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Hydrogenation of CO and CO_2 toward methanol, alcohols and hydrocarbons on promoted copper–rare earth oxides catalysts

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Abstract

The recent development of a copper–rare earth oxid catalyst ($Cu–La_2Zr_2O_7$) with cubic pyrochlore structure allows to synthesize alcohols and hydrocarbons from $CO + H_2$ and $CO_2 + H_2$ feeds. A good activity in methanol synthesis is obtained by promoting the given catalysts by addition of oxides, e.g., ZnO or ZrO_2. C_{2+} alcohols and C_{2+} hydrocarbons are formed in the presence of a transition metal promotor like Co. Finally, a composite catalyst prepared by mixing the $Cu–La_2Zr_2O_7$ methanol catalyst with a HY zeolite yields mainly C_{2+} hydrocarbons.

Keywords: Methanol; Hydrocarbons; Carbon dioxide; Hydrogenation; Copper catalysts; Rare earth oxide catalysts; Composite catalysts

1. Introduction

The possibility of CO and CO_2 hydrogenation into methanol on various copper catalysts is well known from the literature [1–6] despite the dispute which exists about the reaction mechanism in the presence of syngas [7–9]. With a $CO_2 + H_2$ feed a direct hydrogenation of CO_2 without intermediacy of CO is proposed by many authors [10,11]. The problem of activity enhancement by metals or oxides as well as that of aging of the catalytic material must be solved in order to develop suitable catalysts for the MeOH synthesis from $CO_2 + H_2$.

Many important results have been reported in the CO chemistry for the synthesis of higher alcohols and hydrocarbons on Ni or Co promoted copper catalysts (or on Cu promoted Co or Fe catalysts) [12,13]. However, only few informations exist in literature concerning their formation from CO_2. Higher alcohol or hydrocarbon synthesis implies the presence of a catalytic system able to favour the chain growth.

In syngas chemistry on rhodium or Co–Cu/$ZnAl_2O_4$ catalysts, a CO "insertion" mechanism has been proposed by several authors [14,15]. In that mechanistic scheme, the chain growth on a Co–Cu system, is based on the reaction between a C_1 oxygenated species (formyl or CO) which can be formed on the copper surface and a carbene (or hydrocarbon) entity located on Co or at the Co–Cu interface. Therefore, the catalysts have to ensure several functions:

1. Formation of chemisorbed C_1 oxygenated moieties.

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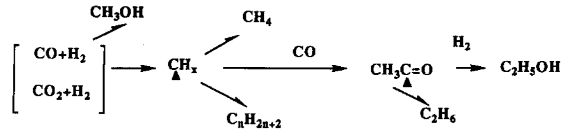

Scheme 1. "Insertion" mechanism of alcohols and hydrocarbons formation from CO and CO_2.

2. Formation of alkene or alkyl species.
3. Insertion of C_1 oxygenates into the hydrocarbon metal bonds.

In the presence of CO_2 an insertion into a metal–alkyl bond, as described with Ni complexes in homogeneous catalysis [16], does not seem reasonable in heterogeneous catalysis. A combined mechanism (Scheme 1) with formation of a CH_x intermediate from CO_2 and a further insertion of CO (formed from CO_2 by reverse water gas shift "WGS" reaction) seems more in line with the results obtained previously in heterogeneous catalysis for the formation of alcohols and hydrocarbons.

An alternative way for the formation of hydrocarbons is the transformation of methanol by the MTG (methanol to gasoline) process [17] in a reaction involving two catalytic reactors or to make use of a composite catalyst associating a methanol catalyst with a zeolite [18–20].

Taking into account these different possibilities, the copper pyrochlore methanol catalyst ($Cu–La_2Zr_2O_7$), developed in our laboratory [3,21], was promoted in order to reach three different objectives:

1. To increase the CH_3OH formation by addition of oxides, e.g., ZnO or ZrO_2.
2. To form C_{2+} alcohols in presence of a transition metal like Co.
3. To yield hydrocarbons on a composite catalyst prepared by mixing the $Cu–La_2Zr_2O_7$ methanol catalyst with a HY zeolite.

2. Experimental

2.1. Catalyst preparation

The $La_2Zr_2O_7$ supports were prepared by coprecipitation by oxalic acid of a mixed solution of $La(NO_3)_3 \cdot 6H_2O$ and $Zr(C_3H_7O)_4$ in ethanol [21]. The precipitate was washed by ethanol, dried at 60°C and calcined at 550°C for 3 hours and at 710°C for 0.5 hour.

