CHEMISTRY LETTERS, pp. 507-510, 1979. Published by the Chemical Society of Japan

THE CATALYTIC ACTIVITIES OF METHANOL REFORMING CATALYSTS AND THEIR PREPARATIONS

Chiaki MINOCHI, Haruo KOBAYASHI, and Nobutsune TAKEZAWA
Department of chemical Process Engineering, Hokkaido
University, Sapporo 060

Methanol reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$ was carried out over copper-containing catalysts which were prepared from hydroxides of copper and from the hydroxide kneaded with silica. From differential thermal analysis, infrared and X-ray photoelectron spectra of the catalysts and other chemical analysis, it was concluded that the anionic group of their starting material readily exchanged with hydroxide ion in the hydroxide precipitate in the course of their preparation and greately influenced the reaction.

It has been reported that the methanol reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$ occurs over copper-containing mixed oxides with high selectivity (1). Hydrogen atoms in water molecule as well as methanol are, therefore, simultaneously converted into gaseous hydrogen.

In the present communication, we concluded that the anions of starting materials are readily held in the catalysts in the course of the preparation and markedly inhibit the methanol reforming reaction.

Hydroxide of copper was precipitated by addition of the solution of copper salt (nitrate, formate or chloride) to that sodium hydroxide until a given pH was attained. The hydroxide was filtered and washed thoroughly with 20 ℓ of distilled water at room temperature. After the precipitate was kenaded with silica (Japan Chromat-Industry Co.) in an atomic ratio Cu : Si = 1 : 2, it was dried at 125°C overnight and calcined in air at 520°C for 3 hrs. In a similar manner, support-free catalyst was prepared. The reaction was carried out at atmospheric pressure in a flow system. Equimolar mixture of methanol and water was fed with a micropump and rapidly vaporized in the nitrogen stream before entering into the catalyst bed. The outlet gases were analyzed by gas chromatography.

In Figure 1, the steady rates of hydrogen and carbon dioxide formations over copper-silica catalysts are plotted against pH at which hydroxides of copper were precipitated from copper nitrate with sodium hydroxide solution. It is seen that the activity markedly increases with the pH. On the other hand, the activation energy and the selectivity of the reaction were practically unaffected by the pH. When support-free copper catalysts were used for the reaction, the similar results were obtained.

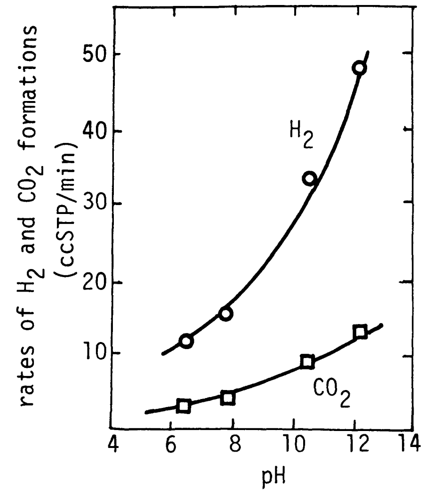

Figure 1 Effect of pH at which hydroxides of copper are precipitated upon the rates of H_2 and CO_2 formations.
Catalyst used : 1 gr, Reaction temp. : 220°C
$P_{CH_3OH} : P_{H_2O} : P_{N_2} = 0.24 : 0.24 : 0.52$

Figure 2 illustrates DTA curves of hydroxides of copper which were prepared at various pH. An endothermic peak is observed around 195°C for hydroxide prepared at higher pH. The peak coincided with that of copper hydroxide $Cu(OH)_2$ in its position. For hydroxide prepared at lower pH, on the other hand, another endothermic peak is observed around 240°C together with the peak that is assigned to copper hydroxide. It was found that copper nitrate $Cu(NO_3)_2$ was not held in the precipitate from DTA curve and the infrared spectrum of the precipitate. However, the presence of monodentate type nitrate (2) was suggested from the infrared absorptions observed around 1420, 1350 and 1048 cm^{-1}. When the

