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Effects of Alkali Metals Added to Silica-Supported Ruthenium Catalysts on Hydrogenation of Carbon Monoxide

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The hydrogenation of carbon monoxide to produce hydrocarbons (Fischer-Tropsch synthesis) has been studied over Ru/SiO_2 catalysts to which alkali metals (Li, Na, K, and Cs) were added. The effects of alkalis were compared by varying the amounts added and by varying the support to Al_2O_3. By the alkali addition, the CO conversion and the selectivity to methane decreased but the propagation probability as well as the olefin/paraffin ratio increased. Among the alkali metals, Li least depressed the catalytic activity of Ru/SiO_2, but was most effective for the suppression of methane formation. In contrast to a K-added catalyst, the infrared band of adsorbed carbon monoxide shifted only slightly upon Li addition, showing its small electronic effect. The results in electron microscopy and X-ray diffraction suggested that the Ru particle size remained almost unchanged upon Li addition, although the amounts of adsorbed carbon monoxide and hydrogen significantly decreased. This indicates that Ru particles were partially covered by a compound of Li. On the basis of these results, it was concluded that the suppression of methane formation by Li was due to a geometric or ensemble effect.

Chemical modification of metal catalysts by adding certain metal ions/oxides often brings about a significant increase in the catalytic activity and selectivity, e.g., for the synthesis of methanol or ethanol from CO and H_2.[1-4] Alkali metals have been reported to be effective additives to Fe,[5-7] Ni,[8,9] and Ru[10-12] catalysts for the formation of olefinic hydrocarbons from CO and H_2.

The effects of alkali metals have been attributed to an electronic effect caused by the electron-donating nature of alkali for supported metal catalysts.[8,9,12,13] However, McClory and Gonzalez suggested that the decrease of catalytic activity upon alkali addition was associated with an ensemble effect rather than an electronic effect in the case of silica-supported Ru catalysts,[14] although the changes in the selectivities were rather small.

We previously reported the effects of the dispersion of metal[15] as well as the effects of such additives as K, P, and B,[12] and transition metals[16] on the adsorption and the hydrogenation of CO over alumina-supported Ru catalysts. As an extension of these studies, we have investigated in the present work CO hydrogenation using silica-supported Ru catalysts in which the contents of Li, Na, K, and Cs were widely changed. The catalysts were characterized by infrared spectroscopy of CO chemisorption, electron microscopy, X-ray diffraction, and adsorption stoichiometries of H_2 and CO. The relationship between the catalytic property and the state of Ru particles is discussed while placing emphasis on the peculiar effect of the Li addition.

Experimental

Catalysts. Silica (Aerosil 200) was used as supports after calcination in air at 500 °C for 20 h. Silica-supported Ru catalysts were prepared by incipient-wetness impregnation with an aqueous solution of $RuCl_3$. In the case of alkali-added catalysts, the silica was first impregnated by an incipient-wetness method with an aqueous solution of alkali carbonate. Then, it was dried and calcined at 500 °C prior to impregnation with a $RuCl_3$ solution. All catalysts contained 2.5% Ru by weight. Hereafter, these catalysts will be designated as, e.g., Ru/SiO_2 or Ru-Li(1 : 0.25)/SiO_2, where the ratios in parentheses are the atomic ratios of Ru to alkali metal. A catalyst (Li/Ru/SiO_2) was additionally prepared by impregnating a reduced Ru/SiO_2 catalyst with a Li_2CO_3 solution (Li/Ru=0.25).

Alumina-supported Ru catalysts were also prepared in the same way as Ru/SiO_2 or Ru-Li/SiO_2. γ-Al_2O_3 (Reference Catalyst of Catalysis Society of Japan, ALO-4) was used after calcination in air at 400 °C for 10 h.

Procedure. The hydrogenation of CO was carried out by using conventional flow reactors. After catalysts of 0.2—1.5 g were reduced at 450 °C for 2 h in flowing H_2, a 1 : 2 mixture of CO and H_2 was fed at 260 °C under 1 or 10 atm. The products were analyzed by gas chromatographs, by using a Molecular Sieve 5A, a Porapak Q, a VZ-10 and a Silicone SE-30 column. The formation of methanol, ethanol, and acetaldehyde was checked by a Porapak R column.