Copper has been added to the supports by conventional impregnation (I) of the support by the necessary amount of a water solution of $Cu(NO_3)_2 \cdot 3H_2O$ (250 g/l), or by cationic exchange (E) between the powdered support and a ammonia-containing solution (pH 14.4) of $Cu(NO_3)_2 \cdot 3H_2O$ (5 g/l) by stirring during 48 hours. The solid was filtered, dried and calcined in air at 350°C.

The coprecipitated $Cu–La_2Zr_2O_7$ catalysts (C) were prepared by coprecipitation by oxalic acid of a mixed solution of $Cu(NO_3)_2 \cdot 3H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Zr(C_3H_7O)_4$ in ethanol [21]. The precipitate was washed and calcined in the same conditions as the support.

$Cu–La_2O_3$ and ZnO promoted catalysts were prepared using the same coprecipitation technique. For the preparation of Co and CoMo promoted catalysts the copper catalyst was impregnated by aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and/or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in suitable amounts. The impregnates were then dried and calcined at 350°C in air.

The composite $Cu–La_2Zr_2O_7$/HY catalysts are obtained by mechanical mixing of the $Cu–La_2Zr_2O_7$ methanol catalyst with HY zeolite (JRC-Z-HY4.8).

2.2. Catalytic activities

The catalytic tests were carried out in a stainless steel continuous flow reactor (6 mm inner diameter) containing 0.5 g of catalyst as described elsewhere [13,21]. The catalysts were reduced in H_2, flow rate = 4 l h^{-1} g $cat.^{-1}$, the reduction temperature was increased (1°C min^{-1}) from 20 to 250°C, and then maintained at 250°C for 6 hours. Standard reaction conditions are: pressure = 6 MPa, CO/H_2 ratio = 1/2 (CO_2/H_2 = 1/4), flow rate = 4 l h^{-1} g $cat.^{-1}$. The formed alcohols were condensed in a cold liquid trap at 10°C. The inlet and outlet gases were analyzed by on-line G.C. The carbon balance was always higher than 95%.

The reaction conditions on composite catalyst were carried out in the conditions described in reference 20. Standard reaction conditions: $P=5$ MPa, flow rate $=3$ l h^{-1} g cat.$^{-1}$, and CO_2/H_2 ratio $=1/3$.

The catalytic activities, given as MeOH yield (%), are expressed as follows: number of moles of CO (CO_2) transformed into MeOH/100 (initial number of moles of CO (CO_2)).

3. Development of a Cu–$La_2Zr_2O_7$ methanol catalyst

The synthesis of methanol from CO and/or CO_2 is an exothermic reaction passing through formates and/or formyl species. According to the literature the active sites are mainly located on the copper [7–9]. The role of the support or of the promoters is to stabilize the reaction intermediates or to favour the hydrogenation of these intermediates.

Copper catalysts supported on (or promoted by) rare earth oxides have been reported in numerous studies to be able to produce methanol [3,6,7]. However, one of the main drawbacks of these systems is their fast deactivation in presence of CO_2 which is believed to be caused by the formation of stable carbonate or hydroxycarbonates [22] covering the active copper sites and reducing thus the global catalytic activity.

To prevent the fatal carbonate formation a mixed oxide of lanthanum oxide and another oxide with acid properties can be synthesized [23]. The cubic $La_2Zr_2O_7$ pyrochlore has been prepared and shown by FT-IR and XRD to have a good resistance against carbonation [20,24]. Therefore, this pyrochlore was believed to be a promising candidate for the preparation of methanol catalysts able to work even in presence of CO_2–H_2 feeds.

3.1. Preparation of Cu–$La_2Zr_2O_7$ methanol catalysts

The $La_2Zr_2O_7$ pyrochlore is a well-definite structure compound described in the literature [23]. However, the conventional "firing-milling" method with heating up to 1000°C used for the preparation leads to crystallized products; the surface areas are as low as 1 m^2 g^{-1} and not suitable for use as catalytic supports. The physical characteristics of the prepared supports strongly depend on the preparation technique and the calcination conditions. Therefore, different procedures have been compared to improve the $La_2Zr_2O_7$ pyrochlore preparation. Calcination of the oxalates obtained by precipitation of $La(NO_3)_3.6H_2O$ and $Zr(OPr)_4$ in ethanol solution leads to the best results.

