Direct Synthesis of Ethanol over a Cu–Zn Catalyst in the Liquid Phase

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Cu–Zn and Cu–Al catalysts generated by reduction of $Cu(acac)_2$ (acac = acetylacetonato) with $ZnEt_2$ or $AlEt_3$, are shown to produce oxygenated compounds from syngas in the liquid phase under pressure; high selectivities for ethanol are observed, especially with the Cu–Zn system (45.7 mol%) in the early stages of the reaction.

Cu–Zn Catalysts give very high selectivity in the gas phase synthesis of methanol from syngas.[1] However, the direct catalytic synthesis of higher alcohols from CO and H_2 using these copper based catalysts requires alkaline promoters, together with high temperatures and pressures. Under these conditions, a 20—30% yield of higher alcohols is obtained.[2] Another heterogeneous system gives rise to higher selectivities towards heavy alcohols,[3] but additional transition metal salts are necessary; in these cases yields of up to 30—40% C_2^+ alcohols are obtained. Our earlier work on the synthesis of cobalt catalysts for the catalytic production of light olefinic hydrocarbons[4,5] and the observation that small amounts of linear alcohols are produced under more drastic conditions[6] prompted us to extend this method of generating catalyst precursors to the Cu–Zn system, in order to produce reduced Cu moieties together with an oxidized form of Zn, which appears to be the combination required for the synthesis of alcohols from syn gas.

The synthesis of this new catalyst was performed as previously described for cobalt.[5] A pink solution of $Cu(acac)_2$ (acac = acetylacetonato) (38 mmol) in dry benzene (200 ml) was mixed with a solution of butadiene (300 mmol, large excess) in the same solvent (10 ml) in a Schlenk tube at room temperature under nitrogen atmosphere, and cooled to *ca.* 0 °C. Pure $ZnEt_2$ (39 mmol) was then added at room temperature with a hypodermic syringe through a septum over 1 min. During this process, the solution became dark brown and remained homogeneous, and a mixture of C_2H_4 and C_2H_6 was evolved. This is consistent with the fact that $Cu(acac)_2$ is reduced,[7] a process for which reaction (1) can be proposed, as for the synthesis of naked nickel from $Ni(acac)_2$ and $AlEt_2OEt$.† Owing to the production of zerovalent Cu by this process, buta-1,3-diene must be introduced in order to prevent copper precipitation.[8] In this case, solubilization of Cu^0 occurs by complexation with the diene, most likely *via* production of a π-allyl intermediate.[9]

$$Cu(acac)_2 + ZnEt_2 \longrightarrow Cu^0 + Zn(acac)_2 + C_2H_4 + C_2H_6 \qquad (1)$$

After 10 min stirring at 0 °C, *o,o'*-terphenyl (50 g) was introduced into the Schlenk tube. Dissolution of this compound was followed by transfer to an autoclave under H_2, where the solution was warmed slowly to 260 °C.‡ During this

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† When the reduction of $Cu(acac)_2$ with $ZnEt_2$ is conducted without buta-1,3-diene, copper precipitates on the side of the Schlenk tube. This catalyst then gives essentially CH_4 from CO/H_2 under the same conditions.

‡ The initial benzene solvent was evaporated under H_2 over 3—4 h. The reactor was then heated from *ca.* 100 to 260 °C over 4 h under H_2. At this stage, H_2 was continuously passed through the autoclave and the exit gases analysed by g.c. This treatment was stopped when no more secondary products were formed, after about 12 h.

Table 1. Catalytic results for hydrogenation of CO on Cu–Zn based catalysts in the liquid phase.

