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A New Method of CO_2 Activation: Alcohol Homologation with a CO_2/H_2 Mixture

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Homologation of methanol and ethanol has been observed by placing a CO_2/H_2 (1:1) mixture in contact with a suspension of copper/zirconium polyhydride, $Cu_3Zr_2H_n$, in an alcohol–benzene solution; the absence of CO and CH_3OH among the reaction products in the ethanol homologation suggests that carbon monoxide and methanol are not involved in the reaction observed.

The homologation of an alcohol by treating it with 'syngas' (CO/H_2) is a well-documented reaction.[1] We describe here a new reaction in which a CO_2/H_2 mixture is used as homologation reagent instead of syngas. Neither carbon monoxide nor methanol are intermediates in the reaction under discussion.

A copper/zirconium polyhydride $Cu_3Zr_2H_n$ ($n \approx 0.3$) with its surface covered by copper crystallites (~240 Å), copper(I) and (II) oxides, and zirconia phases was used as the catalyst (Catalyst I)† in our experiments. Copper metal and copper oxides are widely considered to be catalysts for methanol synthesis by CO_2 or CO hydrogenation.[3] The ability of the zirconium atom in zirconia to play the role of a Lewis acid and to bind to oxygenates is well known.[4] In this context we expected the catalyst under study to reveal some activity.

Our experiments showed that small amounts of methanol and traces of CO and CH_4 are formed by placing a CO_2/H_2 (1:1) mixture in contact with catalyst I at 210°C and 25 atm in the absence of a solvent (Table 1, Entry 1). However, the course of the reaction was changed dramatically in the presence of an alcohol or alcohol–benzene mixture as the solvent. In fact, neither methanol nor CO and CH_4 was detected in reaction products formed by contact of a CO_2/H_2 (1:1) mixture with an ethanol–benzene (1:2) solution containing a suspension of catalyst I under the above-mentioned temperature and pressure. Ethanol was found to convert into a mixture of ethyl and propyl acetate (see Table 1, Entry 2). Ethyl acetate formation was also observed under an Ar atmosphere in the absence of CO_2 and/or H_2 and is presumably a result of ethanol oxidation by surface copper(II) oxide. In agreement with this conclusion, no X-ray pattern corresponding to the CuO phase is found for the samples after these experiments (see Table 2, Entry 3). Propyl acetate formation does not take place in the absence of CO_2 (for example, under an Ar atmosphere), so it seems to be a result of ethanol homologation with the CO_2/H_2 mixture and esterification of initially-formed propanol. Analagously, in experiments in which methanol instead of ethanol was used as the solvent component, methyl formate and diethyl ether formation was observed (Table 1, Entry 3). It was also found that interaction of a suspension of catalyst I in an ethanol–benzene system with a CO/H_2 mixture under the same conditions results in the formation of small amounts of propyl and butyl alcohols as well as ethyl, propyl and butyl acetates (see Table 1, Entry 7).

The palladium complex $Pd[(PhCN)(OAc)]_2$ was found to activate carbon dioxide under the reaction conditions; more than 0.3 mol (mol cat)$^{-1}$ h^{-1} of ethyl formate was formed on placing a H_2/CO_2 mixture in contact with an ethanol–benzene solution containing 100 mg $Pd[(PhCN)(OAc)]_2$ at 150°C and 30 atm. It was therefore of interest to study whether the introduction of the complex into the reaction mixture can influence the catalytic process observed for catalyst I. In fact, the addition of $Pd[(PhCN)(OAc)]_2$ to catalyst I increased the yield of propyl acetate (see Table 1, Entry 4). Interestingly, the substitution of $Pd[(PhCN)(OAc)]_2$ by a complex with phosphine ligands $(PPh_3)_2PdCl_2$ gave rise to another product of homologation, di-n-propyl ester (see Table 1, Entry 5).

According to X-ray data, the treatment of catalyst I with an H_2/CO_2 mixture in the absence of a solvent results in the disappearance of the $Cu_3Zr_2H_n$ phase (see Table 2, Entry 2). The destruction of the polyhydride phase does not take place in the presence of alcohol-containing solvents. Formation of new crystal phases ($PdZr_2$ and Pd_3Zr_6O) was observed (see Table 2, Entries 5 and 6) in systems with palladium complexes. These palladium-containing phases seem to be able to take part in the H_2 molecule activation. It is worth mentioning that $(PPh_3)_2PtCl_2$ addition to the reaction mixture does not lead to the formation of any Pt/Zr containing phases and no products of CO_2 hydrogenation were detected for the last system.