Different methods have been used to introduce copper into different supports. As can be seen from Table 1, a good methanol activity in the $CO+H_2$ reaction is obtained in the atmospheric pressure test for the exchanged catalysts supported on $La_2Zr_2O_7$ (980×10^{-6} g MeOH g cat.$^{-1}$ h^{-1}) but the amount of copper which can be introduced into the catalyst by these technique is limited to about 1 wt%. Higher loadings can be obtained either by impregnation or coprecipitation. Impregnation of the $La_2Zr_2O_7$ support with 10 wt% of Cu results in

Table 1
Characteristics of Cu–$La_2Zr_2O_7$ catalysts

Supports	Cu wt%	Cu loading technique	MeOH formation [a]
$La_2Zr_2O_7$	0.6	E	980
	10	C	300
	10	I	30
	17.6	C	1700
	33	C	2200
	50	C	2700

[a] Expressed in 10^{-6} g g cat.$^{-1}$ h^{-1} ($CO+2H_2$, $P=0.1$ MPa, $T=200$°C).

Loading technique: E = cationic exchange, I = impregnation, C = coprecipitation (see Experimental).

an poor activity. Coprecipitation is much more efficient at the same copper content.

In previous studies [21] the micrographs also show that the oxalate coprecipitated catalysts have a good homogeneity and are dispersed better than those obtained by impregnation. A phase rejection process according the following scheme could explain this result.

$$CuO + La_2O_3 \rightarrow CuLa_2O_4$$

$$CuLa_2O_4 + 2ZrO_2 \rightarrow CuO + La_2Zr_2O_7$$

During the calcination copper oxide reacts between 400°C and 550°C with lanthanum oxide to produce, in a first step, the well defined copper lanthanate. The $La_2Zr_2O_7$ pyrochlore begins to form at about 550°C and CuO is released in a well dispersed phase in the frame of the pyrochlore. After annealing at 710°C, the selected temperature for the preparation of the copper catalysts, the XRD spectrum of the Cu–$La_2Zr_2O_7$ catalysts shows only the characteristic lines of both $La_2Zr_2O_7$ and CuO.

Coprecipitated catalysts with a copper loading of 50% lead to an accessible copper surface area (*S*Cu), measured by N_2O chemisorption, as high as 14 m^2 g $cat.^{-1}$ (Table 2) suitable for methanol synthesis under industrial reaction conditions.

3.2. Catalytic activity of Cu–$La_2Zr_2O_7$ catalysts

The Cu–$La_2Zr_2O_7$ catalysts which allow the synthesis of methanol in presence of $CO + H_2$, $CO + CO_2 + H_2$ and $CO_2 + H_2$ feeds (Fig. 1) are able to compete with conventional catalysts [21]. The formation of CH_3OH is in competition with the water gas shift reaction and the methanol decomposition at high temperature whereas methane is formed only in small amounts and represents less than 1% of the formed products.

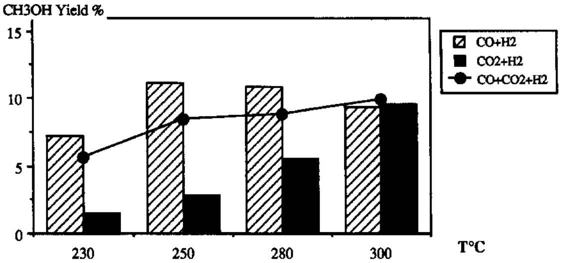

Fig. 1. Catalytic activities of Cu–$La_2Zr_2O_7$ in presence of different feeds. Reaction conditions: $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, feeds: $CO + 2H_2$, $CO_2 + 4H_2$, $25CO + 5CO_2 + 70H_2$.

The highest methanol yield is always obtained with carbon monoxide and the promoting effect of CO_2 described by Klier [25] on Cu–ZnO catalysts in the presence of $CO + CO_2 + H_2$ feeds could not be observed.

In the presence of a $CO_2 + H_2$ feed, compared to a 50% Cu–lanthana model catalyst, the 50% copper-pyrochlore catalyst has a better methanol activity. Fig. 2 shows that the conversion at 280°C is about two times higher whereas the observed methanol selectivities are in the same order of magnitude. The important point of the experiment shown in Fig. 2 is that the pyrochlore supported catalyst recovers its initial activity at $T = 250$°C after a four days run at higher temperatures, whereas a 60% activity decrease is observed, under the same conditions, with the lanthana supported catalyst.

