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Catalytic properties of new Cu based catalysts containing Zr and/or V for methanol synthesis from a carbon dioxide and hydrogen mixture

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Pure unsupported copper is a poor catalyst for CH_3OH synthesis from $CO_2 + H_2$ when it is compared to Cu coprecipitated with Zr or Zr + V in which case its selectivity and yield in methanol are strongly enhanced. The two Zr and V components added to pure Cu are shown to be textural promoters towards zerovalent Cu which participate to the building of the active sites. Methanol formation on these catalysts is a structure insensitive reaction with respect to the metallic Cu dosed by N_2O surface decomposition.

Keywords: Copper catalysts; methanol synthesis; “syn gas” conversion

1. Introduction

It is well known that CO_2 is a very abundant and cheap carbon source which can be used as a reactant to yield methanol and/or hydrocarbons [1,2] in the presence of a conventional methanol synthesis catalyst, i.e. the one associated with the $CO + H_2$ mixture. Recently CO_2 was also tested as a source of methanol on different catalysts than the conventional one. Most of these new catalysts were based on the combination of Cu and zirconia and gave very promising results [3–7]. Besides this support for Cu, other ones such as V, Cr based ones were also recently successfully tested for this reaction starting with CO_2 and H_2 (8–10).

Ternary and binary V–Cu–Zn, Cr–Cu–Al and V–Cu–Zr catalysts were prepared in this laboratory by coprecipitation of well defined complex precursors as described by Kanoun et al. [11,12] which led to well defined catalysts once they were reduced in flowing hydrogen at 300°C for 3 h. For instance towards the dehydrogenation of ethanol into acetaldehyde at 190°C these composite catalysts showed high selectivities ($\approx 100\%$) and good activities as already described by Kanoun et al. [11,12]. The V–Cu–Zn and Cr–Cu–Al systems exhibited also interesting selectivities in methanol synthesis from CO_2 and H_2 as well as good activities at a temperature reaction of 300°C and under a total pressure of 32 bar [8,9].

Zirconia was introduced here in the precursors of the catalysts under the form of an alkoxide, namely zirconium propoxide as a starting Zr material.

2. Experimental and results

2.1. PREPARATION OF THE CATALYSTS

Cu and V complexes were prepared as described in earlier publications while zirconia was introduced as an alkoxide (propoxide) in the ammonia solution containing the copper complex with or without the vanadium one. The binary Cu–Zr catalysts were prepared with the atomic compositions indicated in table 1 while the ternary ones were obtained with an atomic ratio $V/(Cu + Zr) = 1$, the $Cu/(Cu + Zr)$ atomic terms varying from 0 up to 1. Copper free ZrO_2 and V–Zr were also made and tested in the synthesis.

Their textural properties were already described by Kanoun et al. [12], the copper specific areas S m^2/g Cu were determined by the decomposition of N_2O and given in tables 1 and 2.

2.2. CATALYTIC CONVERSION OF CO_2 BY H_2

The GHSV was set at 30000 h^{-1} and the reactant partners analyzed on-line by gas chromatography. The three principal reaction products were: methanol,

Table 1
Catalytic properties of the catalysts in the synthesis of methanol

Catalyst	A_{cat} (g h^{-1} kg^{-1} (cat.))	A_{Cu} (g h^{-1} kg^{-1} (Cu))	S (m^2/g) Cu	TOF (10^3 molec./s at Cu)	Selectivity (%)
Cu	65	65	1	17	6
Cu 0.9 Zr 0.1	86	128	4	10	17
Cu 0.5 Zr 0.5	103	311	29	5	17
Cu 0.1 Zr 0.9	236	4560	86	16	15
V–Cu	156	441	29	5	27
V–Cu 0.9 Zr 0.1	170	521	30	5	12
V–Cu 0.5 Zr 0.5	171	883	49	5	9
V–Cu 0.1 Zr 0.9	170	4396	185	6	13
V–Zr	54	–	–	–	5
ZrO_2	0	–	–	–	–
V_2O_5	39	–	–	–	7

