METHANOL SYNTHESIS FROM CO$_2$-H$_2$ AND FROM CO-H$_2$ UNDER ATMOSPHERIC PRESSURE OVER Pd AND Cu CATALYSTS

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Under atmospheric pressure, methanol was produced from CO$_2$-H$_2$ over Pd/ZnO and from CO-H$_2$ over Pd/MgO catalyst. Similar support effects were observed over Cu catalysts.

INTRODUCTION

Among group 8 metal, Pd and Rh are active for the methanol synthesis from CO$_2$, CO$_2$ + 3H$_2$ → CH$_3$OH + H$_2$O, under elevated pressures [1-3]. To our knowledge, it has not yet been reported that this reaction occurs at atmospheric pressure over these catalysts, although these catalysts are effective for methanol synthesis from CO at atmospheric pressure [4, 5]. The synergy between the metal component and the support has been reported to enhance the catalytic performance of Cu/ZnO for methanol synthesis from CO$_2$ [6]. The synergic effect might be observed for group 8 metal catalysts supported on ZnO. In the present study, CO$_2$-H$_2$ and CO-H$_2$ reactions are carried out over Pd, Rh, Pt, Fe, Co, Ni, Ag and Cu supported on ZnO, and over Pd and Cu supported on other metal oxides under
atmospheric pressure. We show that Pd catalysts exhibit high performance in the methanol synthesis from CO$_2$ and from CO as Cu catalysts, and methanol synthesis over Pd catalysts is strongly affected by the support used in a similar manner to that observed over Cu catalysts.

**EXPERIMENTAL**

Pd, Fe, Co, Ni and Ag catalysts supported on ZnO were prepared by an inverse coprecipitation method in a way similar to that employed by Porta et al. [7]. A mixed solution of nitrates of Pd, Fe, Co, Ni or Ag, and Zn (total metal concentration 1 M) was slowly added to a solution of NaHCO$_3$ (1.2 M) at 338 K under stirring. Precipitates formed were aged in the mixed solution at 338 K for 90 min. The precipitates were then filtered out, washed with distilled water, dried in air at 373 K overnight. Cu/ZnO was prepared by coprecipitation of basic salts of copper and zinc. Details of catalyst preparation were described elsewhere [8]. Pt/ZnO or Rh/ZnO were prepared by impregnation of ZnO, which was obtained as the Cu/ZnO, with an aqueous solution of tetraammine platinum(II) nitrate or with a CH$_2$Cl$_2$ solution of Rh$_6$CO$_{16}$. The catalysts thus prepared were calcined in air at 623 K for 4 h, and then reduced in reactors with H$_2$ according to the schedule adopted in the previous study [8]. The reduction temperature was raised stepwise 10 K/h from 483 K up to 523 K.

Pd/ZrO$_2$, Pd/MgO, Cu/ZrO$_2$ and Cu/MgO were prepared under the same conditions as Pd, Fe, Co, Ni and Ag catalysts supported on ZnO. Pd/SiO$_2$ and Cu/SiO$_2$ were obtained by impregnation of SiO$_2$ with aqueous solutions of Pd nitrate and tetraammine Cu(II) nitrate, respectively. The catalysts were calcined and reduced at the same conditions as the ZnO supported catalysts.

Methanol synthesis from CO$_2$-H$_2$ and from CO-H$_2$ (CO$_2$ or CO = 0.1 atm, H$_2$ = 0.9 atm) was studied in a flow reactor under atmospheric pressure at a contact time of 0.02 g-cat.min/cm$^3$. The effluent from the reactor was analyzed by gas chromatography.