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## Formation of Dimethyl Ether from Hydrogen and Carbon Dioxide over a Graphite-PdCl<sub>2</sub>-Na Catalyst

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Summary Dimethyl ether was formed from  $H_2$  and  $CO_2$  over a graphite-PdCl<sub>2</sub>-Na catalyst under mild conditions; the reactivity and selectivity of this and other similar catalysts has been studied.

THE catalytic formation of  $C_1$ — $C_5$  hydrocarbons from hydrogen and carbon monoxide is known to occur over graphite-alkali metal EDA complexes.<sup>1</sup> This reaction is promoted by adding transition-metal chlorides to these complexes. We report the direct formation of dimethyl ether from hydrogen and carbon dioxide over a graphite PdCl<sub>2</sub>-Na catalyst with high selectivity.

The graphite-PdCl<sub>2</sub>-Na catalyst was prepared as follows: Graphite<sup>†</sup> (2 g) and  $PdCl_2$  (0.5 g) were mixed and heated under vacuum at 250-300° for 12-20 h in a closed system; pure sodium metal (2 g) was distilled onto the mixture, and PdCl<sub>2</sub> and Na were spread on the graphite under vacuum at 300°. When hydrogen gas (1 atm) was admitted to the system at 250°, 50–100 cm<sup>3</sup> (S.T.P.) of  $H_2$  was adsorbed over several hours. When a mixture of  $H_2$  (30 cmHg) and CO<sub>2</sub> (30 cmHg) was then introduced to the system, hydrocarbons such as  $CH_4$ ,  $C_2H_4$ , and  $C_2H_6$  were formed while several hundred cm<sup>3</sup> of CO<sub>2</sub> was simultaneously adsorbed. On introducing a mixture of H<sub>2</sub> and CO<sub>2</sub> several times more to the system, the main species of hydrocarbons changed from  $C_1 - C_2$  to  $C_3 - C_4$  (propene and butenes). Dimethyl ether<sup>‡</sup> was gradually formed during these reactions, finally reaching a steady concentration (5.6 cm<sup>3</sup> of CH<sub>3</sub>OCH<sub>3</sub> at 15 h). Water and a small amount of CO were also formed during the reaction. The reactivity and selectivity to dimethyl ether formation were sensitive to the preparation

and the pretreatment of the catalysts. The presence of oxygen gas markedly inhibited dimethyl ether formation.

The formation of ether was very much enhanced, however, by the presence of methanol or formaldehyde in the mixture of  $H_2$  and  $CO_2$ , and by pretreatment of the graphite-PdCl<sub>2</sub>-Na catalyst with CO. The hydrogenolysis of HCOOCH<sub>3</sub> (a probable intermediate in this reaction as it is easily formed from methanol and formaldehyde) proceeded selectively over this graphite-PdCl<sub>2</sub>-Na system to form dimethyl ether, but dimethyl ether was not formed from a mixture of only methanol and hydrogen under the reaction conditions. X-Ray analysis of the catalyst after the reaction indicated the presence of NaCl, palladium metal, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>. These results suggest that the dimethyl ether is formed through CH<sub>3</sub>O- and/or HCO-intermediates formed from CO<sub>2</sub> and H<sub>2</sub> on palladium in its low oxidation states (*e.g.* Pd<sup>1</sup> and Pd<sup>0</sup>) over graphite and sodium.

Other transition-metal chlorides were also used to prepare the catalysts with graphite and sodium. NiCl<sub>2</sub> and PtCl<sub>4</sub> (ca. 0.5 g) had some reactivity but poor selectivity to form dimethyl ether (0.8—1.1 cm<sup>3</sup> of CH<sub>3</sub>OCH<sub>3</sub> and 2.6—10 cm<sup>3</sup> of hydrocarbons in 15 h at 300°). RhCl<sub>3</sub>, IrCl<sub>3</sub>, OsCl<sub>3</sub>, CoCl<sub>2</sub>, and FeCl<sub>3</sub> showed little reactivity (less than 0.2 cm<sup>3</sup>). Pd metal or PdO instead of PdCl<sub>2</sub>, potassium instead of sodium, active carbon instead of graphite were examined, but no dimethyl ether was obtained under similar reaction conditions. Graphite–PdCl<sub>2</sub>–Na is therefore the most effective catalyst for the direct formation of dimethyl ether from hydrogen and carbon dioxide.

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† The pure graphite used (from the Union Carbide Co.) contained less than 5 p.p.m. of Fe and Si as ash. ‡ Identified by i.r., m.s. and g.c.

<sup>&</sup>lt;sup>1</sup> M. Ichikawa, M. Sudo, M. Soma, T. Onishi, and K. Tamaru, J. Amer. Chem. Soc., 1969, 91, 1538.