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Selective Production of C_4-C_{10} Hydrocarbons in Hydrogenation of Carbon Monoxide over Ruthenium Supported on Al_2O_3-Intercalated Montmorillonite

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C_4 to C_{10} hydrocarbons (main fractions of gasoline) were selectively produced by hydrogenation of CO over Ru supported on Al_2O_3-intercalated montmorillonite, presumably due to shape-selective secondary reactions of hydrocarbons in the pores of the support.

Montmorillonite (natural clay) has a layer structure and an ion-exchange ability. By using these properties, several oxide pillars can be introduced into the interlayer spaces of montmorillonite.1-4) Since the resulting intercalated montmorillonites showed pore structures, high thermal stabilities1,2,5) and acidities,6) these intercalated montmorillonites have attracted much attention to possible use as shape-selective solid acid catalysts for cumene cracking,7) methanol conversion to hydrocarbons,8) alkylation,9,10) disproportionation of trimethylbenzene11) or supports for metal catalysts.12,13) However, only a few successful results have been reported as for the shape-selectivity. We reported previously shape-selective hydrogenation of methyl-substituted benzenes over a Ru supported on Al_2O_3-intercalated montmorillonite.13) As for the hydrogenation of carbon monoxide over Fe_3O_4-intercalated montmorillonite, a patent has been applied,14) but the shape-selectivity is not obvious.

Here we wish to report a high selectivity found for the production of C_4-C_{10} hydrocarbons in the CO hydrogenation over the Ru supported on Al_2O_3-intercalated montmorillonite (abbreviated as Ru/Mont-Al_2O_3 hereafter). The distribution of carbon number of the product hydrocarbons deviated significantly from that expected from the Schulz-Flory distribution, and the activity and selectivity were stable at least for 45 h.

Al_2O_3-intercalated montmorillonite prepared according to the literature15) (OH/Al = 1.85, Al/montmorillonite = 3.0, abbreviated as Mont-Al_2O_3) was kindly supplied by Kunimine Kogyo Co. Ltd. and used after calcination at 400 °C for 4 h. It showed a fairly strong XRD line corresponding to the interlayer space of 8.1 Å (the distance of basal planes; 17.7 Å) and a surface area of 316 $m^2 \cdot g^{-1}$. Ru was loaded on the support by an ion-exchange method using an aqueous $Ru(NH_3)_6Cl_3$ solution at 70-80 °C. After filtration, washing and drying at 110 °C, the catalyst was reduced by H_2 at 400 °C in the reactor just before the catalytic use. The amount of Ru loaded was 0.6 wt%. For comparison purpose, Ru/SiO_2 (Ru: 1 wt%) prepared by impregnation of SiO_2 with an aqueous $RuCl_3$ solution, as well as Ru/NaY zeolite (Ru: 1.0 wt%) prepared by the ion-exchange method, were used as catalysts. Hydrogenation of CO was carried out by a flow method at 240 °C and 10^3 kPa. The feed gas was a mixture of H_2 and CO (1.9 : 1).

Figure 1 shows the changes of reaction rate and the composition of product hydrocarbons with time for CO hydrogenation over Ru/Mont-Al_2O_3. The reaction rate did not change greatly for at least 45 h. The product distribution became nearly constant after about 30 h, methane being significant at the initial stage. In the case of Ru/SiO_2, the reaction rate reached a stationary value at about 5 h after a slight decrease during the initial stage of the reaction. It was observed that the product composition over Ru/SiO_2 was nearly constant after 5 h.