Table 2
Charateristics of coprecipitated Cu–$La_2Zr_2O_7$ catalysts [a]

Cu (%)	S_{BET} [a] (m^2 g $cat.^{-1}$)	*S*Cu g $cat.^{-1}$ (m^2 g $cat.^{-1}$)	*S*Cu g Cu^{-1} (m^2 g Cu^{-1})	MeOH yield (%) $(CO + H_2)/(CO_2 + H_2)$
0	30			
10	31	4	40.5	2.7/2.2
33	28	13	39	7.5/4.9
50	26	14	28	8.2/5.2
54	14	10.6	19.5	7.6/5

[a] Calcined at 710°C. MeOH synthesis conditions: $CO + 2H_2$ ($CO_2 + 4H_2$) feed, flow rate = 4 l h^{-1} g $cat.^{-1}$ at $T = 280$°C, $P = 6$ MPa.

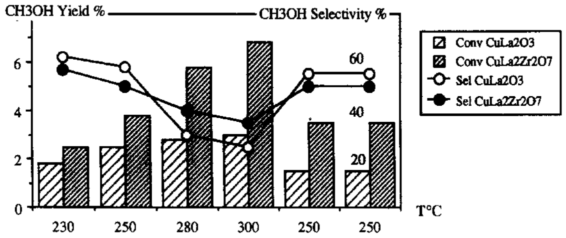

Fig. 2. Catalytic activities of Cu–$La_2Zr_2O_7$ and Cu–La_2O_3 in presence of CO_2+H_2. Reaction conditions: $P=6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, CO_2+4H_2.

3.3. Influence of the copper loading on the catalytic activity

The physical characteristics (BET surface area, exposed metallic copper surface area) as well as the catalytic behaviour of Cu–$La_2Zr_2O_7$ catalysts with increasing copper contents prepared by coprecipitation are shown on Table 2.

The methanol productivity increases with the copper content both in presence of $CO+H_2$ and CO_2+H_2 feeds. Under high pressure conditions (6 MPa), the best productivities, based on the weight of catalyst, are obtained for 33% and 50% copper loading (Fig. 3). This is in agreement with literature results obtained on conventional Cu–ZnO catalysts [1,7]. Considering the accessible copper surface area it can be observed that a high copper surface area corresponds to a good methanol productivity even if the correlation is not strictly linear (Table 2, Fig. 3). Copper loadings higher than 50% lead to sintering of the copper metal particles and hence in a decrease of methanol formation.

3.4. Promoting effect of oxides

3.4.1. Influence of an overstoichiometric amount of ZrO_2 or La_2O_3

The relatively loose cubic structure of the pyrochlore allows the formation of a well-definite structure compound over a wide range of composition (Zr/La atomic ratio between 0.75 and 1.25) [23,24].

It can be seen in Fig. 4 that, as well as in the reactions in presence of $CO+H_2$ and CO_2+H_2, the catalytic activity of a 50 wt% Cu catalyst with a Zr/La ratio of 0.75 is lower than that of the ideal $La_2Zr_2O_7$ structure.

The detrimental influence of lanthana in excess from the $La_2Zr_2O_7$ stoichiometric composition can be explained by two different effects.

1. Formation of a $CuLa_2O_4$ phase which has a poor activity as observed previously [21].
2. Migration of La_2O_3 or probably of La hydroxycabonates [22] onto the active copper sites.

An excess of zirconia, rather than lanthana can have a positive effect on methanol production. Thus, a ZrO_2 over-stoichiometry of about 25% ($La_{1.8}Zr_{2.2}O_7$) represents the best composition for catalyst development.

Aging experiments show also that carbonates

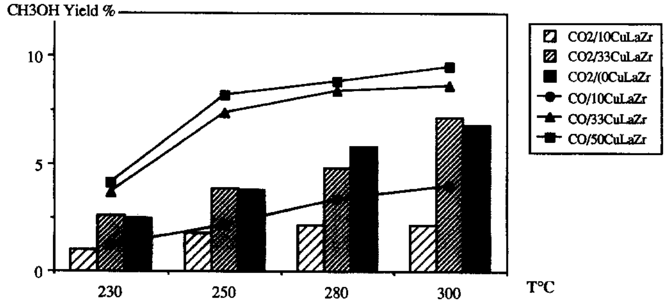

Fig. 3. Influence of the copper loading on the activity in presence of $CO+H_2$ and CO_2+H_2. Catalysts: xCu–$La_2Zr_2O_7$. Reaction conditions: $P=6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, feeds: $CO+2H_2$, CO_2+4H_2.

