrogenolysis was accelerated by the addition of K at a content level varying from 0.2 to 0.5. This trend was the same in the two different preparation methods.

The effects of the kinds of alkali are illustrated in Fig. 2, where the content of alkali was 0.2. The addition of Cs accelerated the hydrogenolysis, while Li and Na showed little effect. In contrast, the activity for benzene formation decreased monotonically as the atomic number of alkali increased.

Figure 3 shows the effects of the K content on TOF (turnover frequency), where TOF was defined as the number of molecules reacted per exposed Ru atom per second. The TOF of CO hydrogenation, obtained previously,[17] is also plotted in this figure. From Fig. 3, the reactions may be classified into two groups. The first group includes the hydrogenation of benzene and the hydrogenolysis of cyclohexane. In this group the changes of TOF were not significant, that is, within one order of magnitude. The dehydrogenation of

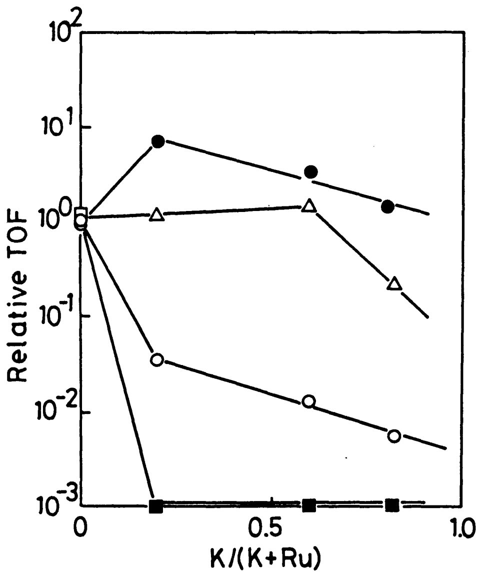

Fig. 3. Changes of TOF of various reactions as a function of K content in Ru-K/SiO_2.
○: $CO+H_2$ at 533 K, ●: hydrogenolysis of cyclohexane at 573 K, ■: dehydrogenation of cyclohexane at 573 K, △: hydrogenation of benzene at 358 K.

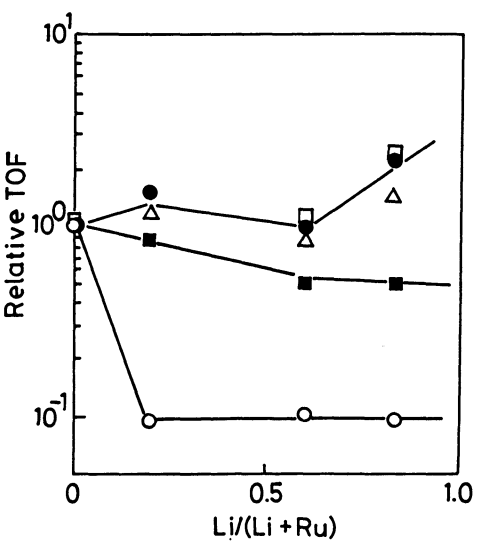

Fig. 4. Changes of TOF of various reactions as a function of Li content in Ru-Li/SiO_2.
○: $CO+H_2$, ●: hydrogenolysis of cyclohexane, ■: dehydrogenation of cyclohexane, △: hydrogenation of benzene, □: hydrogenolysis of butane.

cyclohexane and the CO hydrogenation belong to the second group. The rates of these reactions were markedly suppressed by the addition of K.

In Fig. 4, the effects of Li are summarized. Similarly to the case of K, the TOF's of CO hydrogenation and dehydrogenation of cyclohexane decreased and those of hydrogenolysis of cyclohexane and butane increased as the alkali content increased. However, these changes in both reaction groups were distinctly smaller than in the case of K.

Discussion

The dehydrogenation of cyclohexane is an important reaction involved in the reforming process. Recent studies have shown that the addition of Au to Pt[19] or Cu to Ru(0001)[23] results in enhanced catalytic activities for the formation of benzene from cyclohexane. Miura et al.[20] also observed an enhancement in dehydrogenation and a suppression of hydrogenolysis upon Pt-addition to Ru/SiO_2. However, there has been no report on the effect of alkali-addition for this reaction.