The data available do not permit us to arrive at a definite

† $CuZr_2$ alloy was oxidized and hydrogenated to give the initial form of the catalyst as described elsewhere.[2]

Table 1 Catalytic activity of Cu/Zr catalyst-containing systems[a]

Entry	Catalyst	Solvents	Products[b]
1	Catalyst I	—	CO[c], CH_4[c], MeOH[d]
2	Catalyst I	C_6H_6–EtOH (2:1)	H_2O, AcOEt, AcOPr[e]
3	Catalyst I	C_6H_6–MeOH (3:1)	H_2O, HCO_2Me,[c] Et_2O[c]
4	Catalyst I + $Pd[(PhCN)(OAc)]_2$	C_6H_6–EtOH (2:1)	H_2O, AcOEt, AcOPr[f]
5	Catalyst I + $(PPh_3)_2PdCl_2$	C_6H_6–EtOH (2:1)	H_2O, $(Pr^n)_2O$[g]
6	Catalyst I + $(PPh_3)_2PtCl_2$	C_6H_6–EtOH (2:1)	H_2O, AcOEt, AcH[e,h]
7	Catalyst I[i]	C_6H_6–EtOH (2:1)	H_2O, PrOH, BuOH, AcOEt, AcOPr, AcOBu

[a] Experiments were carried out with the experimental technique described in ref. 6 (autoclave 16 cm^3)at 210°C, $CO_2/H_2 = 1$, $p = 25$–35 atm, time = 10 h; 0.2–0.4 g of catalyst I. [b] Liquid samples were analysed using an Automass 150 (Delsi–Nermag, France), OV-1: 0.25 mm × 25 m, $E\,I^+ = 70$ eV. [c] Traces. [d] 15 mmol (g cat)$^{-1}$ h^{-1}. [e] 0.06 mmol (g cat)$^{-1}$ h^{-1}. [f] 0.3 mmol (g cat)$^{-1}$ h^{-1}. [g] 0.2 mmol (g cat)$^{-1}$ h^{-1}. [h] Product of EtOH dehydrogenation. [i] Experiment was carried out with a $CO/H_2 = 1$ mixture at 210°C, $p = 20$ atm.

Table 2 Phase composition of samples

Entry	Catalyst and conditions of treatment	Crystal phases detected						
		Cu	CuO	Cu_2O	ZrO_2	$Cu_3Zr_2N_n$	$PdZr_2$	Pd_3Zr_6O
1	Catalyst I (initial form)	+	+	+	+	+		
2	Catalyst I; $CO_2/H_2=1$, 210°C, 25 atm	+			+			
3[a]	Catalyst I; CO_2, 30 atm	+		+	+			
4[a]	Catalyst I; $CO_2/H_2=1$, 30 atm	+	+	+	+	+		
5[a]	Catalyst I; $CO_2/H_2=1$, $+Pd[(PhCN)_2(OAc)]_2$, 35 atm	+			+	+	+	+
6[a]	Catalyst I; $CO_2/H_2=1$, $+(PPh_3)_2PdCl_2$, 35 atm	+	+		+			+

[a] After reaction with an ethanol–benzene containing mixture at 210°C.

conclusion concerning the reaction mechanism. However, tentative suggestions can be drawn taking into consideration the following facts.

(i) Neither carbon monoxide nor methanol are detected in liquid phase reaction products; their absence suggests that CO and MeOH are not involved as intermediates in the reaction observed. In agreement with this conclusion the product composition of the liquid phase CO_2/H_2 reaction differs markedly from that of CO/H_2 homologation (*cf.* Table 1, Entries 2 and 7).

(ii) Carbon dioxide is known to react with an alcohol to form a monoalkyl hydrocarbonate,[5] eqn. (1).

$$CO_2 + ROH \rightarrow ROCO_2H \quad (1)$$

The key problem of the reaction is the mechanism of the new C—C bond formation. Different schemes can be used for the speculations including one presuming intermediate coordinated carbene-species [HC(R)O→Zr] formation and its isomerization to form a coordinated aldehyde which undergoes reduction into the coordinated alcohol.

The observed ether or ester is assumed to be formed by a surface reaction between adsorbed/coordinated alkoxy and carboxylic groups.

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