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METHANOL REFORMING REACTION OVER COPPER-CONTAINING MIXED OXIDES

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Methanol was decomposed into hydrogen and carbon dioxide in the presence of water at atmospheric pressure over copper-containing mixed oxides, indicating that the reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$ proceeded to an appreciable extent. The mixed oxides were active and selective for the reforming reaction whereas the single oxides which constituted the mixed oxides were much less active for the reaction.

Methanol is decomposed into hydrogen, carbon monoxide and/ or formadehyde over metal catalyst and various metal oxides.[1,2] However, when it is decomposed in the presence of water, it can be converted into hydrogen and carbon dioxide through the methanol reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$. This reaction is thermodynamically fovarable but few reports have been published on this subject.[3]

In the present report, we communicate that the methanol reforming reaction occurred selectively at atmospheric pressure over copper oxide mixed with some other metal oxides.

The reforming reaction was carried out in a flow system. The equimolar mixture of liquid methanol and water was admitted by a microfeeder into the upper part of the reactor where they were readily vaporized. The reaction was always carried out over 1 gr. of catalyst at the partial pressure of 0.24 atm. for each reactant. Nitrogen was used as a diluent gas and the total flow rate was always kept at 96 ml/min. In a similar fashion, the decomposition of methanol, methyl formate or of the latter species in the presence of water vapor was carried out. The gaseous composition was determined by means of gas chromatography. The mixed oxides were composed of the oxides of copper and of other metals with the atomic ratio of 1 to 2. Prior to the experiments, the catalysts were heated at 500°C in air.

Table 1 illustrates the results over Cu-Mn mixed oxide and its consituent oxides. In the third column of the table, the rates of carbon dioxide formation are listed. The fourth to the seventh columns represent the gaseous composition at the outlet of the catalyst bed. In the last two columns, the ratios H_2/CO_2 and $CO_2/(CO + CO_2)$ are listed. These ratios should be 3 and 1, respectively, when the reforming reaction selectively occurs. As seen from the table, the activity was considerably increased and the selectivity of the reforming reaction was improved when copper oxide was kneaded with manganese dioxide.

In Table 2, the ratios $CO_2/(CO + CO_2)$ and H_2/CO_2 obtained over various catalysts are listed together with the respective activation energies of the reforming reaction. As is evident from Table 2, the activation energy is lowered when copper oxide is mixed with the other metal oxide. With the copper-containing reducible oxide such as Cu-Co and Cu-Ni mixed oxide the H_2/CO_2 and $CO_2/(CO + CO_2)$ ratios deviate largely from 3 and 1, respectively. However, the other nine mixed oxides are favorable for the reforming reaction. In particular, the reaction occurred more selectively over Cu-Zn, Cu-Si, Cu-Cr and Cu-Sn mixed oxides at 200°C.

Table 1.

Catalyst	Temp.(°C)	Rate	H_2(%)	HCHO(%)	CO_2(%)	CO(%)	H_2/CO_2	$CO_2/(CO + CO_2)$
Cu	283	0.19	58	33	9	0	7.1	1.0
Mn	270	0.0	50	50	0	0	——	——
Cu-Mn	283	8.82	67.6	13.5	16.8	2.1	4.0	0.89

Table 2.

Catalyst[a]	H_2/CO_2[b]	$CO_2/(CO + CO_2)$[b]	Activation Energy[c] kcal/mole
Cu	7.1	1.0	19.8-20.9
Mn[d]	——	——	——
Cu-Cr	3.0	1.0	18
Cu-Mn	4.0	0.95	13.1-16.7
Cu-Zn	3.3	1.0	17.4
Cu-Fe	4.3	1.0	15.3
Cu-Al	2.7	1.0	8.0
Cu-Ti	3.4	1.0	18.8
Cu-Si	3.0	1.0	13.1
Cu-Ca	3.7	0.98	15.6
Cu-Sn	3.0	1.0	14.3
Cu-Co	5.5	0.28	8.4
Cu-Ni	20.0	0.08	11.9

a) Used as oxide.
b) At 200°C.
c) Determined from the rate of CO_2 production.
d) CO and CO_2 were not produced.

