

Methanolization under pressure of carbon oxides and their mixture on Cu-ZnO-Al₂O₃ catalysts. Role of carbon dioxide.

* J. THIVOLLE-CAZAT, R. BARDÈT, Y. TRAMBOUZE.

Institut de Recherches sur la Catalyse

2, Av. A.Einstein 69626 VILLEURBANNE Cédex FRANCE

The hydrogenation of carbon oxides into methanol is a reaction known for a long time. Formely it was believed that methanolization of CO₂ proceeded via the intermediacy of CO (1). More recently, Bashkirov et Al.(2) have shown that reduction of CO₂ into CO and methanol could not be consecutive reactions since they both took place when contact time tended to zero; they reported as Temkin et Al.(3) that methanol formation from CO decreased dramatically if the presence of CO₂ or water was strictly eliminated from the reactive gases. Then it was concluded that methanolization of CO₂ proceeded through a direct pathway whereas that of CO involved the intermediacy of CO₂ through the water gas shift reaction. On the contrary, Klier et Al.(4) proposed that the role of CO₂ in a mixture of carbon oxides is to keep the catalyst in an oxidation state favourable to CO hydrogenation which was regarded as the main reagent leading to methanol. We report here some results which support the hypothesis of Bashkirov but do not exclude the oxidative role of CO₂.

EXPERIMENTAL

The CuO-ZnO-Al₂O₃ (65/25/10) catalyst used is an industrial one prepared by precipitation of nitrates mixture by potassium carbonate at pH 7. Its surface area is about 50 m²/g. 5mg of this catalyst diluted in 500 mg of quartz powder are introduced in a 1/4" differential flow reactor and reduced for 12 hr at 300°C in a hydrogen stream (3l/hr; heating rate: 3°C/mm). Then the mixture of reactive gases (CO + 2H₂, CO₂ + 3H₂, or 23CO + 7CO₂ + 70H₂) kept in a pressurized steel container is passed through the catalytic bed (22bar, 2l/hr), depressurized downstream the reactor in a heated upstream pressure regulating valve and chromatographically analyzed on line.

Higher conversion experiments are performed in a 3/8" integral flow reactor (22bar, 2l/hr, 2,2g of catalyst); downstream the reactor, the products are partially trapped at ambient temperature and effluent gases are analyzed as above. All reactive gas mixtures are used with their residual moisture.

RESULTS AND DISCUSSION

The results obtained in the differential flow reactor (22bar, 2l/hr, 5mg of catalyst) are represented in the figure. As observed under atmospheric pressure (5), the formation of methanol under 22bar, from either CO or CO₂ shows a maximum versus temperature. The maximum obtained from CO₂ is higher and situated at a lower temperature than that from CO. Moreover the only significant by-product from CO₂ is CO, whereas hydrocarbons and higher alcohols are formed in important proportions

from CO. Thus the methanolization of CO_2 under the present conditions proves to be more active, more selective and to proceed at a lower temperature than that of CO. These results support the hypothesis of Bashkirov (2) according which CO_2 can be hydrogenated directly into methanol, without the intermediacy of CO; indeed the methanolization of CO_2 proceeds at a temperature which does not allow significant hydrogenation of CO. Thus the hydrogenation of CO and CO_2 must involve two distinct reaction pathways, the latter being more rapid. Nevertheless these results are in disagreement with those of Klier et Al. (4) who observed that hydrogenation of CO into methanol was more active and selective than that of CO_2 and concluded in the opposite way. The difference in catalyst composition and preparation may be the reason of such a divergence since Sneed et Al. (6) observed that the ratio of methanol formation maxima from CO and CO_2 could be reversed by changing the nature of the catalyst.

Experiments were also performed in the integral reactor (22bar, 21/hr; 2,2g of catalyst), whose results are reported in table 1.

Table 1: Conversion of carbon oxides into methanol(x%) and methanol concentrations measured(C%) or theoretical equilibrium values(Ceq) at determined temperatures.

Reagents	T °C	x%	C%	Ceq
$\text{CO} + 2\text{H}_2$	246	11,8	4,5	11
$\text{CO}_2 + 3\text{H}_2$	225	7,2	3,5	3,8
$23\text{CO} + 7\text{CO}_2 + 70\text{H}_2$	230	31,3	11,6	12

The theoretical equilibrium values of methanol concentrations were calculated from relations reported in reference 4.

It can be seen that the thermodynamic equilibrium is nearly reached in the case of CO_2 or CO, CO_2 mixture, but not with CO. These results confirm the high reactivity of CO_2 already observed in differential conditions which are governed by kinetics; in the integral reactor the CO_2 conversion is lower than that of CO because of thermodynamic limitations.