Table 2
Catalytic properties of the catalysts in methane formation

Catalyst	A_{cat} (g h^{-1} kg^{-1} (cat.))	A_{Cu} (g h^{-1} kg^{-1} (Cu))	S (m^2/g) Cu	TOF (10^3 molec./s at Cu)	Selectivity (%)
Cu	125	125	1	68	24
Cu 0.9 Zr 0.1	72	107	4	16	25
Cu 0.5 Zr 0.5	100	302	29	6	22
Cu 0.1 Zr 0.9	215	4150	86	16	28
V–Cu	35	99	29	2	11
V–Cu 0.9 Zr 0.1	270	827	30	17	36
V–Cu 0.5 Zr 0.5	136	699	49	9	18
V–Cu 0.1 Zr 0.9	115	2974	185	10	20
V–Zr	148	–	–	–	25
ZrO_2	0	–	–	–	–
V_2O_5	88	–	–	–	31

methane and carbon monoxide (coming from the reverse WGS reaction). Traces of ethanol and dimethylether were also detected in particular with catalyst Cu 0.1 Zr 0.9. All values indicated in tables 1 and 2 were recorded at steady state, at a reaction temperature of 300°C with a feed containing 10% of CO_2 in H_2 under a total pressure of 32 bar.

3. Discussion

Tables 1 and 2 show clearly that pure zirconia is neither a catalyst by itself for CH_3OH nor for CH_4 formation in the experimental conditions and as described elsewhere vanadia on the contrary develops some activity towards these two reactions [8]. The binary V–Zr catalyst exhibits better A_{cat} but lower selectivities for the two reaction tests than pure vanadium oxide. The most interesting catalyst of all in methanol synthesis is the binary Cu 0.1 Zr 0.9 system and one can see that the lower the Cu content of these binary catalysts the better the results in terms of A_{Cu} and A_{cat} while it seems that the corresponding selectivities are quite without modification. Addition of a constant amount of V to the former binary catalysts results in a levelling of A_{cat} at a constant value and an increase of the A_{Cu} values except for the V–Cu 0.1 Zr 0.9 where a small decrease is recorded when compared to Cu 0.1 Zr 0.9 without V at all. The TOF data are also levelled by introduction of V in the binary Cu systems. This behaviour of V has also been recorded for other ternary complex catalysts such as V–Cu–Zn [8] for the same reaction. Finally the methanol synthesis appears once more to be a structure insensitive reaction. The TOF numbers of table 1 are of the order of magnitude of those found in the literature for several other

Cu–Zr catalysts involving CO_2 and H_2 feeds as mentioned by Amenomyia et al. [4] and Gasser and Baiker [6]. The yield of catalyst Cu 0.1 Zr 0.9 in terms of A_{Cu} is much higher than that quoted by Denise and Sneeden [5] for the same reaction under quite similar conditions.

Comparing tables 1 and 2 shows one that the whole series of catalysts is more selective towards methanation than methanol formation no matter their actual compositions. Again the best results are obtained for the binary composite Cu 0.1 Zr 0.9 while adjunction of V does not exert the same effect as mentioned above and acts in a more complicated way. Here the introduction of a constant amount of V on the three CuZr compounds is followed by a decrease of A_{cat} which is not recovered for the A_{Cu} results. The reaction is again non sensitive to the structure according to the TOF data indicated in table 2.

It is, however, worth mentioning that the most interesting catalyst of the whole series is Cu 0.1 Zr 0.9 in terms of CH_3OH production as well as in terms of CH_4 formation but its A_{Cu} in methane formation though its selectivity in the hydrocarbon is higher than the one in the alcohol.

Nevertheless, as the selectivities of the catalysts in methanol and in methane are relatively low (in general less than 50%) it appears that they are all relatively selective towards the reverse WGS reaction.

4. Conclusions

Zirconia is a valuable promoter for copper catalysts with respect to the synthesis of methanol from CO_2 and H_2 in particular.

This oxide provides a textural effect upon the dispersion of Cu and also contributes to the building of the Cu zerovalent active sites by increasing markedly the poor selectivity of Cu alone in the synthesis of methanol. When V is added to the binary Cu–Zr composite catalysts the main properties supplied by ZrO_2 are quite preserved in the ternary composite catalysts.

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