Synthesis of Light Olefins from CO and H$_2$ over Highly Dispersed Ru/K–Al$_2$O$_3$ derived from Ru$_3$(CO)$_{12}$

By Toshio Okuhara,* Kenji Kobayashi, Tomoo Kimura, Makoto Misono,* and Yukio Yoneda

(Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, Japan)

Summary A highly dispersed Ru/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$Fe(CO)$_4$ supported on Al$_2$O$_3$ was active and selective for C$_2$—C$_4$ olefins (50%). Recently, Yasumori *et al.*[3] demonstrated that Mo$_2$C produced 52% ethylene but that the activity was very low. Mixed oxide catalysts such as Fe$_3$O$_4$–TiO$_2$–ZnO–K$_2$O[4] and Co–Mn–Al$_2$O$_3$–K$_2$O[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$_2$O$_3$ 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$_2$O$_3$ (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$_2$O$_3$ supports were obtained by the addition of an aqueous solution of K$_2$CO$_3$ to the γ-Al$_2$O$_3$ and were treated in the same way as γ-Al$_2$O$_3$.

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$_2$O$_3$ 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$_2$O$_3$ or RuCl$_3$/K–Al$_2$O$_3$. 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/Al₂O₃.ᵃ

| | | | | % Product distributionᶠ | | | | | | | |
| | | | | Saturated | | Unsaturated | | | | | Total olefins |
Catalystᵇ	Dispersion	Rateᵉ	$S(CO_2)$ᶠ (%)	C_1	C_2-C_6ᵍ	C_2	C_3	C_4	C_5	C_6	(%)
Ru₃(CO)₁₂ᶜ	0·9	2·3	1·8	8·2	12·3	2·3	28·5	24·8	15·6	8·3	79·5
RuCl₃ᶜ	0·15	1·3	0·2	24·0	23·8	1·9	18·4	17·9	11·9	2·1	52·2
Ru₃(CO)₁₂ᵈ	0·9	12·2	1·4	29·0	20·3	3·0	22·3	14·1	7·6	3·7	50·7
RuCl₃ᵈ	0·15	11·3	2·5	33·2	26·8	4·2	18·4	11·1	5·2	1·1	40·0
RuNO(NO)₃ᵈ	0·20	2·3	7·9	20·9	44·6	0·4	8·7	13·4	9·5	2·5	34·5
Ru₃(CO)₁₂–Kᵈ	0·9	4·5	5·0	18·9	6·7	9·3	28·9	14·0	13·1	9·1	74·4
RuCl₃–Kᵈ	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-Al₂O₃. Loading amounts of Ru are 2·5 wt.% for Ru₃(CO)₁₂ and RuCl₃, 0·9 wt.% for RuNO(NO₃)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) = $100 \times N(CO_2)/[\Sigma\{nN[C_n (\text{sat.})] + nN[C_n (\text{unsat.})]\} + N(CO_2)]$. Percentage of C_n (sat.) or C_n (unsat.) = $100 \times \{nN[C_n(\text{sat.})] \text{ or } nN[C_n(\text{unsat.})]\}/\Sigma\{nN[C_n(\text{sat.})] + nN[C_n(\text{unsat.})]\}$ where C_n(sat.), C_n(unsat.) = paraffin, olefin with n carbon atoms, $N[C_n(\text{sat.})]$, $N[C_n(\text{unsat.})]$ = 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 Ru₃(CO)₁₂/Al₂O₃ is very high compared with conventional catalysts. Addition of K (1 wt.%) did not change the dispersion of Ru for either Ru₃(CO)₁₂/Al₂O₃ or RuCl₃/Al₂O₃. In CO hydrogenation, Ru₃(CO)₁₂/Al₂O₃ was more active and selective for olefins than conventional catalysts; thus at 200 °C, Ru₃(CO)₁₂/Al₂O₃ produced olefins with 80% selectivity, compared with 52% on RuCl₃/Al₂O₃. The selectivities declined to 55% for Ru₃(CO)₁₂/Al₂O₃ and 40% for RuCl₃/Al₂O₃ at 260 °C.

Addition of K to Ru₃(CO)₁₂/Al₂O₃ significantly enhanced the preferential formation of olefins, but the selectivity was not affected by the presence of K on RuCl₃/Al₂O₃. The selectivity for olefins formed on Ru₃(CO)₁₂/K–Al₂O₃ was ca. 75% which is very high compared with 46% found with RuCl₃/K–Al₂O₃ at 260 °C. The activities of both Ru₃(CO)₁₂/

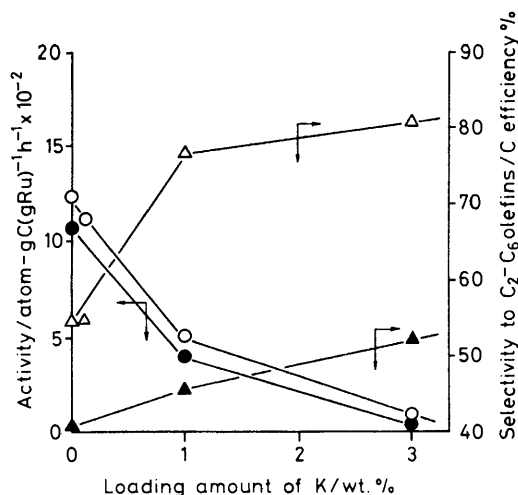Figure. Changes in catalytic activities and selectivities with loading amount of K for Fischer–Tropsch synthesis. $CO + H_2 = 500$ mmHg ($H_2:CO = 2$), 260 °C. ○,△: Ru₃(CO)₁₂/K–Al₂O₃ (Ru: 2·5 wt.% metal); ●,▲: RuCl₃/K–Al₂O₃ (Ru: 2·5 wt.% metal).

Al₂O₃ and RuCl₃/Al₂O₃ were similarly depressed by the addition of K. Thus, K has different effects on the activity and selectivity in the hydrogenation of CO.

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 RuCl₃/Al₂O₃. On the contrary, addition of more than 1 wt.% of K to Ru₃(CO)₁₂/Al₂O₃ 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 Al₂O₃. The surface area of 1% K–Al₂O₃ was 150 m²/g, which is close to that of Al₂O₃.

Ru₃(CO)₁₂/K–Al₂O₃ was found to be less active than Ru₃(CO)₁₂/Al₂O₃ 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 Ru₃(CO)₁₂/Al₂O₃ 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 Ru₃(CO)₁₂/Al₂O₃ 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 Ru₃(CO)₁₂/Al₂O₃, but only a little (a few percent) was removed in the case of Ru₃(CO)₁₂/K–Al₂O₃.

From these results, we suggest that addition of K to Ru₃(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.

[1] D. Commereuc, Y. Chauvin, F. Hughes, M. Basset, and D. Oliver, J. Chem. Soc., Chem. Commun., 1980, 154.
[2] G. B. McVicker and M. A. Vannice, J. Catal., 1980, 63, 25.
[3] I. Kojima, E. Miyazaki, and I. Yasumori, J. Chem. Soc., Chem. Commun., 1980, 573.
[4] Ruhrchemie, Dutch Patent Appl. 75/10,634 (1975).
[5] A. L. Dent and M. Lin, Adv. Chem. Ser., 1978, 178.