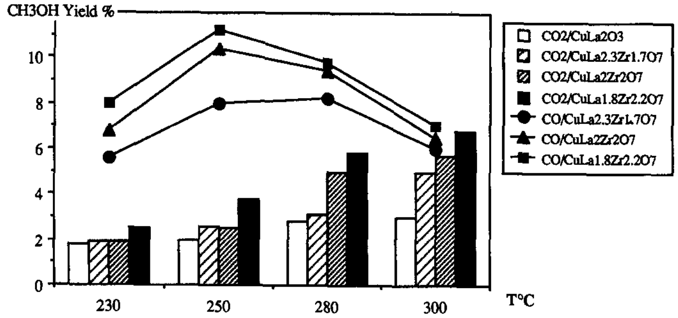

Fig. 4. Influence of the support composition on the activity. Catalysts: xCu–$La_2Zr_2O_7$, Reaction conditions: $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, feeds: $CO + 2H_2$, $CO_2 + 4H_2$.

and hydroxycarbonates are not formed on catalysts containing an excess of zirconia.

3.4.2. *Influence of the addition of ZnO*

ZnO addition has little effect on the BET surface areas and on the accessible copper metal surface areas (Table 3) in accordance with previous results [21]. The addition of 5 to 33% of ZnO does not hinder the formation of $La_2Zr_2O_7$ as shown by XRD and scanning electron micrographs show also a good homogeneity of the catalyst.

The methanol activity with a $CO + 2H_2$ feed decreases upon ZnO addition and less than 40% of the catalytic activity of the unmodified catalyst remains with the 33% Zn promoted catalyst (Fig. 5).

In presence of a $CO_2 + H_2$ feed a ZnO promoting effect is clearly observed. It can be related with the formation, in agreement with literature [7,26], of anionic vacancies favourable for CO_2 chemisorption and hydrogenation.

The most interesting effect is observed if 3–5 mole % of CO_2 is added to the $CO + H_2$ feed, an important increase in methanol formation is observed comparable with that described with the conventional copper–zinc catalyst [25].

Table 3
Characteristics of Zn promoted Cu–$La_2Zr_2O_7$ catalysts

Catalyst [a]/% Zn	BET area	S. Cu.	XRD [b]
A/0	19	9.1	CuO, $La_2Zr_2O_7$
A/14	15	8	CuO, ZnO, $La_2Zr_2O_7$
B/0	28	15	CuO,$La_2Zr_2O_7$
B/33	20	13	CuO, ZnO, $La_2Zr_2O_7$

[a] A: Cu–$La_2Zr_2O_7$ calcined at $T = 730$°C; B: Cu–$La_{1.8}Zr_{2.2}O_7$ calcined at $T = 710$°C.

[b] Compounds evidenced after calcination at 710 or 730°C.

4. Promoted catalyst for the synthesis of higher alcohols from $CO_2 + H_2$ feeds

In both the CO and CO_2 hydrogenation methane and methanol are obtained together with higher alcohols and hydrocarbons.The effect of group VIII and group VI metal oxides (e.g., through cobalt oxide and/or molybdenum oxide) addition to a Cu–$La_2Zr_2O_7$ catalyst leads to a decrease of the production of methanol and an increase of the formation of methane and of C_1–C_5 alcohol and hydrocarbon mixtures [12,13,27]. Our results on Co and Co + Mo promoted Cu–$La_2Zr_2O_7$ catalysts are in good

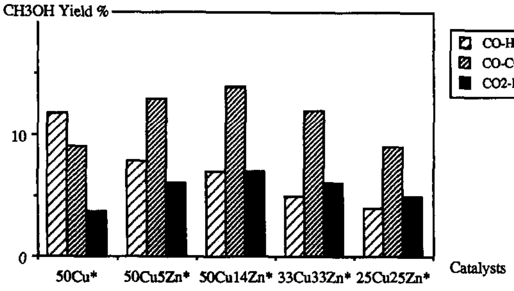

Fig. 5. Reaction of ZnO promoted catalysts with different feeds. Reaction conditions: $T = 280$°C, $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, feeds: $CO + 2H_2$, $CO_2 + 4H_2$, $25CO + 5CO_2 + 70H_2$.