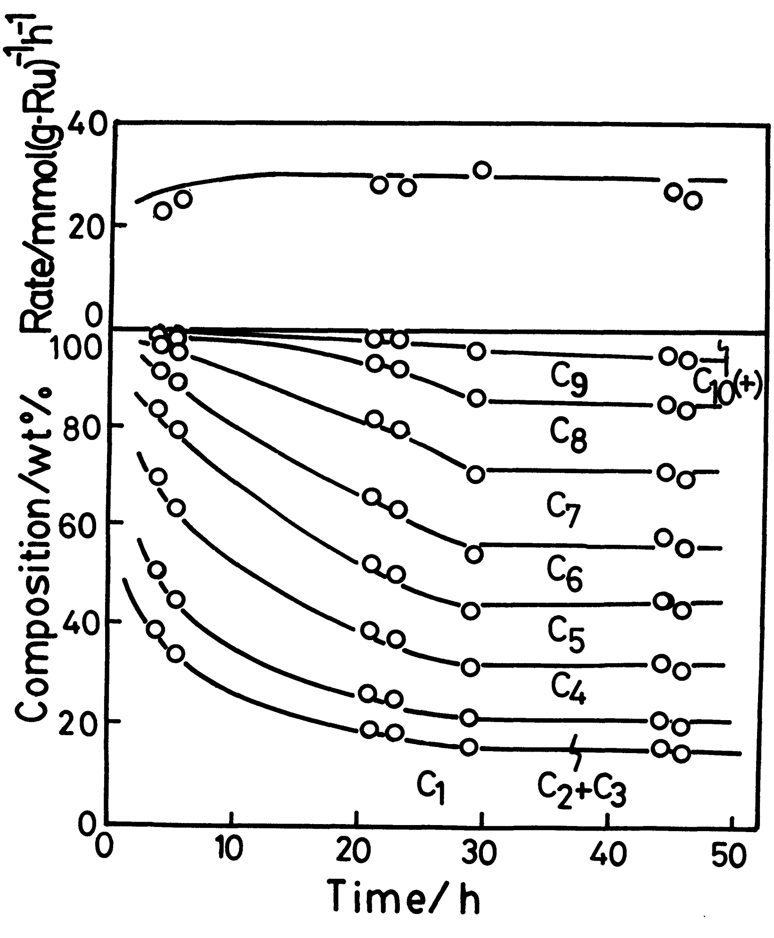

Fig. 1. Changes of the rate and product composition with reaction time in CO hydrogenation over 0.6%Ru/Mont-Al_2O_3.
Reaction conditions: 240 °C, 10^3 kPa (H_2/CO = 1.9), W/F = 418 g-cat·h·CO-mol^{-1}

The distributions of carbon number are compared for Ru/Mont-Al_2O_3 and Ru/SiO_2 in Fig. 2 and the related data are summarized in Table 1. These data were obtained at the conversion level of 5 - 10%. It was confirmed that the selectivity was almost unchanged for 2 - 10% conversion. Data shown are the stationary values. The distribution of carbon number ($\geq$3) for Ru/SiO_2 followed the Schulz-Flory distribution with a propagation probability of 0.85. In contrast, in the case of Ru/Mont-Al_2O_3, the production of hydrocarbons higher