	$Cu(acac)_2$–$ZnEt_2$[a]				$Cu(acac)_2$–$AlEt_3$[b]		
Run number	1	2	3	4	5	6	7
T°C	260	260	280	300	260	270	300
p/atm	60	60	60	80	60	60	60
Space velocity[c] h^{-1}	193	401	396	2038	225	567	202
Turnover rate[d]/h^{-1}	0.07	0.06	0.06	0.11	0.02	0.04	0.06
Selectivity							
Hydrocarbons[e]	7.3	18.5	36.7	51.6	48.4	50.9	65.1
Oxy products[e]	86.3	69.7	44.3	35.5	33.8	31.1	24.7
CO_2[e]	6.4	11.8	19.0	12.9	17.8	18.0	10.2
MeOH[f]	31.9	36.3	93.4	94.5	67.5	73.9	60.9
EtOH[f]	45.7	57.2	6.2	5.1	21.4	21.2	29.7
Pr^nOH[f]	Trace	0.1	0.15	0.1	0.6	1.4	0.8
Bu^nOH[f]	Trace	0.1	0.05	0.05	1.1	1.1	0.9
Branched alcohols[f]	0.3	—	—	0.1	Trace	Trace	—
MeCHO[f]	1.2	1.7	0.15	0.05	0.9	0.5	1.1
$MeCO_2Me$[f]	2.0	1.0	—	0.05	2.1	0.4	2.0
$MeCO_2Et$[f]	18.9	3.6	—	—	0.4	Trace	0.5
Ketones[f]	—	—	0.05	0.05	6.0	1.5	4.1

[a] $Cu(acac)_2$ (38 mmol), $ZnEt_2$ (39 mmol), butadiene (300 mmol); for each run H_2:CO = 1; reaction time = 60 min.
[b] $Cu(acac)_2$ (38 mmol), $AlEt_3$ (26 mmol), butadiene (264 mmol); for each run; H_2:CO = 2; reaction time = 60 min.
[c] ml of syngas × (ml of liquid phase)$^{-1}$ × h^{-1}.
[d] Cmmol × (Cu mmol)$^{-1}$ × h^{-1}:
[e] Selectivities expressed in C_1 units.
[f] Selectivities expressed in mol% within the oxyproducts.

process, byproducts were formed and detected by g.l.c., mainly $(Me)_2CO$, CH_4, and C_2H_6. This corresponds to hydrogenolysis of $Zn(acac)_2$, which affords ZnO together with the same product mixture.§ The homogeneous solution was transformed into a slurry, in which CO hydrogenations were conducted under dynamic conditions. The results are given in Table 1. Hydrocarbons, CO, CO_2, and H_2 were analysed by on-line g.l.c., the oxygenated products were trapped before analysis. Although the conversion is lower than that observed using cobalt catalysts,[6] it appears that ethanol is produced with good selectivity in the early stages of the process. 86% of consumed CO is converted to oxygenated products at the beginning of the reaction, but this selectivity decreases to 35% after 10 h. Of the oxygenates, ethanol is produced with a *ca.* 40—60% molar selectivity on a fresh catalyst, as after a few hours, methanol becomes the major product. Other experiments have shown that modification of the H_2 : CO ratio does not significantly affect the oxygenate selectivity and overall activity.[10]

Upon using $AlEt_3$ instead of $ZnEt_2$ as reducing agent, the selectivity to oxygenates is reduced. However, the ethanol production remains quite high, even for long periods (run 7, the results are those obtained after 30 h). X-Ray photoelectron spectroscopic (x.p.s.) analysis of the used catalysts shows that the amount of stable Cu^+ (915, 9 eV) is greater in Cu–Zn than Cu–Al mixtures; in accordance with previous investigations reported by Herman *et al.*,[11] the active species in these systems may be Cu^+ dissolved in the ZnO lattice which favours MeOH production.[12]

The ability of the Cu–Zn combination to produce ethanol thus decreased with time to that of a classical methanol synthesis. However, at least in the early stages of the catalytic reaction, the reaction produces ethanol with good selectivity. This is an unprecedented and rather unexpected result, which may be enhanced by the introduction of additional transition metals, which are known to favour such reactions.[13]

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§ The products acetone, methane, and ethane begin to appear at temperatures as low as 180 °C; X-ray analysis of the resultant solid clearly shows that ZnO is produced.

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