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Reaction of Carbon Dioxide and Hydrogen on Supported Palladium Catalysts

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Reaction of CO_2–H_2 with Pd/La_2O_3 gives MeOH with 89% selectivity, but acidic supported catalysts (Pd/SiO_2) favour the formation of CH_4.

At atmospheric pressure, the reactions of carbon oxides on Pd catalysts give mainly CH_4.[1,2] Poutsma[3] and Bell[4] have reported the synthesis of methanol on this type of catalyst but they used medium or high pressures (10—1088 bar) and synthesis gas (CO–H_2). The activity of CO_2 under these conditions was not tested.

We have reported earlier,[5] in agreement with other authors,[6,7] that methanol synthesis from CO_2 occurs by a direct reaction and not through prereduction to CO and consecutive hydrogenation. Consequently, the activity and selectivity for CO_2 reactions do not necessarily have the same characteristics as those for CO reactions in similar catalytic systems. We have now studied the reactions of CO_2–H_2 mixtures on supported palladium catalysts.

The results in Table 1 show that at a pressure of 120 bar and 350 °C, catalysts supported on SiO_2, Al_2O_3, and ThO_2 are able to form detectable quantities of methane, but systems based on La_2O_3, or those promoted by an alkali metal (Li–Pd/SiO_2) show a selectivity for methanol formation of $>80\%$.

Under our reaction conditions, the formation of higher hydrocarbons or alcohols by a chain-growing process is negligible. The reaction of CO, under the same conditions, shows a selectivity of up to 5% for formation of this type of product.[8] The observed formation of CO in the present reactions can be attributed to the water gas shift reaction.

These results and especially the particular selectivity towards formation of C_1 products are in accordance with a direct synthesis from CO_2 to methane or methanol. The mechanism proposed earlier for carbon oxides–hydrogen reactions[9] is in agreement with these facts. In this mechanism, the first step is the formation of formates by CO_2 insertion into a hydride site. We have detected formate species on Pd/SiO_2 and Pd/Al_2O_3 by chemical trapping[10] and Solymosi[11] has confirmed this proposition on Rh catalysts by i.r. spectroscopy. Another possible route to formate species is *via* the reduction of carbonates formed by CO_2 insertion into hydroxide sites.[9]

The conversion of the formate species into methanol (or methane) can be interpreted as taking place *via* bridged oxygenated and methoxy-species.[9,12] The stabilisation of these intermediates can explain the favourable effect of the basic supports. Chain-growing processes from C_1 products to higher alcohols or hydrocarbons by insertion of CO_2 into a

Table 1. Reaction of CO_2 on supported Pd catalysts.[a]

Catalyst: 5% Pd/support	Conversion (%)			Selectivity (%)				
	CH_4	MeOH + Me_2O	CO	CH_4	RH (C_2—C_5)	MeOH	Me_2O	ROH (C_2—C_5)
Pd/SiO_2	7.6	0.6	3	92.5	Trace	6.3	1.1	Trace
Pd/Al_2O_3	5.5	5.3	18	50.3	Trace	38.9	10.2	—
Pd/ThO_2	6.3	6.2	6.8	49.8	0.5	49.1	—	0.3
Pd/La_2O_3	0.7	6.1	4	10.5	0.1	89.4	—	—
$LiPd/SiO_2$	1.2	7.2	13.3	13.9	1.7	83.9	—	0.2

[a] $T = 350$ °C; $P = 120$ bar; $H_2/CO_2 = 3$; gas space velocity 4 l h^{-1} (g catalyst)$^{-1}$. The supports were commercial products, SiO_2 (Roth 0201), and γ-Al_2O_3 (Fluka 1095), or were prepared (La_2O_3, ThO_2) by calcination (12 h at 550 °C) of the hydroxides obtained by precipitation from commercial nitrates (Rhône-Poulenc) with NH_4OH at pH = 8. Catalysts were prepared by impregnation under reduced pressure (20 mbar) of the oxides, with a solution of $PdCl_2$ in 0.2 M-HCl (Li_2PdCl_4 in aqueous media for the final entry), and dried (150 °C at 0.1 mbar for 3 h, then 400 °C in air for 4 h). Reactions were carried out in a stainless steel reaction vessel as described previously,[5] after reduction *in situ* at 400 °C for 5 h. The products were analysed by g.l.c. as described in ref. 5.

metal–C or metal–O bond which occur with transition-metal complexes[13] are not observed on solid catalysts under our conditions.

Thus, supported palladium catalysts are able to produce methanol from CO_2–H_2 synthesis gas, with a selectivity which depends on the nature of the support.

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