As was reported by Klier (5) and other workers (1), the CO, CO_2 mixture leads to the best results; according to the former the role of CO_2 in such a mixture is to keep the catalyst in an oxidized form Cu^{I} which would favour CO hydrogenation. In the light of our results we can propose a complementary explanation: taking into account its high reactivity, CO_2 may well be the main reagent leading to methanol. Each reduced CO_2 molecule leads to one of methanol and one of water; this latter can react in the presence of CO according to the water gas shift reaction which is kinetically and thermodynamically favoured under the present conditions. Thus, the equilibrium $\text{CO}_2 + 3\text{H}_2 = \text{MeOH} + \text{H}_2\text{O}$ can be displaced to the right and then the low thermodynamic limitations in the case of pure CO_2 can

be overstepped. In order to evaluate the realism of such a proposal, the influence of water content on the methanolization of CO was studied under atmospheric pressure (table 2).

Table 2: Influence of water content in CO + 2H₂ mixture on CO hydrogenation at 220°C (1bar, 2l/hr, 175mg of catalyst).

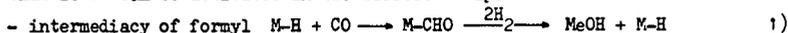
Water content	.5ppm (a)	residual moisture	6000ppm	2%
Methanol concentration (ppm)	60	400	500	300

(a) dehydration of gas is performed by trapping in acetone-dry ice bath.

It must be pointed out that for each water content, CO₂ is obtained almost quantitatively from reaction of water and CO. Thus no kinetic limitation can restrict the conversion of CO into CO₂ during the hydrogenation of CO, CO₂ mixtures.

The results in table 2 show that methanolization rate of CO is very low in the absence of water; but traces of water are sufficient to reactivate the process; in this case the intermediacy of CO₂ is unlikely because of its low partial pressure. Higher water contents inhibit methanol formation probably for kinetic reasons.

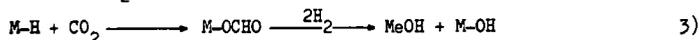
These results support the mechanism already proposed by Sneed et Al.(6), that is CO can be activated in two different ways:



This process may occur mainly in the absence of water and proves to be very slow; it may also lead to C-C bond formation.



The same formate intermediate shown by Deluzarche et Al.(7) by chemical trapping can be formed from CO₂:



The processes 2 and 3 prove to be rapid according to our results. The M-OH species which allows rapid activation of CO may be an oxidized form of copper as proposed by Klier (4); in agreement with these workers the conservation of such a species may involve the presence of CO₂ or water as can be illustrated by equations 3' and 4



CONCLUSION

The comparative study of hydrogenation under pressure of CO and CO₂ has shown that CO₂ leads to methanol more rapidly, more selectively and at a lower temperature than CO. These results support the hypothesis of Bashkirov which suggests that methanolization of CO₂ proceed without the intermediacy of CO.

Moreover the hydrogenation of CO proves to be dramatically dependent of the presence of CO₂ or water; the role of these products may be to keep the catalyst in a suitable oxidized form. At high conversion the hydrogenation of CO in CO,CO₂ mixtures may also proceed at least partially through water gas shift reaction via the intermediacy of CO₂.

REFERENCES

- 1/ G. NATTA Catalysis, Emmett (Reinhold New-York) III, 349, 1955
- 2/ A.N. BASHKIROV et Al. Kinetics and Catal. 16, 704 and 706, 1975, *ibid* 17, 380 and 1132, 1976
- 3/ V.D. KUZNETSOV, F.S. SHUB and M.I. TEMKIN *ibid* 23, 788, 1982
- 4/ K. KLIER et Al. J. Catal. 74, 343, 1982
- 5/ R. BARDET, J. THIVOLLE-CAZAT, Y. TRAMBOUZE J. Chim Phys 78, 135, 1981
- 6/ B. DENISE and R.P.A. SNEEDEN J. Mol. Catal. 17, 359, 1982
- 7/ A. DELUZARCHE et Al. React. Kinet. Catal. Lett 16, 207, 1981

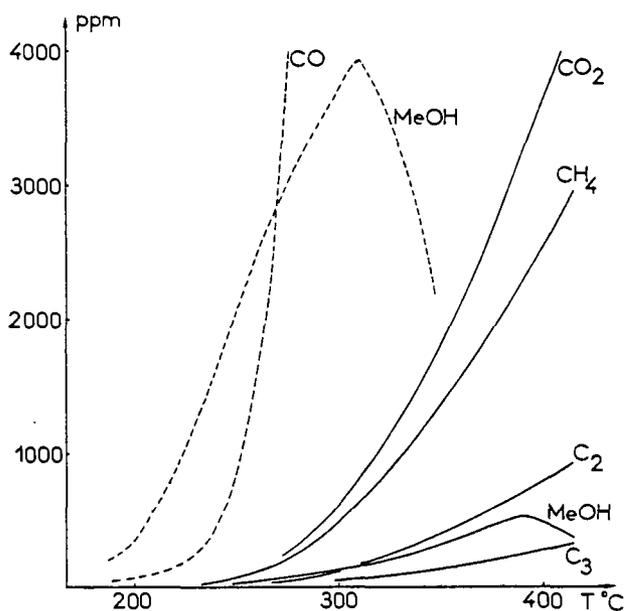


Figure: Evolution of products concentration versus temperature, during CO (—) or CO₂ (---) hydrogenation (22bar, 2l/hr, 5mg of Cu-ZnO-Al₂O₃ catalyst).