Ruthenium-based Catalyst for the Gas-phase Synthesis of Alcohols from CO and H_2

Masashi Inoue, Takanori Miyake, Tomoyuki Inui,* and Yoshinobu Takegami

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Hydrogenation of CO with H_2 at 86 kg/cm^2 and 255 °C over a catalyst composed of Ru, Mo, and Na_2O gives a series of straight-chain primary alcohols as essentially the only liquid products (>99%, excluding water).

Because of the recent rapid increase in the price of petroleum (and naphtha) the conversion of synthesis gas (CO–H_2) into organic chemicals has become an important applied research topic. It is well known that low-temperature Fischer–Tropsch

Table 1. Activities and selectivities of the catalysts in Fischer–Tropsch synthesis.[a]

Catalyst[b]	*SV*[c]	CO conversion (%)	Condensate		α[f]	*STY*[g]	Carbon atom selectivity (%)				
			Vol.[d]	Alcohol selectivity[e] (%)			Alcohols	Other oxygenates	CH_4	Other hydrocarbons	CO_2
I	1 700	71	114[h]	98.5	0.39	26.7	6.3	0.03	31	17	46
I	6 300	16	166[h]	99.8	0.37	38.7	13	0.02	34	20	33
I	18 200	7.2	235[h]	99.6	0.36	68.7	18	0.13	26	24	32
I	39 800	1.6	87.9[h]	97.7	0.34	15.6	6.9	0.06	45	17	31
II	16 000	3.8	125[i]	98.5	—[j]	6.96	3.2	0.03	57	18	22
III	17 300	7.1	198[h]	99.0	—[k]	94.4	19	0.13	23	18	40
IV	22 600	99.9	2510[h]	—[l]	—	0.0	0.0	0.0	72	0.02	28
V	27 700	0.2	Trace	—	—	—	—	—	*ca.* 16	*ca.* 41	*ca.* 43

[a] Conditions: 255 °C; 86 kg/cm^2; H_2–CO (2:1); 0.25—0.35 ml of catalysts. [b] Catalysts are as follows: I, 3% Ru–5% Mo–1.25% Na_2O/Al_2O_3 (B); II, 5% Ru–5% Mo–1.25% Na_2O/Al_2O_3 (B); III, 5% Ru–5% Mo–1.25% Na_2O/Al_2O_3 (G); IV, 5% Ru/Al_2O_3 (B); V, 5% Mo–1.25% Na_2O/Al_2O_3 (B); (B) and (G) refer to Al_2O_3 obtained by calcination of boehmite and gibbsite, respectively. [c] Space velocity in h^{-1}. [d] Space time volume yield of condensate in (ml condensate) (l cat.)$^{-1}$ h^{-1}. [e] Excluding water. [f] Chain-growth probability for formation of higher alcohols. [g] Space–time yield of alcohol, (g alcohol) (l cat.)$^{-1}$ h^{-1}. [h] The condensate was homogeneous. [i] The condensate was turbid presumably because of the formation of an emulsion of higher alcohols. [j] A semi-logarithmic carbon number distribution plot for alcohols showed a line with an abrupt change in slope at n-pentanol from $\alpha = 0.444$ for lower alcohols to $\alpha = 0.233$ for higher alcohols; this was assumed to be caused by solubility problems for higher alcohols because the condensate contained only small amounts of lower alcohols. [k] A semi-logarithmic carbon number distribution plot showed downward curvature with $\alpha = 0.256$ at the methanol end and $\alpha = 0.467$ for n-decanol, indicating that the rate of termination relative to the rate of chain-growth decreased with increasing carbon chain length of the alcohol. [l] Condensate was essentially pure water.

synthesis (synol process) with conventional iron (or cobalt) based catalysts produces oxygenated compounds together with hydrocarbons.[1–3] However, these oxygenates are usually complex mixtures of alcohols, fatty acids, esters, aldehydes, and ketones. We report here a new composite catalyst system which exhibits high selectivity for alcohol formation in the Fischer–Tropsch reaction.

The catalysts were prepared by impregnation of γ-alumina (82 m^2/g, obtained by calcination of boehmite;[4] or 223 m^2/g, obtained by calcination of gibbsite) with an aqueous solution of $RuCl_3$, $(NH_4)_6Mo_7O_{24}$, and $NaNO_3$. The supported salts were decomposed at 400 °C, and the catalysts were then reduced by H_2 at 400 °C prior to the reaction. The reactions were carried out in a fixed-bed microreactor made from 316 stainless steel tubing of 7.0 mm internal diameter. The exhaust gases were analysed by gas-adsorption chromatography every 30 min. All the Ru-based catalysts studied were active for the formation of high molecular weight hydrocarbons in the early stages of the reactions. However, this activity decreased quite rapidly, and became negligible before the reactions reached the steady state.[5,6] After the steady state had been attained (usually in 1.5 h from the introduction of synthesis gas to the reactor), the outlet was connected to an acetone–solid CO_2 condenser. The resulting condensate was analysed after the required period of reaction (6 h). The catalyst activity and the product distribution remained almost constant during this period. The results for this reaction together with the results obtained using Ru/Al_2O_3 and $Mo–Na_2O/Al_2O_3$ as catalysts are summarized in Table 1.

