Formation of Dimethyl Ether from Hydrogen and Carbon Dioxide over a Graphite–$PdCl_2$–Na Catalyst

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Summary Dimethyl ether was formed from H_2 and CO_2 over a graphite–$PdCl_2$–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.[1] 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 $PdCl_2$–Na catalyst with high selectivity.

The graphite–$PdCl_2$–Na catalyst was prepared as follows: Graphite† (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 $PdCl_2$ 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^3 (S.T.P.) of H_2 was adsorbed over several hours. When a mixture of H_2 (30 cmHg) and CO_2 (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^3 of CO_2 was simultaneously adsorbed. On introducing a mixture of H_2 and CO_2 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‡ was gradually formed during these reactions, finally reaching a steady concentration (5·6 cm^3 of CH_3OCH_3 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–$PdCl_2$–Na catalyst with CO. The hydrogenolysis of $HCOOCH_3$ (a probable intermediate in this reaction as it is easily formed from methanol and formaldehyde) proceeded selectively over this graphite–$PdCl_2$–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_2CO_3, and $NaHCO_3$. These results suggest that the dimethyl ether is formed through CH_3O– and/or HCO–intermediates formed from CO_2 and H_2 on palladium in its low oxidation states (*e.g.* Pd^I and Pd^0) over graphite and sodium.

Other transition-metal chlorides were also used to prepare the catalysts with graphite and sodium. $NiCl_2$ and $PtCl_4$ (*ca.* 0·5 g) had some reactivity but poor selectivity to form dimethyl ether (0·8—1·1 cm^3 of CH_3OCH_3 and 2·6—10 cm^3 of hydrocarbons in 15 h at 300°). $RhCl_3$, $IrCl_3$, $OsCl_3$, $CoCl_2$, and $FeCl_3$ showed little reactivity (less than 0·2 cm^3). Pd metal or PdO instead of $PdCl_2$, potassium instead of sodium, active carbon instead of graphite were examined, but no dimethyl ether was obtained under similar reaction conditions. Graphite–$PdCl_2$–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.

[1] M. Ichikawa, M. Sudo, M. Soma, T. Onishi, and K. Tamaru, *J. Amer. Chem. Soc.*, 1969, **91**, 1538.