When methanol was brought into contact with Cu-Mn mixed oxide, hydrogen, carbon monoxide and methyl formate were formed in appreciable amounts with small amount of formaldehyde. When the reaction was carried out in the presence of water, carbon dioxide was formed at the expense of carbon monoxide. Methyl formate formation was also markedly suppressed and was practically negligible. Similar results were obtained over other copper containing mixed oxides. When methyl formate was brought into contact with the catalysts, it decomposed into methanol and carbon monoxide with a certain amount of formaldehyde. As Schwab et al.4) observed on copper, silver, gold, nickel, palladium and platinum metals the reaction $HCOOCH_3 = CH_3OH + CO$ primarily occurs on the present catalysts. However, when methyl formate was decomposed in the presence of water, carbon dioxide was formed on Cu-Mn mixed oxide at the expense of carbon monoxide. These results indicate that water gas shift reaction is involved in the reforming reaction. Considering that methyl formate can be produced through the Tishchenko reaction5,6,7) or hemiacetal formation,8) we assumed that the reforming reaction is consisting of the following reaction.

$$CH_3OH \longrightarrow HCHO + H_2 \quad \text{----------} \quad a)$$

$$\left.\begin{array}{l} 2HCHO \longrightarrow HCOOCH_3 \\ (\text{or } HCHO + CH_3OH \longrightarrow HC(OH)(OCH_3) \\ \longrightarrow HCOOCH_3 + H_2) \end{array}\right\} \text{----------} \quad b)$$

$$HCOOCH_3 \longrightarrow CO + CH_3OH \quad \text{----------} \quad c)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \text{----------} \quad d)$$

Table 3.

Catalyst a)	Temperature (°C)	$-\Delta G_1$ b)	$-\Delta G_2$ c)
Cu	285	20.4	3.17
Mn d)	—	—	—
Cu-Cr	205	20.5	4.2
Cu-Mn	200	13.4	3.7
Cu-Zn	226	15.3	0.5
Cu-Fe	300	14.2	0.4
Cu-Al	288	19.0	0.02
Cu-Ti	255	16.1	0.07
Cu-Si	220	14.4	0.5
Cu-Ca	201	15.1	2.7
Cu-Sn	274	24.3	5.3
Cu-Co	211	10.9	8.0
Cu-Ni	201	8.3	8.2

a) Used as oxide.

b) (a) + (b) + (c) : $CH_3OH = CO + 2H_2$: $-\Delta G_1 = RT\ln(P_{CO}P_{H_2}^2/K_{P_1}P_{CH_3OH})$.
K_{P_1} : Equilibrium constant of the reaction $CH_3OH = CO + 2H_2$

c) (d) : $CO + H_2O = CO_2 + H_2$: $-\Delta G_2 = RT\ln(P_{CO_2}P_{H_2}/K_{P_2}P_{CO}P_{H_2O})$.
K_{P_2} : Equilibrium constant of the reaction $CO + H_2O = CO_2 + H_2$

d) The reaction $CH_3OH = HCHO + H_2$ occurred.

The free energies ΔG_1 of the methanol decomposition $CH_3OH \longrightarrow CO + 2H_2$, which is the overall process of the reactions a), b) and c), and ΔG_2 of water gas shift reaction d) were estimated from the gaseous composition at the outlet of the catalyst bed. Table 3 demonstrates that both ΔG_1 and ΔG_2 values are negative. Over the catalysts other than Cu-Co and Cu-Ni mixed oxide, $-\Delta G_1$ values are always much greater than $-\Delta G_2$ values. This suggests that either of the reaction a), b) or c) is the rate determing step of the reforming reaction. In addition, since formaldehyde was observed but methyl formate was practically negligible in the reforming reaction products, the reaction b) seems to be rate determining. Further work on the mechanism of the reforming reaction and the nature of the active site is now in progress.

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