Other Measurements. The surface areas of SiO_2 and Li/SiO_2 were measured by N_2 adsorption. The adsorption of CO and H_2 was volumetrically measured at room temperature after the catalysts were reduced by H_2 at 450 °C for 2 h. Infrared spectra (IR) of CO adsorbed were recorded in the same way as described previously.[15] Transmission electron micrographs (EM) were obtained with a JEOL JEM 1250 electron microscope (1000 keV, final magnification: ×150000). The particle-size distributions were calculated by counting 300—400 particles of Ru on several micrographs for each catalyst. Powder X-ray diffraction (XRD) was obtained on an X-ray diffractometer (Rotaflex, Rigaku denki). Mean diameters of Ru particles were estimated from the half width of the main peak of Ru metal (2θ=44.0°).

Results

Hydrogenation of CO. The reaction rates and the

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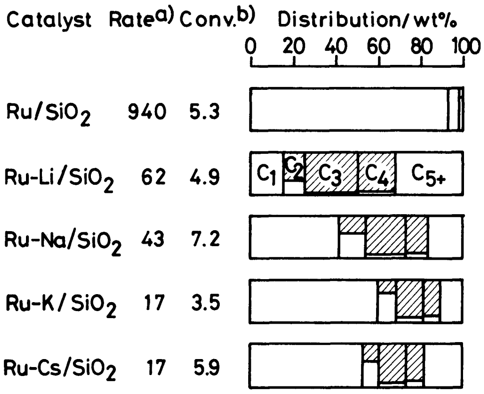

Fig. 1. Effects of alkali addition to Ru/SiO_2 on catalytic activity and product distribution in the CO hydrogenation (260 °C, 1 atm, alkali/Ru = 0.25). Shaded parts indicate olefins in C_2–C_4 products. a) Reaction rate/10^{-3} mol g-Ru^{-1} h^{-1}. b) Conversion/%.

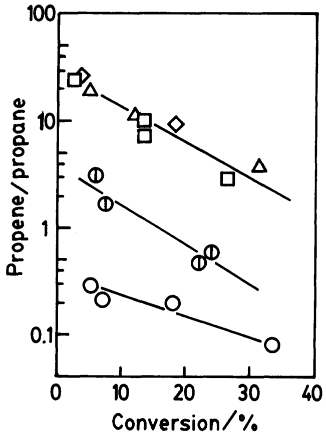

Fig. 2. Propene/propane ratio vs. conversion for the CO hydrogenation on Ru/SiO_2 and Ru-Li/SiO_2 catalysts under 1 atm at 260 °C. ○: Ru/SiO_2, ⦶: Ru-Li (1:0.1)/SiO_2, □: Ru-Li (1:0.25)/SiO_2, △: Ru-Li (1:1.5)/SiO_2, ◇: Ru-Li (1:4.5)/SiO_2.

product distributions of CO hydrogenation performed under 1 atm on Ru/SiO_2 and alkali-added Ru/SiO_2 are summarized in Fig. 1. The formation of methanol, ethanol and acetaldehyde was negligible, and the yield of CO_2 was only about 0.1%. In the case of Ru/SiO_2, methane was the main product, and the contents of olefins in C_2-C_4 hydrocarbons were low. When alkali metals were added, the reaction rates decreased by more than a factor of ten. At the same time, the selectivity to methane considerably decreased, and the selectivities to higher hydrocarbons and olefins increased.

