Synthesis of Light Olefins from CO and H_2 over Highly Dispersed Ru/K–Al_2O_3 derived from $Ru_3(CO)_{12}$

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Summary A highly dispersed Ru/Al_2O_3 catalyst, prepared from $Ru_3(CO)_{12}$ was much more active and selective for C_2—C_5 olefins in the hydrogenation of CO than conventionally prepared Ru/Al_2O_3 catalyst, and addition of K to the carbonyl-derived catalyst enhanced significantly the preferential formation of light olefins (*ca.* 80% at 260 °C).

Recently, much attention has been directed towards the selective synthesis of light olefins like ethylene and propene in the Fischer–Tropsch reaction. Only a few catalysts have been reported to show high selectivity for light olefins.

Commereuc *et al.*[1] reported novel Fe catalysts prepared from $Fe_3(CO)_{13}$ which exhibited high selectivity for propene (45%) at the initial stage of the reaction. Vannice *et al.*[2] found that $K_2Fe(CO)_4$ supported on Al_2O_3 was active and selective for C_2—C_4 olefins (50%). Recently, Yasumori *et al.*[3] demonstrated that Mo_2C produced 52% ethylene but that the activity was very low. Mixed oxide catalysts such as Fe_3O_4–TiO_2–ZnO–K_2O[4] and Co–Mn–Al_2O_3–K_2O[5] have been known to yield C_2—C_4 olefins preferentially. We report here that catalysts prepared by thermal decomposition of $Ru_3(CO)_{12}$ on Al_2O_3 have very high dispersion and afford light olefins in the hydrogenation of CO. Moreover, addition of K to this catalyst enhanced the preferential formation of light olefins.

γ-Al_2O_3 (170 m^2/g, reference catalyst ALO-4, The Catalysis Society of Japan) was calcined in air at 500 °C for 10 h and then subjected to a stream of N_2 for 2 h. K–Al_2O_3 supports were obtained by the addition of an aqueous solution of K_2CO_3 to the γ-Al_2O_3 and were treated in the same way as γ-Al_2O_3.

The catalysts were prepared by impregnation of the supports with $Ru_3(CO)_{12}$ (Stream Chemical Co.) in n-hexane solution and the solvent was removed in the stream of N_2. Conventional Ru/Al_2O_3 catalysts were prepared by the standard incipient wetness technique from $RuCl_3$ and $RuNO(NO_3)_3$. These catalysts were evacuated and reduced by H_2 at 450 °C for 2 h prior to the reaction and H_2-chemisorption. Hereafter, these catalysts are described as, *e.g.*, $Ru_3(CO)_{12}$/Al_2O_3 or $RuCl_3$/K–Al_2O_3. The reaction was carried out in a conventional circulating system (200 ml) at an initial pressure of 500 mmHg (H_2:CO = 2) at 200 or 260 °C; the products other than methane were collected in a trap kept at liquid nitrogen temperature to suppress secondary reactions. The products were analysed by gas chromatography, and the activities and selectivities were determined at the 10—25% conversion level in the second run in which the reaction proceeded with a steady rate.

Typical results are given in the Table. The chemisorption of H_2 was measured in a static system (60 ml) at room temperature. The dispersion was calculated from the

TABLE. Activities and selectivities in Fischer–Tropsch synthesis over Ru/Al$_2$O$_3$.[a]

				% Product distribution[f]							
				Saturated		Unsaturated					
Catalyst[b]	Dispersion	Rate[e]	S(CO$_2$)[f] (%)	C$_1$	C$_2$–C$_6$[g]	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	Total olefins (%)
Ru$_3$(CO)$_{12}$[c]	0·9	2·3	1·8	8·2	12·3	2·3	28·5	24·8	15·6	8·3	79·5
RuCl$_3$[c]	0·15	1·3	0·2	24·0	23·8	1·9	18·4	17·9	11·9	2·1	52·2
Ru$_3$(CO)$_{12}$[d]	0·9	12·2	1·4	29·0	20·3	3·0	22·3	14·1	7·6	3·7	50·7
RuCl$_3$[d]	0·15	11·3	2·5	33·2	26·8	4·2	18·4	11·1	5·2	1·1	40·0
RuNO(NO)$_3$[d]	0·20	2·3	7·9	20·9	44·6	0·4	8·7	13·4	9·5	2·5	34·5
Ru$_3$(CO)$_{12}$–K[d]	0·9	4·5	5·0	18·9	6·7	9·3	28·9	14·0	13·1	9·1	74·4
RuCl$_3$–K[d]	0·14	4·0	1·2	39·8	16·9	0·6	15·4	14·2	7·6	5·5	45·5

[a] CO + H$_2$ = 500 mmHg, H$_2$:CO = 2. [b] Support: γ-Al$_2$O$_3$. Loading amounts of Ru are 2·5 wt.% for Ru$_3$(CO)$_{12}$ and RuCl$_3$, 0·9 wt.% for RuNO(NO$_3$)$_3$. Loading amount of K is 1 wt.%. [c] T = 200 °C. [d] T = 260 °C. [e] × 10^{-2} g atom of C/(g Ru)h. [f] S(CO$_2$) (selectivity to CO$_2$) = 100 × N(CO$_2$)/[Σ{nN[C_n (sat.)] + nN[C$_n$ (unsat.)]} + N(CO$_2$)]. Percentage of C$_n$ (sat.) or C$_n$ (unsat.) = 100 × {nN[C$_n$(sat.)] or nN[C$_n$(unsat.)]}/Σ{nN[C$_n$(sat.)] + nN[C$_n$(unsat.)]} where C$_n$(sat.), C$_n$(unsat.) = paraffin, olefin with n carbon atoms, N[C$_n$(sat.)], N[C$_n$(unsat.)] = number of hydrocarbon molecules with n carbon atoms, and N(CO$_2$) = number of CO$_2$ molecules formed. [g] Total paraffins with carbon atoms from 2 to 6.