In contrast with the reactions using conventional Fischer–Tropsch catalysts reported so far,† >99% of the liquid product (with the exclusion of water) comprised a series of straight-chain primary alcohols.‡ The remainder comprised traces of acetone, methyl ethyl ketone, acetic acid, a series of n-alkanes, and methyl, ethyl, and propyl acetates.

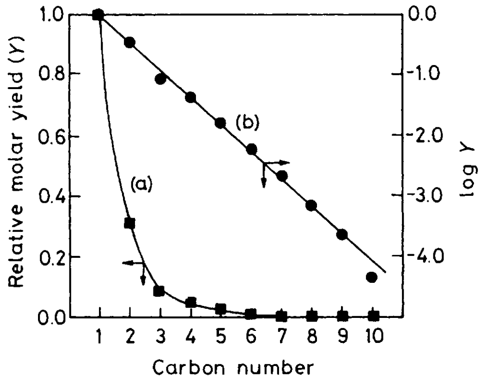

Figure 1. Carbon number distribution for alcohols obtained by using 3% Ru–5% Mo–1.25% Na_2O/γ-Al_2O_3 at 255 °C, 86 kg/cm^2, space velocity 18 200 h^{-1}: (a) ordinary plot; (b) semi-logarithmic plot; the slope of the plot leads to an α value of 0.355.

The carbon number distribution of the alcoholic products obeyed a Schultz–Flory-type distribution[8] with α = 0.3—0.4 (Figure 1), significantly lower than α values for conventional Fischer–Tropsch reactions (*ca.* 0.75),[9] and therefore the catalysts reported here produced only a negligible amount of undesired high boiling point materials. The yield of methanol was in accordance with that expected from the Schultz–Flory distribution. This is in sharp contrast with the results from the conventional Fischer–Tropsch catalysts, which produce methanol in much smaller quantity than expected from the α value obtained from the yields of higher alcohols.[9]

As shown in Table 1, the Ru/Al_2O_3 catalyst had quite a high activity for methanation,[10] but no activity for alcohol synthesis,§ whereas the $Mo–Na_2O/Al_2O_3$ catalyst was inactive. The addition of Mo and Na_2O to the Ru/Al_2O_3 catalyst decreased the methanation activity and induced activity for alcohol

---

† For example; Gall *et al.*[3] reported that the condensate obtained from a Fischer–Tropsch reaction at 160—170 °C using a standard Co–ThO_2–MgO–kieselguhr catalyst, was composed of 40.0% alcohols, 0.5% acids, 0.8% esters, 2.0% carbonyl compounds, and 56.7% hydrocarbons, excluding water.

‡ Recently, selective formation of straight-chain primary alcohols from synthesis gas using modified methanol catalysts was reported.[7] We thank a referee for drawing our attention to this point.

§ Ruthenium catalysts supported on Al_2O_3 have been reported to show activity for alcohol synthesis,[5,11] and so the activity of Ru/Al_2O_3 catalysts for alcohol synthesis seems to depend on the ruthenium source and the catalyst-preparation method.

synthesis. A fairly high space-time yield of alcoholic products, *ca.* 90 g (l cat.)$^{-1}$ h^{-1}, was achieved with this Ru-based catalyst. As the liquid product composed of water and alcohols was essentially uncontaminated by hydrocarbons and other oxygenated products, the refining of the alcoholic products would become much simpler than with conventional Fischer–Tropsch reaction (synol synthesis).

Received, 1st October 1982; Com. 1156

References

1 W. Wenzel, *Angew. Chem.*, 1948, **B20**, 225.

2 R. B. Anderson, *Catal. Rev. Sci. Eng.*, 1980, **21**, 53.

3 D. Gall, E. J. Gibson, and C. C. Hall, *J. Appl. Chem.*, 1952, 371.

4 T. Inui, T. Miyake, K. Fukuda, and Y. Takegami, *Appl. Catal.*, in the press.

5 C. S. Kellher and A. T. Bell, *J. Catal.*, 1981, **71**, 288.

6 Compare the following papers: T. Okuhara, K. Kobayashi, T. Kimura, M. Misono, and Y. Yoneda, *J. Chem. Soc., Chem Commun.*, 1981, 1114; H. E. Ferkul, D. J. Stanton, J. D. McCowan, and M. C. Baird, *ibid.*, 1982, 955.

7 A. Sugier and E. Freund, Brit. Pat., 1 547 687 (1978).

8 G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 136.

9 R. B. Anderson, in 'Catalysis,' ed. P. H. Emmett, vol. IV, Reinhold, New York, 1956, chs. 2 and 3.

10 Y. T. Shah and A. J. Perrotta, *Ind. Eng. Chem., Prod. Res. Dev.*, 1976, **15**, 123; T. Inui, M. Funabiki, M. Suehiro, and T. Sezume, *J. Chem. Soc., Faraday Trans.* 1, 1979, **75**, 787.

11 A. Bossi, F. Grabassi, and G. Petrini, Preprints of 7th Internat. Congress on Catalysis, Tokyo, 1980, E-4.