As for the relative extents of the effects, the following trends are noted. The reaction rate decreased in the order of none > Li > Na > K ≈ Cs, while the selectivity to methane was in the order of none > Cs ≈ K > Na > Li. The turnover frequency (TOF) calculated from H_2 chemisorption varied in the same order as the rate (none > Li > Na > K ≈ Cs), since the difference in the H/Ru ratio between alkalis was much smaller than the activity change. It is remarkable that Li showed the least suppression of activity, but was most effective for the suppression of methane. The rates of methane formation were 865 and 9.3 mmol g-Ru^{-1} h^{-1} for Ru/SiO_2 and Ru-Li(1 : 0.25)/SiO_2, respectively, exhibiting a decrease of 1/90 by Li addition. On the other hand, the rate of C_{2+} formation decreased only to 70%; 75 and 53 mmol g-Ru^{-1} h^{-1} for Ru/SiO_2 and Ru-Li (1 : 0.25)/SiO_2, respectively. The Li/Ru/SiO_2 catalyst, which was prepared in the reversed order of impregnations, showed the same activity and selectivity as Ru-Li/SiO_2 (reaction rate: 63 vs. 62 mmol g-Ru^{-1} h^{-1}, selectivity to methane: 16 vs. 15%).

The selectivity to methane was almost independent of the extent of conversion. For example, the selectivity was 93±1% for Ru/SiO_2 and 15±2% for Ru-Li (1 : 1.5)/SiO_2, in the conversion range from 3 to 35%. Distributions of the carbon number of hydrocarbons were also independent of the conversion. This fact shows that the distributions of the carbon number are of the primary products. In Fig. 2, the propene/propane ratios in the products are plotted against the % conversion. Most Ru-Li/SiO_2 catalysts showed high propene/propane ratios, but the ratios tended to decrease with an increase in the conversion for both Ru/SiO_2 and Ru-Li/SiO_2. This fact indicates that the hydrogenation of olefins proceeded significantly under the reaction conditions. Li also enhanced the ethylene/ethane and butenes/butane ratios, which similarly decreased with increasing conversion.

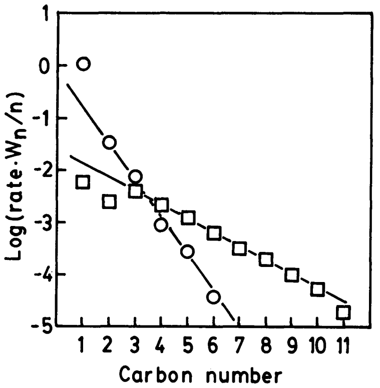

Fig. 3. Schultz-Flory plots (logarithm of (Rate W_n/n), where W_n is weight percentage, and n is carbon number). ○: Ru/SiO_2, □: Ru-Li(1:0.25)/SiO_2.

The distributions of product hydrocarbons for Ru/SiO_2 and Ru-Li(1 : 0.25)/SiO_2 are shown according to Schultz-Flory plots in Fig. 3. The distributions obeyed the Schultz-Flory distribution for C_{3+} products. The production of C_1 produced on Ru/SiO_2 deviated upward from that predicted by the Schultz-Flory plot, but downward on Ru-Li(1 : 0.25)/SiO_2. This implies that Li addition induced a selective suppression of methane formation.

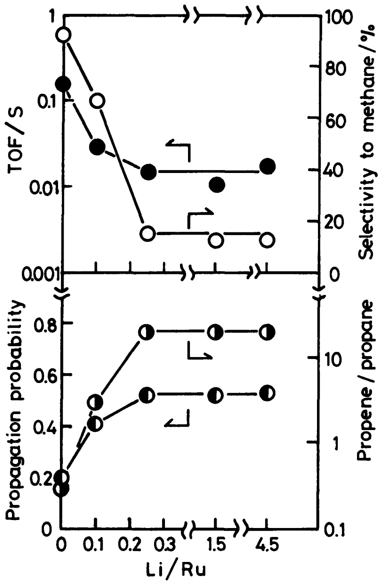

Fig. 4. Effects of the content of Li in Ru-Li/SiO$_2$ on TOF, selectivity to methane, propagation probability, and propene/propane ratio (at 5% conversion) in the CO hydrogenation under 1 atm at 260 °C. ●: TOF, ○: selectivity to methane, ◐: propagation probability, ◑: propene/propane ratio.