equilibrium amount of H$_2$ adsorption at an H$_2$ pressure of *ca.* 60 mmHg by assuming that one hydrogen atom was adsorbed on each Ru atom on the surface. It is apparent that the Ru dispersion in Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ is very high compared with conventional catalysts. Addition of K (1 wt.%) did not change the dispersion of Ru for either Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ or RuCl$_3$/Al$_2$O$_3$. In CO hydrogenation, Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ was more active and selective for olefins than conventional catalysts; thus at 200 °C, Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ produced olefins with 80% selectivity, compared with 52% on RuCl$_3$/Al$_2$O$_3$. The selectivities declined to 55% for Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ and 40% for RuCl$_3$/Al$_2$O$_3$ at 260 °C.

Addition of K to Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ significantly enhanced the preferential formation of olefins, but the selectivity was not affected by the presence of K on RuCl$_3$/Al$_2$O$_3$. The selectivity for olefins formed on Ru$_3$(CO)$_{12}$/K–Al$_2$O$_3$ was *ca.* 75% which is very high compared with 46% found with RuCl$_3$/K–Al$_2$O$_3$ at 260 °C. The activities of both Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ and RuCl$_3$/Al$_2$O$_3$ were similarly depressed by the addition of K. Thus, K has different effects on the activity and selectivity in the hydrogenation of CO.

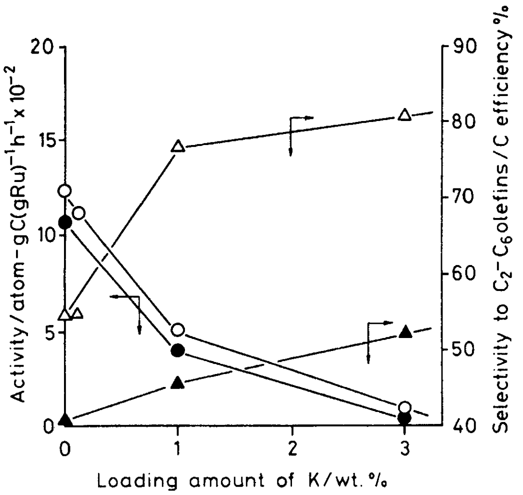

FIGURE. Changes in catalytic activities and selectivities with loading amount of K for Fischer–Tropsch synthesis. CO + H$_2$ = 500 mmHg (H$_2$:CO = 2), 260 °C. ○,△: Ru$_3$(CO)$_{12}$/K–Al$_2$O$_3$ (Ru: 2·5 wt.% metal); ●,▲: RuCl$_3$/K–Al$_2$O$_3$ (Ru: 2·5 wt.% metal).

The Figure shows the variation of activity and selectivity as a function of the loading amount of K. A similar drop in activity with increase in loading amount was observed for both catalysts. No promotional effect of K on the selectivity was observed in the case of RuCl$_3$/Al$_2$O$_3$. On the contrary, addition of more than 1 wt.% of K to Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ increased the formation of olefins. These changes in activity and selectivity on addition of K indicate that K affects the electronic state or morphology of Ru on Al$_2$O$_3$. The surface area of 1% K–Al$_2$O$_3$ was 150 m^2/g, which is close to that of Al$_2$O$_3$.

Ru$_3$(CO)$_{12}$/K–Al$_2$O$_3$ was found to be less active than Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ for the hydrogenolysis of ethane at 150 °C, by a factor of about 4, possibly because addition of K reduces the activation of H$_2$. The rate of the disproportionation of CO on Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ at 230 °C was not affected by the addition of K at the initial stage. The total amount of CO$_2$ formed from CO was increased by addition of K by a factor of 1·3.

The i.r. band due to adsorbed CO on Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ appeared at 2044 cm^{-1}, and was shifted to 2000 cm^{-1} by the addition of K (1 wt.%). However, adsorbed CO on both catalysts could be removed in a similar manner with increase in evacuation temperature. When hydrogenation of the adsorbed CO which remained at 200 °C was carried out at 200 °C for 1 h, half of the band intensity due to adsorbed CO disappeared in the case of Ru$_3$(CO)$_{12}$/Al$_2$O$_3$, but only a little (a few percent) was removed in the case of Ru$_3$(CO)$_{12}$/K–Al$_2$O$_3$.

From these results, we suggest that addition of K to Ru$_3$(CO)$_{12}$ causes depression of the H$_2$ dissociation and an increase in unreactive adsorbed CO, decreasing the activity for the hydrogenation of CO. This suppression of activity does not necessarily result in an increase in selectivity for olefins (Table, Figure). Therefore, the enhancement of the olefin selectivity may be explained by an acceleration in β-hydrogen abstraction from the surface alkyl intermediate.

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