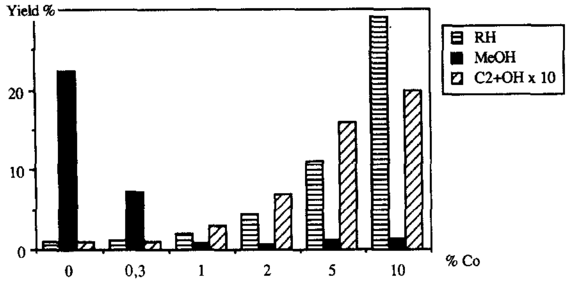

Fig. 6. "Promoting" effect of Co on Cu–$La_2Zr_2O_7$ catalysts. Catalysts: $x Co_{50}Cu–La_2Zr_2O_7$. Reaction conditions: $T = 280°C$, $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, feeds: $CO + 2H_2$, $CO_2 + 4H_2$, $25CO + 5CO_2 + 70H_2$.

agreement with the mechanistic proposal given before.

Cu–$La_2Zr_2O_7$ catalysts, with increasing cobalt contents up to 10%, have been tested in presence of a $CO + H_2$ feed as shown in Fig. 6. It can be seen that the addition of only a slight amount of cobalt sharply decreases the methanol formation. This has also been observed by Lin and Pennella [27] on Co–Cu/ZrO_2 and was attributed to the covering of the methanol active copper sites by cobalt species responsible for hydrocarbon formation. However, the higher alcohol ($C_2 + OH$) and hydrocarbon ($C_2 + HC$) yields increase with the amount of cobalt as well as the $C_2 + OH$ proportion in the total alcohol fraction. A good 60% content of $C_2 +$ alcohols in the alcohol mixture but a low alcohol selectivity is observed with a 10% Co loading (Fig. 6). Finally, the best compromise between activity and selectivity was obtained with the catalyst loaded with 5% cobalt. An additional promoting effect is observed in presence of 3% molybdenum which seems to increase the hydrogenating properties of the catalyst [28].

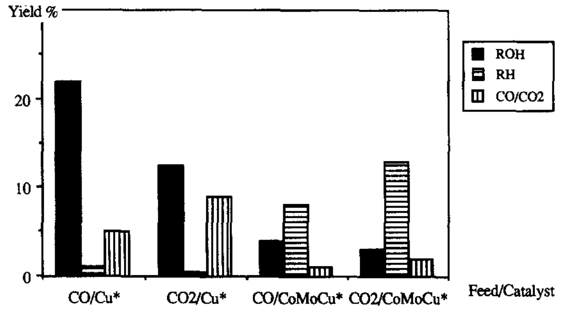

Fig. 7. Reaction of $CO + H_2$ and $CO_2 + H_2$ on Cu–$La_2Zr_2O_7$ and CoMo/Cu–$La_2Zr_2O_7$ catalysts. Influence on the catalyst activity. Reaction conditions: $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, $CO + 2H_2$, $CO_2 + 4H_2$.

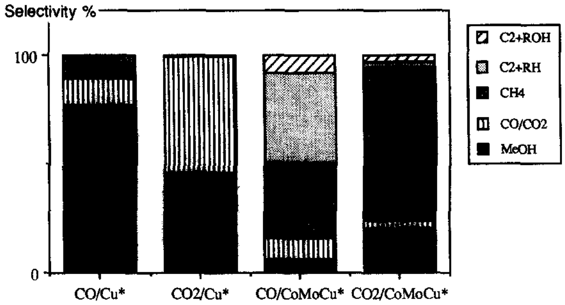

Fig. 8. Reaction of $CO + H_2$ and $CO_2 + H_2$ on Cu–$La_2Zr_2O_7$ and CoMo/Cu–$La_2Zr_2O_7$ catalysts. Influence on the product selectivities. Reaction conditions: $P = 6$ MPa, flow rate = 4 l h^{-1} g $cat.^{-1}$, $CO + 2H_2$, $CO_2 + 4H_2$.

The activity in alcohol synthesis on the MoCo/Cu–$La_2Zr_2O_7$ catalyst, as shown in Fig. 7, is higher with CO than that in presence of CO_2 whereas methane is formed in larger amounts with carbon dioxide rich feeds. This observations fit well with the proposed mechanism since CO, and not CO_2, is responsible for the chain growth.

Concerning the selectivities (Fig. 8), higher percentages of C_{2+} compounds are obtained in the presence of $CO + H_2$ feed than with $CO_2 + H_2$. The presence of cobalt is also essential for the chain growth whereas the direct and the reverse WGS reaction is decreased in presence of this promotor.