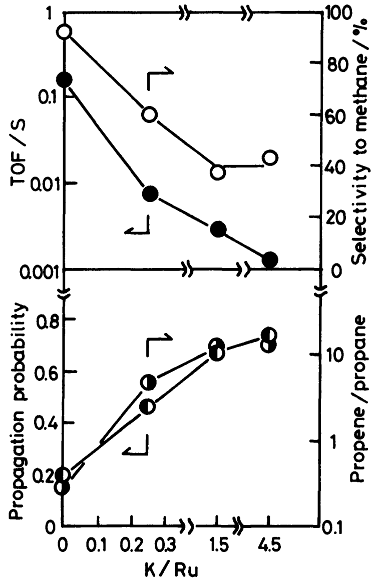

Fig. 5. Effects of the content of K in Ru-K/SiO$_2$ on TOF, selectivity to methane, propagation probability, and propene/propane ratio (at 5% conversion) in the CO hydrogenation under 1 atm at 260 °C. ●: TOF, ○: selectivity to methane, ◐: propagation probability, ◑: propene/propane ratio.

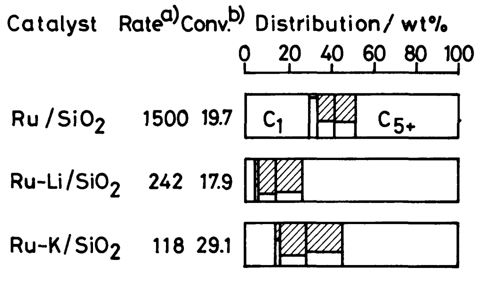

Fig. 6. Effects of alkali addition to Ru/SiO$_2$ on catalytic activity and product distribution in the CO hydrogenation (260 °C, 10 atm, alkali/Ru= 0.25). Shaded parts indicate olefins in C$_2$–C$_4$ products. a) Reaction rate/10^{-3} mol g-Ru^{-1} h^{-1}. b) Conversion/%.

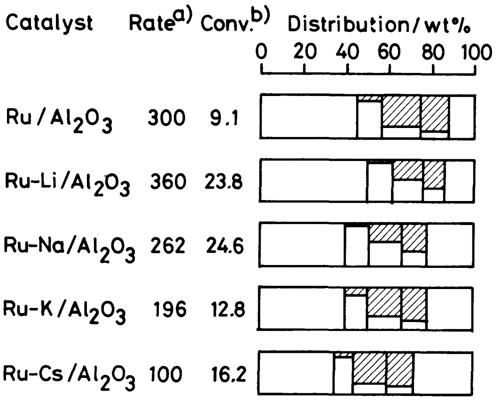

Fig. 7. Effects of alkali addition to Ru/Al$_2$O$_3$ on catalytic activity and product distribution in the CO hydrogenation (260 °C, 1 atm, alkali/Ru= 3). Shaded parts indicate olefins in C$_2$–C$_4$ products. a) Reaction rate/10^{-3} mol g-Ru^{-1} h^{-1}. b) Conversion/%.

In Fig. 4, TOF, selectivity to methane, propagation probability (calculated from Fig. 3), and propene/propane ratio at 5% conversion are plotted against the Li/Ru atomic ratio. In the range of Li/Ru less than 0.25, TOF and the methane formation greatly decreased, while the latter two values increased with an increase in Li/Ru. For Li/Ru greater than 0.25, these values were almost independent of Li/Ru.

Figure 5 shows the effect of K. In the case of K, the selectivity to methane decreased only to about 40%, even when the K/Ru atomic ratio was increased to 4.5. The decrease of TOF was greater and TOF continued to decrease with the amounts of K. The propagation probability and the propene/propane ratio increased monotonously with the amount of K.

Figure 6 shows the results of reactions performed under 10 atm. The reaction rates increased and the formation of higher hydrocarbons was promoted for all catalysts, as compared with the results obtained under 1 atm (Fig. 1). Even under 10 atm, the suppression of methane formation by Li was remarkable; the selectivity to methane decreased from 30 to 5% for Ru-Li(1 : 0.25)/SiO$_2$. The Schultz-Flory plots for Ru/SiO$_2$ and Ru-Li/SiO$_2$ showed essentially the same trend as in Fig. 3, although the slopes were less steep.

