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Production of Synthesis Gas with Various Compositions of H_2, CO, and CO_2 from Methanol and Water on a Ni-K/Al_2O_3 Catalyst

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Mixtures of H_2, CO, and CO_2 were produced over a Ni-K/Al_2O_3 catalyst from methanol and water. The composition of the mixtures, in particular the H_2/CO ratio, was extensively varied by changing reaction conditions such as starting ratio of methanol/water.

There have been several investigations on gasification of methanol over solid catalysts. Decomposition of methanol affords a 2 : 1 mixture of H_2/CO over various catalysts including nickel and palladium.$^{1)}$

$$CH_3OH \quad = \quad 2H_2 \quad + \quad CO \quad - \quad 90.6 \text{ kJ mol}^{-1} \qquad (1)$$

On the other hand, steam reforming of methanol affords a 3 : 1 mixture of H_2/CO_2 over catalysts containing Cu.$^{2)}$

$$CH_3OH \quad + \quad H_2O \quad = \quad 3H_2 \quad + \quad CO_2 \quad - \quad 49.4 \text{ kJ mol}^{-1} \qquad (2)$$

The combination of these two reactions may result in production of mixtures of H_2, CO, and CO_2 with various compositions, in particular H_2/CO ratio, depending on the contribution of each reaction. We report here that the two reactions took place simultaneously on a Ni-K/Al_2O_3 catalyst, yielding mixtures of H_2, CO, and CO_2. The composition of the products was extensively changed by the reaction conditions of reactant CH_3OH/H_2O ratio, reaction temperature, and space velocity.

The catalyst was prepared by impregnating aqueous solutions of nickel nitrate and potassium nitrate with extrudate γ-alumina (Ketjen lot no. 6550; 1.5 mm diameter x 2.4 mm length; BET surface area 260 m^2g^{-1}), followed by drying at 110 °C for 24 h. The loading amounts of nickel and potassium were 4 and 5 mg-atoms(g-Al_2O_3)$^{-1}$, respectively. Potassium was effective in eliminating the dehydration reaction of methanol by neutralizing acid sites on the support, and in improving the surface area of metallic nickel on the catalyst.$^{3)}$ The catalyst was reduced by flowing methanol at 350 °C for 5 h. The reactions were carried out on a conventional flow system at atmospheric pressure. Mixture of the reactants and balance argon was fed to a tubular-type quartz reactor (26 mm i.d.). Outlet composition of products and unreacted materials was analyzed on gas chromatograghs.

Table 1 shows catalytic activities of Ni-K/Al_2O_3 in the reaction of methanol and water. In the absence of water the catalyst was active in decomposition of methanol, giving a 2 : 1 molar ratio of H_2 and CO.[3)] Although a slight decrease in methanol conversion was observed in the decomposition with increased pressures, probably due to a poisoning of product CO on the surface,[3,4)] the decomposition obeyed almost zero-order in partial pressure of methanol in the range from 0.3 to 1.0 atm. When water was admitted with methanol, the conversion of methanol was greatly increased. Since the free energy changes in the decomposition and steam reforming reactions are -28 and -49 kJ mol^{-1} at 250 °C, respectively, the addition of water makes the reaction thermodynamically more favorable. However, detail mechanism for this enhancement is not clear. Under these conditions, rate of methane formation was negligibly slow (<0.1 mmol $h^{-1}g^{-1}$), and neither C_2-, C_3-hydrocarbons, HCHO, nor $HCOOCH_3$ was detected. Most interesting feature of the reaction between methanol and water was that on increasing partial pressure of water, rate of CO formation decreased whereas those of H_2 and CO_2 formation

Table 1. Reaction of CH_3OH and H_2O over Ni-K/Al_2O_3 Catalyst[a)]

Run No.	Partial press. of reactants[b)]/atm		Conversion of CH_3OH/%	Rate of products formation mmol $h^{-1}g^{-1}$			Molar ratio of H_2/CO
	CH_3OH	H_2O		H_2	CO	CO_2	
1	1.00	0	15.7	5.8	2.7	0.1	2.1
2	0.50	0	15.2	5.6	2.8	0.1	2.0
3	0.50	0.50	41.2	18.7	2.8	5.0	6.8
4[c)]	0.50	0.50	92.4	43.2	5.3	11.4	8.1
5	0.30	0	17.4	6.4	3.1	0.1	2.1
6	0.30	0.15	24.5	11.2	3.1	1.7	3.7
7	0.30	0.30	31.3	14.6	2.6	3.1	5.6
8	0.30	0.45	35.5	17.6	2.2	4.2	8.2
9	0.30	0.59	36.1	18.7	1.3	5.3	14.2

a) Catalyst 25 ml (34.1 g), reaction temp 250 °C. b) CH_3OH feed rate 18.2 ± 0.2 mmol $h^{-1}g^{-1}$, balance argon. c) Reaction temp 300 °C.