The observed product repartition is that of a conventional ASF distribution in presence of $CO + H_2$ syngas whereas with $CO_2 + H_2$ the amount of produced C_1 compounds is higher than expected by the ASF law [13].

5. Formation of hydrocarbons on a Cu–$La_2Zr_2O_7$/HY composite catalyst

The use of composite catalysts is an alternative method to produce hydrocarbons in a non-

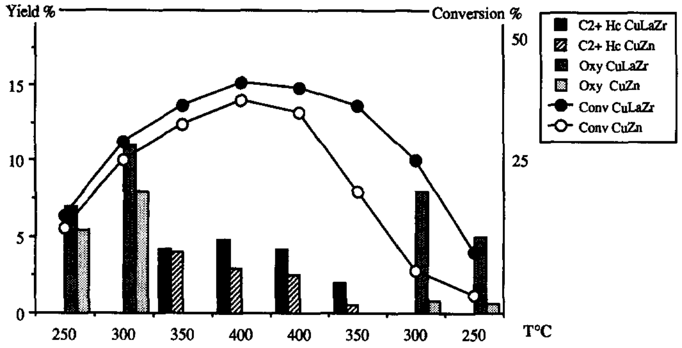

Fig. 9. Reaction of $CO_2 + H_2$ on $Cu\text{–}La_2Zr_2O_7/HY$ composite catalyst. Reaction conditions: $P = 5$ MPa, flow rate $= 3\ l\ h^{-1}$ g cat.$^{-1}$, $CO_2 + 3H_2$.

Anderson–Schulz–Flory distribution and consists of converting methanol formed from $CO_2 + H_2$ into hydrocarbons by MTG reaction [17]. A challenge is to perform the reaction in a one stage reactor using composite catalyst, formed of a methanol synthesis catalyst and HY zeolite, in spite of the fact that these catalysts exhibit their catalytic activity under completely different conditions (e.g., $T = 250°C$, $P = 5$ MPa; $T = 400°C$, $P = 0.1$ MPa, respectively).

Given the good thermal and chemical stability of the $Cu\text{–}La_2Zr_2O_7$ of methanol catalysts they can be proposed as an efficient component for preparing composite catalysts able to produce hydrocarbons from $CO_2 + H_2$.

Composite catalysts obtained by mixing the $Cu\text{–}La_2Zr_2O_7$ methanol catalyst and HY Zeolite were active for the formation of oxygenates and hydrocarbons. Working at increasing temperatures stepwise from 250°C to 400°C (Fig. 9), it can be seen that methanol and dimethylether (by dehydration of methanol) were formed at 250–300°C. Hydrocarbons were predominant at higher temperatures (350–400°C) at which the MTG reaction occurs.

The results obtained at 400°C on $Cu\text{–}La_2Zr_2O_7/HY$ are in accordance with a plausible reaction path.

$$CO_2 + 3H_2 \xrightarrow{\text{Methanol catalyst}}$$

$$[\text{MeOH}] \xrightarrow{\text{Zeolite}} \text{Hydrocarbons}$$

Ethane was the major component in the hydrocarbon fraction at 400°C, and the selectivities of other hydrocarbons were comparatively low.

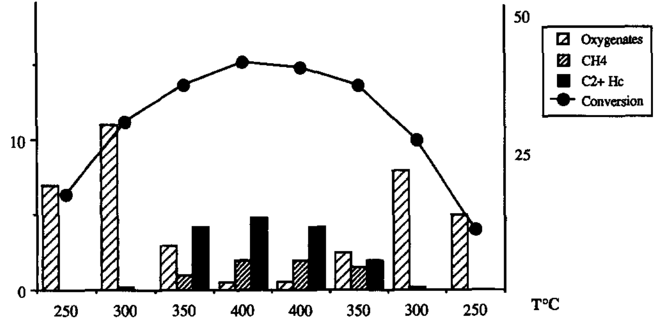

Fig. 10. Reactivity of $Cu\text{–}La_2Zr_2O_7/HY$ and $Cu\text{–}ZnO[CO_3]/HY$ composite catalysts. Reaction conditions: $P = 5$ MPa, flow rate $= 3\ l\ h^{-1}$ g cat.$^{-1}$, $CO_2 + 3H_2$.