The effects of alkali-addition to Ru/Al$_2$O$_3$ are compared in Fig. 7. As already reported, Ru/Al$_2$O$_3$ formed less methane than Ru/SiO$_2$.[12] The extents of methane suppression by alkalis were significantly less than those observed for Ru/SiO$_2$, although the amounts of

Table 1. BET Surface Areas and Amounts of CO and H_2 Adsorbed on Ru-Li/SiO_2 Catalysts

Li wt%	0	0.018	0.045	0.26	0.77
Li/Ru[a]	0	0.1	0.25	1.5	4.5
Surface area[b]	160	152	136	143	88
H/Ru[c]	0.17	0.15	0.12	0.12	0.06
CO/Ru[d]	0.14	0.11	0.05	0.06	0.05

a) Atomic ratio. b) Surface areas/$m^2 g^{-1}$; measured before impregnation of Ru. c) Total adsorption at 25 °C. d) Irreversible adsorption at 25 °C.

alkali metals were twelve times greater than that for Ru/SiO_2.

Characterization of Catalysts. Surface areas of SiO_2 and Li-SiO_2 before Ru impregnation are shown in Table 1. The supports containing 0.018, 0.045, 0.26, and 0.77 wt% of Li correspond to atomic ratios of Li to Ru 0.1, 0.25, 1.5, and 4.5, respectively, when 2.5 wt% of Ru is loaded. The decrease in the surface area was not significant when Li was not more than 0.26 wt%. The data of H_2 and CO adsorption are also given in Table 1. The amounts decreased with the Li content. The decrease was a little greater for CO as reported for K-added Ni/SiO_2,[13] but the reason is not clear at present.

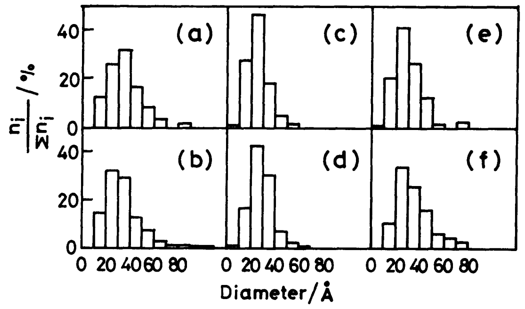

Fig. 8. Distribution of diameters of Ru particles on (a) Ru/SiO_2 after H_2 reduction at 450 °C, (b) Ru/SiO_2 after CO hydrogenation at 260 °C, (c) Ru-Li (1:1.5)/SiO_2 after H_2 reduction at 450 °C, (d) Ru-Li (1:1.5)/SiO_2 after CO hydrogenation at 260 °C, (e) Ru-Li (1:4.5)/SiO_2 after H_2 reduction at 450 °C, and (f) Ru-Li (1:4.5)/SiO_2 after CO hydrogenation at 260 °C.

Figure 8 shows the size distributions of Ru particles on Ru/SiO_2 and Ru-Li/SiO_2 catalysts measured by EM before and after use for CO hydrogenation. For all catalysts, the distributions little changed by the use for CO hydrogenation. The distributions were centered at ca. 30 Å, and a few Ru particles were present above 60 Å. The distributions for Ru/SiO_2 were slightly wider than those on Ru-Li/SiO_2, but there was no essential difference.

Table 2. Mean Diameters of Ru Particles of Ru-Li/SiO_2 Catalysts

Li/Ru[a]	0	0.1	0.25	1.5	4.5
Mean diameters/Å					
H_2 adsorption	49	57	70	68	131
EM[b]	35	—	—	25	28
EM[c]	34	—	—	28	35
XRD	50	45	50	43	45

a) Atomic ratio. b) Diameters measured after H_2 reduction at 450 °C. c) Diameters measured after CO hydrogenation at 260 °C.

Table 2 summarizes the mean diameters of Ru particles, which were determined by H_2 adsorption, EM, and XRD. The diameters determined by EM decreased upon the addition of Li, but the change was small. Those determined by XRD, which were slightly greater than those by EM, showed no significant change either. On the other hand, the apparent diameter determined by H_2 adsorption definitely increased upon the addition of Li.