Table 2. Water Gas Shift Reaction over Ni-K/Al_2O_3 at 250 °C

Partial press. of reactants[a)]/atm		Composition of CO and CO_2 in effluent/% Equilibrium[b)]		Observed		Rate of CO conversion
CO	H_2O	CO	CO_2	CO	CO_2	mmol $h^{-1}g^{-1}$
0.09	0.15	1.1	98.9	40.6	59.4	3.62
0.09	0.29	0.4	99.6	0.6	99.4	5.55
0.09	0.44	0.2	99.8	0.2	99.8	5.53
0.09	0.59	0.2	99.8	0.2	99.8	5.60

a) Catalyst 25 ml (34.1 g); CO feed rate 5.64 mmol $h^{-1}g^{-1}$, balance argon.
b) Equilibrium constant K = 86.92.

increased, giving rise to higher H_2/CO ratios. The higher ratios were also obtained at elevated temperatures, as exemplified by Run 4 in Table 1. Takahashi et al.[5)] demonstrated two different pathways of the steam reforming reaction. Methanol was converted over a Cu/SiO_2 catalyst to methyl formate and formic acid intermediates, the latter being successively decomposed into final products of CO_2 and H_2.

$$2CH_3OH = HCOOCH_3 + 2H_2 \tag{3}$$
$$HCOOCH_3 + H_2O = HCOOH + CH_3OH \tag{4}$$
$$HCOOH = CO_2 + H_2 \tag{5}$$

However, CO never participates in this mechanism, and in fact only a small amount of CO was observed on the Cu/SiO_2 catalyst even in the absence of water.[5)] By contrast, on a Pt/SiO_2 catalyst was proposed another mechanism, which involves a sequence of methanol decomposition (1) and water gas shift (WGS) reaction (6), though product distribution on changing reactant CH_3OH/H_2O ratio was not reported in the literatures.[5,6)]

$$CO + H_2O = CO_2 + H_2 + 41.2\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

Since nickel supported on Al_2O_3 was reported to be active in the WGS reaction,[7)] we have confirmed the reaction on the present catalyst. The results are listed in Table 2. The partial pressure and feed rate of CO in this experiment corresponded to those in the reaction of methanol and water at ca. 30% conversion level. The reaction was extremely rapid and equilibrium compositions were easily obtained with increased partial pressures of water. Therefore, it is most likely that the steam reforming of methanol proceeded through the methanol decomposition and the subsequent WGS reaction.

Another evidence for this pathway comes from

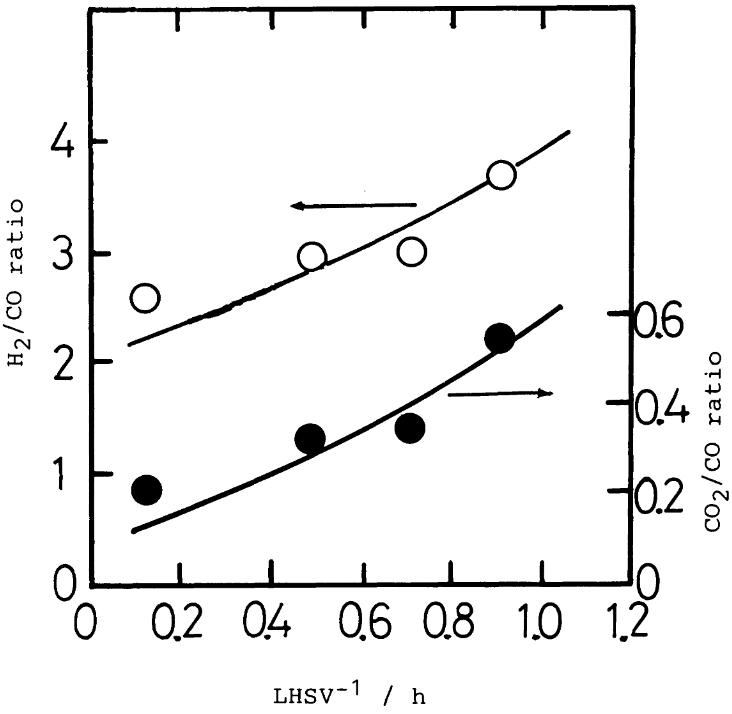

Fig. 1. Change in selectivity of H_2, CO, and CO_2 as a function of LHSV of mehanol in the reaction between methanol and water at 200 °C.

Ni-K/Al_2O_3 catalyst 12.5 ml (16.3 g), reactants methanol/water = 0.30/0.05 atm.

the dependence of product distribution on contact time of the reactants, as illusbtrated in Fig. 1. When the liquid hourly space velocity (LHSV) was increased, the product ratio of H_2/CO approached to the value of 2, and that of CO_2/CO was reduced almost to zero. The conversion of methanol was below 8%, but it increased monotonically with the contact time, i.e. reciprocal of LHSV. This finding indicates that only decomposition of methanol took place at an early stage of the reaction.

As for the reaction of methanol and water shown in Table 1, CO_2 compositions between CO and CO_2 in the equilibrium are calculated to be more than 96%. However, the effluent compositions did not attain the equilibriums, and rates of CO_2 formation were slower in the reaction of methanol and water than in the WGS reaction. This suggests a competitive adsorption between CO and reactant methanol on the catalyst, which retarded the WGS reaction (6) rather than the decomposition reaction (1). Thus the composition of H_2, CO, and CO_2 produced from methanol and water, in particular H_2/CO ratio, may be governed both by the reactions (1) and (6).

In conclusion, mixtures of H_2, CO, and CO_2 with a variety of compositions were selectively produced from methanol and water. The present one-step generation of syn-gas from methanol at lower temperatures is a simple process in which one can obtain a desired ratio of H_2/CO higher than 2. The compositions may be adapted to many industrial processes, for instance, methanation in which the H_2/CO ratio of 3 is needed.[8)] Further study including relation between the methanol conversion and the WGS reaction on various catalysts is under investigation.

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