Table 4
Change of the accessible copper surface areas under different reaction conditions

Conditions	Cu–ZnO[CO_3] SCu (m^2 g^{-1})	Cu–$La_2Zr_2O_7$ SCu (m^2 g^{-1})
H_2 [270°C] [a]	18	10
H_2 [400°C] [a]	10	9
$CO_2 + H_2$ [400°C] [a]	6	6
$CO_2 + H_2$ [400°C] [b]	< 1	5

[a] After 5 h.

[b] Composite catalysts after use for the reaction (Fig. 9Fig. 10).

This distribution, which is analogous to the results previously obtained in Cu–Zn–Cr oxide systems [20], is different from that of MTG reaction [17]. A fast hydrogenation of intermediary ethylene into ethane in the presence of high pressure H_2 and metallic Cu species can explain the decreased formation of higher hydrocarbons as well as the unusual distribution and the low coke formation as mentioned here after.

Comparing a Cu–La_2ZrO_7/HY catalyst with a composite catalyst based on a conventional methanol catalyst, prepared in presence of Na_2CO_3 (Cu–ZnO[CO_3]/HY), it can be observed in Fig. 10:

1. A better conversion into hydrocarbons is obtained on Cu$La_2Zr_2O_7$/HY than on conventional Cu–ZnO[CO_3]/HY, whereas Cu–ZnO[CO_3] and Cu–$La_2Zr_2O_7$ has similar activities in the absence of HY zeolite (the yields in methanol formation on Cu–$La_2Zr_2O_7$ and Cu–ZnO[CO_3], at 250°C are, respectively, 5.9% and 6.0%)
2. The Cu$La_2Zr_2O_7$/HY catalyst presents the most favourable aging properties with a 10% activity decrease, at 300°C, after a 400°C test (Fig. 10) compared to the 60% activity loss of the Cu–ZnO[CO_3]/HY catalyst.

By comparing copper surface areas of both Cu–ZnO[CO_3]/HY and Cu–La_2ZrO_7/HY catalysts, it seems that the presence of residual Na (0.1 wt%) in the Cu–ZnO[CO_3]/HY catalyst favours the decrease of the copper surface areas, by interaction of the copper catalyst with the HY zeolite (Table 4), as well as a deactivation of the acidic sites of the zeolite [20]. It appears that on the Cu–ZnO[CO_3]/HY catalyst the thermal sintering was low compared with the deactivation by the interaction with zeolite, whereas the moderate decrease of copper surface area, observed for Cu–$La_2Zr_2O_7$/HY, seems to be mainly due to the thermal effect.

The difference in the coking of the catalysts can also be related with the previous phenomena. It can be observed that, after reaction, the catalysts prepared by Na_2CO_3 were always black whereas the samples obtained from the oxalate technique were grey and the carbon analysis, after the catalytic tests of Fig. 9, shows a carbon content of 3.1% for Cu–ZnO[CO_3]/HY and 0.1% for Cu–La_2ZrO_7/HY.

The favourable properties of the Cu–$La_2Zr_2O_7$/HY catalyst can be more or less attributed to the original preparation technique, by oxalic acid precipitation, which avoids the presence of residual Na and gives a good stability by forming a well-defined structure compound with a reasonable BET surface area.

6. Conclusion

Copper supported on a stable $La_2Zr_2O_7$ pyrochlore is an active catalyst for methanol synthesis able to work with CO–H_2, CO + CO_2 + H_2 and $CO_2 + H_2$ feeds.

The CO_2 deactivating effect which can mainly be ascribed to the formation of lanthanum carbonates and hydroxycarbonates can be avoided in the presence of an overstoichiometric amount of ZrO_2 and by the use of an adequate preparation technique. Therefore, the composition of the support as well as the annealing temperature are very important.

Co promoted Cu–$La_2Zr_2O_7$ methanol catalysts produce higher alcohols but a secondary formation of CH_4 and alkanes is observed. The mechanistic results are in good accordance with a CO insertion mechanism. The chain growth step can be attributed to the insertion of a C_1 oxygenated species (mainly CO from the feed or formed previously from CO_2) into a metal–alkyl bond. According to our results, it seems that CO_2 alone does not allow the chain growth.

The Cu–$La_2Zr_2O_7$ methanol synthesis catalyst is an advantageous component for composite catalysts for the hydrogenation of CO_2 into lower hydrocarbons by a process including methanol synthesis and MTG reaction. The properties of our composite catalysts leading to a high performance can be attributed to the preparation techniques which avoid the presence of residual Na responsible for the coking and the deactivation of the catalysts.

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