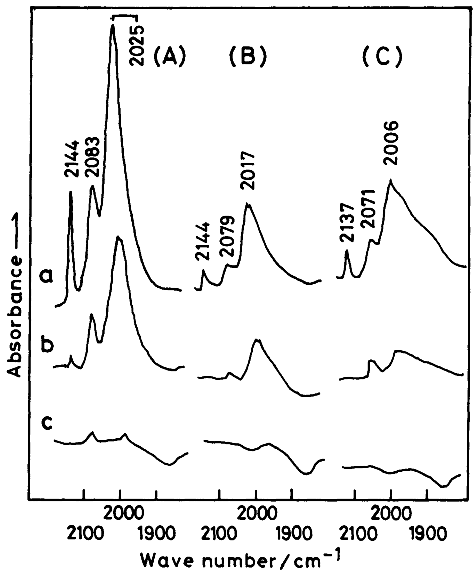

Fig. 9. IR spectra of CO adsorbed on (A) Ru/SiO_2, (B) Ru-Li (1:0.25)/SiO_2, and (C) Ru-K (1:0.25)/SiO_2. The spectra of CO were taken after evacuation at (a) 25 °C, (b) 100 °C, and (c) 200 °C.

Figure 9 shows IR spectra of CO adsorbed on Ru/SiO_2, Ru-Li(1 : 0.25)/SiO_2, and Ru-K(1 : 0.25)/SiO_2. Three peaks at 2025, 2083, and 2144 cm^{-1} were observed for CO on Ru/SiO_2 after evacuation at room temperature. The intensity decreased with an increase in the evacuation temperature, and almost disappeared after evacuation at 200 °C. In the case of Ru-Li/SiO_2, a band was observed at 2017 cm^{-1}, together with two small peaks at 2079 and 2144 cm^{-1}. The relative integrated intensity agreed with the amount of adsorbed CO shown in Table 1. The shift of the main peak was less than about 8 cm^{-1}. On the other hand, the main peak at 2006 cm^{-1} for Ru-K/SiO_2 showed a shift of about 20 cm^{-1} and the peak envelope extended to the lower wavenumber side. The two peaks at 2083 and 2144 cm^{-1}, which were assigned to CO adsorbed on $Ru^{\delta+}$,[17,18] also shifted but to a lesser extent for $Ru\text{-}K/SiO_2$.

Discussion

The principal effects of alkali addition were: (i) a decrease in the catalytic activity, (ii) a suppression of methane formation, (iii) an increased selectivity to higher hydrocarbons, and (iv) an increase in the olefin/paraffin ratio. These effects agreed with those mentioned in the literature.[5-12] As for the kind of alkali metals and the order of catalytic activity: none > Li > Na > K≈Cs, is consistent with those reported for CO hydrogenation on Rh/TiO_2[19] and for methanol formation on Pd/SiO_2.[1] However, it is remarkable that the extent of methane suppression was Li > Na > K≈Cs > none, Li exhibiting the greatest effect. If the suppression of both activity and methane formation was controlled by one common factor like an electronic effect, these effects should show the same orders. In fact, the two orders for Ru/Al_2O_3 were the same. Thus, an additional effect must be considered in the case of $Ru\text{-}Li/SiO_2$.

Effects of Alkalis on the Adsorption of H_2 and CO. The possible effects caused by the addition of alkalis are (i) a change of particle size, (ii) an electronic effect on Ru, and (iii) a geometric or ensemble effect.