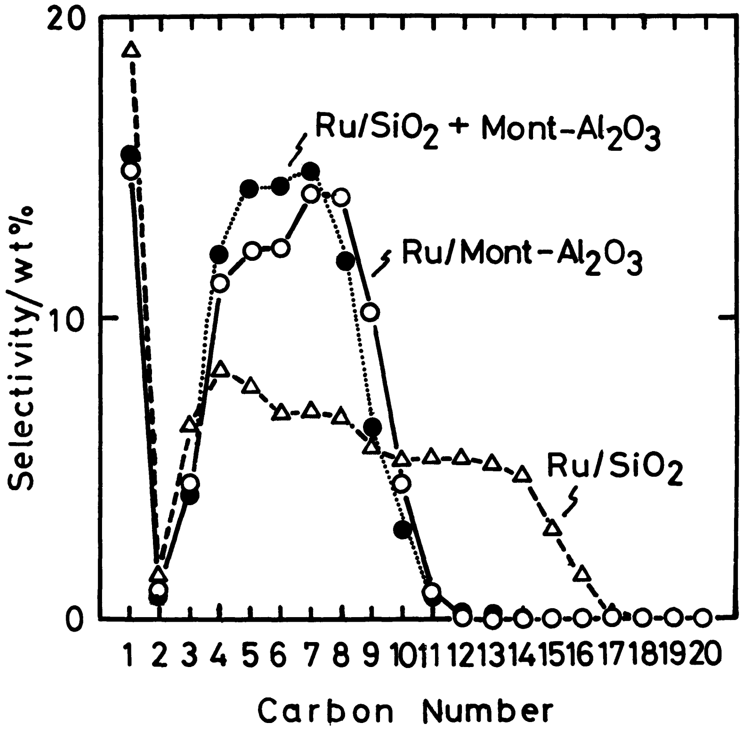

Fig. 2. Distribution of carbon number in the product hydrocarbons of CO hydrogenation (conversion; 5.9% for 0.6%Ru/Mont-Al_2O_3, 6.2% for 1%Ru/SiO_2, 3.9% for 1%Ru/SiO_2 + Mont-Al_2O_3).
Reaction conditions: 240 °C, 10^3 kPa (H_2/CO = 1.9)

Table 1. Rates and Products of CO Hydrogenation over Ru Catalysts

	Activity[a]	Selectivity/wt%				iso/normal[b]
		C_1	C_2,C_3	C_4-C_{10}	C_{11}(+)	
Ru/SiO_2	170	19	8	47	26	0
Ru/Mont-Al_2O_3	26	15	5	79	1	1.4
RuNaY zeolite	120	16	12	67	5	0.1
Ru/SiO_2 + Mont-Al_2O_3[c]	130	15	5	77	3	1.5

a) Reaction rate; mmol·g-$Ru^{-1}h^{-1}$. b) In C_4 hydrocarbons. c) 1wt%Ru/SiO_2 :Mont-Al_2O_3 = 0.09 : 1.
Reaction conditions: 240 °C, 10^3 kPa (H_2/CO = 1.9).

than C_{10} was remarkably suppressed, and selectivity to C_4-C_{10} hydrocarbons increased to 79%. This value was much higher than 47% for Ru/SiO_2.

Tominaga et al. reported that a Ru/HY zeolite produced selectively C_4-C_{10} hydrocarbons in CO hydrogenation.16) The distribution obtained by them was very similar to the present result for Ru/NaY zeolite (Table 1), although the two zeolites must have very different acidity. This fact indicates that the pore structure of the supports (Mont-Al_2O_3, SiO_2,and zeolite) instead of the acidity determined the selectivity. Hence, the selective formation of C_4-C_{10} over Ru/Mont-Al_2O_3 may be also due to its unique pore structure.

The iso to normal ratio of C_4 was 1.4 for Ru/Mont-Al_2O_3, while the ratio was zero for Ru/SiO_2. This fact suggests that secondary isomerization and cracking of hydrocarbons took place on the acid sites6) of Mont-Al_2O_3. Since the acid sites of Mont-Al_2O_3 are mostly located in the interlayer space,6) these reactions mainly occurred there and brought about the unique selectivity controlled by the pore structure. So we examined the hydrogenation of CO using a mechanical mixture of Ru/SiO_2 and Mont-Al_2O_3 (0.09 : 1 in weight). The amount of Mont-Al_2O_3 was the same and the amount of Ru/SiO_2 was chosen so that the rate of hydrocarbon formation became the same as in the case of Ru/Mont-Al_2O_3. As expected, the distribution of carbon number over the mixed catalyst agreed very well with that observed for Ru/Mont-Al_2O_3 (Fig. 2 and Table 1).

The average particle size of Ru estimated from H_2 adsorption17) was 25 Å as reported previously.13) Although it is not clear at present whether the Ru particles are present in the pores in the layers of Mont-Al_2O_3 or on its outer surface, the shape-selectivity of Ru/Mont-Al_2O_3 was revealed presumably when the hydrocarbons formed on Ru were secondarily isomerized and cracked in the pores of the support.

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