Notable points concerning the present results are (1) the addition of K or Cs enhanced the activity for the hydrogenolysis of cyclohexane, while dehydrogenation to benzene was completely suppressed and (2) the activity changes caused by the alkali depended markedly on both the kinds of alkali and the kinds of reaction. The first result is in contrast with those of the bimetallic catalysts described above.

Effect of K on Conversion of Cyclohexane. Goodman et al.[23] reported that the dehydrogenation of cyclohexane over Ru was enhanced by surface overlayers of carbon or Cu. Over fresh Ru(0001) surface, only hydrogenolysis took place, and benzene (dehydrogenation) began to be formed after an induction period. During this period, a surface layer of carbon was gradually formed, and the dehydrogenation rates increased, indicating that the carbonaceous layer is necessary for benzene formation. On the other hand, the hydrogenolysis rates decreased as the amount of carbon increased. Therefore, the carbonaceous layer effectively suppresses the C-C bond scission of cyclohexane. Goodman et al.[23] also showed that Cu on Ru(0001) played a role similar to that of the carbonaceous layer. Over Cu/Ru(0001), of which Ru(0001) was precovered with submonolayer quantities of Cu, benzene was formed from the beginning of the reaction and the hydrogenolysis reaction did not take place.

If, as described above, the carbonaceous layer is necessary for benzene formation and acts as a poison for the hydrogenolysis reaction, it may be concluded that K suppresses the formation of the carbonaceous layer.

Acceleration of C-C Bond Scission. As shown in Table 1, the addition of K or Cs gave rise to a decrease in dispersion. Therefore, an increase in the activity for the hydrogenolysis (in the unit of per weight of Ru) is not due to an increase in the number of active sites. A certain step of the hydrogenolysis reaction must have been accelerated by the addition of K or Cs. It is accepted for the hydrogenolysis reaction that a hydrogen-deficient species is formed in the initial step by a scission of the C-H bond; subsequently, the C-C bond is broken, and finally the hydrocarbon fragments, thus formed, are hydrogenated.[24-27] Over metallic catalysts, the scission of the C-H bond and the hydrogenation of hydrocarbon fragments are considered to be rapid. Therefore, the rate-determining step is presumably the C–C bond breaking.[27,28] Since K really increased the rates of hydrogenolysis, K must have accelerated the C–C bond breaking step. Probably the carbonaceous layer was not formed on Ru/SiO_2 promoted by K due to the rapid C–C bond breaking.

Effect of Kinds of Alkali. As shown in Fig. 2, the suppression of dehydrogenation and the enhancement of hydrogenolysis became more significant as the atomic number of alkali increased. If one considers the fact that the ability of electron donation of the alkali cation M^+ and/or M_2O, increases as the atomic number increases,[1,2] the results in Fig. 2 may be considered to be mainly brought about by the electronic effects of the alkali. As a matter of fact, the IR band positions of the CO adsorbed on Ru/SiO_2 were not affected by the addition of Li, but these shifted considerably to lower frequencies upon the addition of K.[17] In addition, electron transfer from K to Ru in XPS measurements of Ru/SiO_2[16] and by the IR band positions of the CO or NO adsorbed on Ru/Al_2O_3.[7,15]

A comparison of Figs. 3 and 4 makes clear the influence of the electronic effect on the various kinds of reactions. Although the TOF of the CO hydrogenation decreased by the addition of both Li and K, the decrease was remarkable for K, showing that CO hydrogenation was strongly influenced by an electronic effect.[7] Since H_2 adsorption data indicated that Li and K covered the Ru particles to a similar extent,[17] these alkalis probably bring about similar ensemble effects. Actually, the addition of Cu to Ru also resulted in a great decrease in the rate of CO hydrogenation by the ensemble effect.[29] Thus, the greater effect of K may be due to its stronger electronic effect.

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