As shown in Table 2, the particle size calculated from the amounts of adsorbed H_2 (given in Table 1) definitely increased upon Li addition (more than two times), but the particles sizes determined by EM and XRD changed little or slightly decreased. Therefore, the decreases in the amounts of adsorbed CO and H_2 upon Li addition were not ascribable to the increase in the size of Ru particles. One possible explanation may be an electronic effect. Due to a change in the electronic state of Ru caused by Li, a Ru surface might lose the ability to adsorb H_2 and CO. However, the electronic effect was not significant for $Ru\text{-}Li/SiO_2$ as inferred from IR of adsorbed CO. The IR band for $Ru\text{-}Li/SiO_2$ shifted only by 8 cm^{-1} (Fig. 9), as compared to 20 cm^{-1} for $Ru\text{-}K/SiO_2$ and 40 cm^{-1} for $Ru\text{-}K/Al_2O_3$.[12]

If one considers the small electronic effect of Li as well as the small change in the particle size, it is more likely that the decreases in the amounts of adsorbed CO and H_2 were due to partial coverage of the Ru surface by Li. This is similar to a "decoration model" proposed for the SMSI effect.[20-22] It is possible that during the preparation and/or activation process of the catalyst, a portion of Li is transported in a form close to Li_2O to the surface of the Ru particles without changing the particle size. The small change observed when the impregnation order was reversed may be consistent with this explanation.

A possible reason for the smaller effects of alkali for Ru/Al_2O_3 (Fig. 7) than for Ru/SiO_2 (Fig. 1) may be that the migration of Li onto the Ru surface was suppressed by the higher affinity of Li to Al_2O_3 support.

Effects of Alkalis on the Catalytic Property in CO Hydrogenation. It has been known for Ru/Al_2O_3 that TOF of CO hydrogenation changes inversely with the particle size of Ru.[15,23,24] In contrast, when Li was added to Ru/SiO_2, although the particle size decreased slightly (Table 2), TOF considerably decreased (Fig. 4). Therefore, the decrease in TOF was not due to the change in the particle size.

We previously reported that the effects of the addition of K, P, and B to Ru/Al_2O_3 were due to an electronic effect. However, the electronic effect of Li seems much smaller than that of K (as discussed above) in spite of the fact that Li was much more effective than K for the suppression of methane. Therefore, the electronic effect is not likely to be the primary function of Li.

We also studied the effect of V addition to Ru/Al_2O_3 and explained the results in terms of a geometric effect that is similar to an ensemble effect.[16] The effects of Li observed in the present study are rather similar to those of V with regard to activity and methane formation. Therefore, a similar geometric effect may be considered to be the primary function of Li in $Ru\text{-}Li/SiO_2$. The model proposed in the preceding section, that a Li compound partially covered the Ru surface, is consistent with the presence of a geometric effect.

McClory and Gonzalez reported that the addition of alkali to Ru/SiO_2 decreased the activity, enhanced the selectivities to olefins, and slightly suppressed methane formation.[14] In their study, however, changes in selectivities were much smaller and little difference was observed among the alkali metals. The differences between their and our results are attributable to the amounts of alkalis added. The amounts were 0.1 in atomic ratio to Ru in their study as compared with 0.1—4.5 in the present study. As shown in Fig. 4, the effects became significant when Li/Ru ratio was 0.25.

McClory and Gonzalez explained the above effect of alkali by an ensemble effect which lowered the ability for hydrogenation.[14] The suppression of methane formation and the enhancement of the olefin/paraffin ratio is consistent with the lower ability for hydrogenation. Therefore, the same explanation may be applicable to the effect of alkali observed in the present study. The selective suppression of methane formation, as observed in the present study, indicates that the geometric or ensemble effect was greater for methane formation; methane formation may need larger ensembles or more adjacent sites to supply more hydrogen atoms for the hydrogenation of the CH_x intermediate to methane. Another possibility is that sites which selectively produced methane were present on the Ru surface and Li preferentially poisoned these sites. The fact that methane formation was suppressed by a factor of 90 while the C_{2+} formation decreased only to 70% favors this explanation. However, there is no direct evidence in the present study to show the presence of those sites.

An increase in the olefin/paraffin ratio was also found in the case of K addition to Ru/Al_2O_3 in our previous study.[12] In the case of Ru/Al_2O_3, the principal effect of K was the suppression of the secondary hydrogenation of olefin due to the increased CO coverage. But, in the case of $Ru-Li/SiO_2$, secondary hydrogenation was little suppressed. This fact also indicates that the effect is different for K and Li.

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