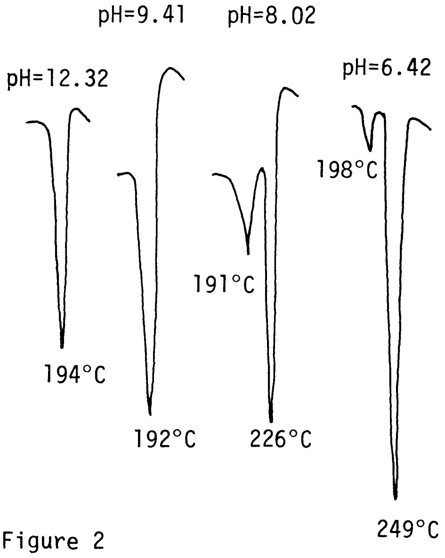

Figure 2
DTA curves for hydroxides of Copper precipitated at various pH

hydroxide was heated around 240°C, the absorptions start to decrease and nitrogen oxides were evolved. The peak around 240°C was, therefore, attributed to monodentate nitrate. Similar results were also obtained for copper-silica catalysts. When hydroxide which was prepared at lower pH was soaked in sodium hydroxide solution, nitrate ion was eluted and pH of the solution was lowerd. The amount of nitrate ion eluted was estimated to be pracitically equal to that of the decrease in hydroxide ion. When copper hydroxide was soaked in copper nitrate solution, the pH of the solution increased and nitrate ion was held in the hydroxide. These results were also confirmed by DTA. In these respects, it was concluded that monodentate nitrate was formed via the exchange $Cu(OH)_2 + NO_3^- = Cu(OH)NO_3 + OH^-$ in the course of the precipitation. Copper hydroxide was preferentially formed at higher pH whereas nitrate ion was held in the hydroxide at lower pH.

Hydroxides of copper were also prepared from copper formate or chloride and were kneaded with silica. As Table 1 shows, the activities of these catalysts are also strongly influenced by pH of preparation. The activities of the catalysts prepared at higher pH were less affected by copper salts employed as starting materials whereas the catalysts prepared at lower pH differed in their activities appreciable with copper salts employed. The XPS spectra of the catalysts which prepared from copper nitrate and chloride were obtained after

Table 1

Starting materials employed in the precipitation of hydroxides of copper and the methanol reforming reaction

	pH at which hydroxides of copper were precipitated			
	pH = 6.5		pH = 12.16	
copper salts	r_{H_2}*)	r_{CO_2}*)	r_{H_2}	r_{CO_2}
$Cu(NO_3)_2 \cdot 3H_2O$	10.85	3.01	48.29	12.96
$CuCl_2 \cdot 2H_2O$	0.88	0.06	24.75	6.94
$Cu(HCOO)_2 \cdot 4H_2O$	22.08	6.94	55.24	17.51

*) r_{H_2} and r_{CO_2} represent the steady rates (ccSTP/min) of hydrogen and carbon dioxide formations at 220°C, respectively.

$P_{CH_3OH} : P_{H_2O} : P_{N_2} = 0.24 : 0.24 : 0.52$

the reaction was carried out. The intensity ratios Cl_{2p}/Si_{2s} and N_{1s}/Si_{2s} obtained are listed in Table 2. It was evidently shown that the catalyst prepared at lower pH retains the anionic group or its fragments on the surface more than that prepared at higher pH even after the reaction or the calcination was carried out. When nitrogen oxides were introduced in the course of the reaction, the reforming reaction was apprecibly decreased. In these respects, it is concluded that the reaction is markedly influenced by pH or the starting material employed since the anionic group in the starting materials strongly retained on the surface. The Auger spectra presented further evidence that no alkali cation was present on the surface. Potassium hydroxide was employed as a precipitant in place of sodium hydroxide. In fact, the precipitant exerted no influence upon the reaction. The effect of alkali cation is, therefore, can be ignored in the present experiment.

Table 2

The XPS results of methanol reforming catalysts which were prepared from hydroxide of copper and silica

Starting material	pH at which hydroxides of copper were precipitated	Peak intensity Cl_{2p}/Si_{2s}	Peak intensity N_{1s}/Si_{2s}
$CuCl_2 \cdot 2H_2O$	6.5	0.094	—
	12.16	0.026	—
$Cu(NO_3)_2 \cdot 3H_2O$	6.5	—	0.37
	12.16	—	0.11

Acknowledgement The present work was supported in part by Asahi Glass Incentive Grant and also in part by a Grant-in-Aid for Research from the Ministry of Eduction of the Japanese Goverment to which the authors gratefully acknowledged. A special thanks is extended to Dr. H.Konno for measuring the XPS spectra of the catalysts.

References

1) H.Kobayashi, N.Takezawa, and C.Minochi, Chem.Letters, 1347(1876).

2) B.M.Gatehouse, S.E.Livingstone, and R.S.Nyholm, J.Chem.Soc., 4222(1957).
N.F.Curtis and Y.M.Curtis, Inorg.Chem., 4, 804(1965).

(Received March 1, 1979)