Performance of ternary Cu–Ga$_2$O$_3$–ZrO$_2$ catalysts in the synthesis of methanol using CO$_2$-rich gas mixtures

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ABSTRACT

The synthesis of methanol via catalytic hydrogenation of carbon oxides was evaluated in two groups of Cu–Ga$_2$O$_3$–ZrO$_2$ ternary catalysts containing 2 wt% Cu. Copper was incorporated in the first group either by incipient wetness (IW) or by ion exchange (IE), both on the pure oxides (Ga$_2$O$_3$ and ZrO$_2$) and the x-Ga$_2$O$_3$/ZrO$_2$ mixed oxides (where x = 1, 6 or 9 wt% Ga$_2$O$_3$). In a second group of materials galia was incorporated onto Cu/ZrO$_2$ previously dried or dried/calcined. The catalytic evaluations were performed in a tubular microreactor at 3 MPa, 523 K, GHSV = 20,000 h^{-1} using two different gas mixtures. The first mixture contained CO$_2$ and CO (**M1**: H$_2$/CO$_2$/CO = 75/22/3), while in the second one carbon monoxide was replaced by He (**M2**: H$_2$/CO$_2$/He = 75/22/3).
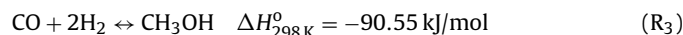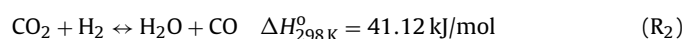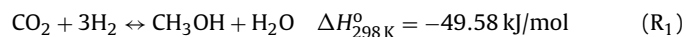
The yield to methanol was progressively higher with gallia loading, but the best catalyst tested had an intermediate loading of Ga$_2$O$_3$ deposited onto a dried and calcined Cu/ZrO$_2$ precursor which was obtained, in turn, by ion exchanging copper nitrate to the zirconia. The catalysts for which gallium were added to the dried and calcined IE Cu/ZrO$_2$ precursor were the most stable.

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1. Introduction

The use of CO$_2$ to make liquid derivatives and intermediate chemicals has received special attention during the last two decades, so as to contribute to mitigating the impact of excess carbon dioxide in the environment. In this context, a viable alternative is the efficient conversion to methanol, via selective hydrogenation of the CO$_2$ liberated from point emission sources, such as power stations, cement and steel industries, or natural gas field related processes, among others.

On industrial scale, the production of methanol is generally achieved using synthesis gas ('syn-gas': H$_2$/CO/CO$_2$ = 69/25/6 [1]), which is obtained via the steam reforming of natural gas, using Cu/ZnO/Al$_2$O$_3$ catalysts. The reactions that this gas mixture undergoes, when there is no appreciable production of dimethyl ether, are: the synthesis of methanol from CO$_2$ (R$_1$), the reverse water gas shift reaction, RWGS (R$_2$), and the 'dry' methanol synthesis reaction from CO (R$_3$) [2]:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^o_{298\,K} = -49.58\,\text{kJ/mol} \quad (R_1)$$

$$CO_2 + H_2 \leftrightarrow H_2O + CO \quad \Delta H^o_{298\,K} = 41.12\,\text{kJ/mol} \quad (R_2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H^o_{298\,K} = -90.55\,\text{kJ/mol} \quad (R_3)$$

Chinchen et al. have shown in a classic experiment by isotope labeling that exclusively CO$_2$ acts as the carbon source of methanol on the commercial catalyst [3]. The role of CO has been discussed to scavenge water by RWGS [4] and to adjust the O-coverage of the Cu surface [5].

If a CO$_2$-rich feed gas was used instead (that is, a feed gas in which the main carbon source is carbon dioxide), the main synthesis reaction must be (R$_1$). The conventional heterogeneous catalysts, based on copper and zinc oxides, have been optimized to operate efficiently within a narrow range of feed compositions [6]. Therefore, to get high conversion and selectivity with feed gas mixtures other than syn-gas new, alternative catalysts must be developed.

Conventional methanol synthesis catalysts are quite sensitive to the presence of poisons such as those that can be found at CO$_2$ point emission sources [7,8]. Even though this shortcoming can be corrected with gas purifying trains located upstream the synthesis reactors, some novel formulations of supported palladium (viz., Pd/Ga$_2$O$_3$ or Ga–Pd/SiO$_2$) have been found to be more active and selective than the classical, copper-based catalysts [9], overcoming – besides – the poisoning problem [10].

The main drawback of these novel materials is that outside the differential conversion regime they invariably generate CO as the main by-product. In any industrial process, of course, catalysts must

operate in integral reactors and with a substantial recycle of non-condensable gases to save both hydrogen and carbon source(s). In consequence, the active material is in contact with the reaction products. Under high pressure, the CO produced covers a significant proportion of the Pd sites onto which H_2 is dissociated, which leads to a decreasing ability to hydrogenate the carbonaceous species adsorbed onto the support or – in other words – to a substantial diminution of the catalytic activity [11].

So, aimed to developing an efficient and selective catalytic system able to convert both CO_2 *and* CO to methanol, our research work is presently devoted to new materials comprised by $Cu–Ga_2O_3–ZrO_2$, on the grounds of several promissory hard facts such as the following: on a set of supported Pd catalysts, ZrO_2 – which has an amphoteric character – emerged as the most promising oxide support to favor the hydrogenation of CO to methanol [12] while, likewise, Ga_2O_3 – which also bears an amphoteric character – showed to strongly favor the hydrogenation of CO_2 [11].

Besides the intrinsic catalytic properties of zirconia as support, it is also well known that it confers mechanic and thermal stability to heterogeneous catalysts [13]. Gallia, meanwhile, acting both as catalyst support [14] or as 'promoter' [15–17], has shown that it can give a good catalytic activity to methanol – with remarkable stability – during long operating times on stream [11].

These were the foundations for our interest in preparing Ga_2O_3/ZrO_2 mixed formulations, onto which the metallic function can be in turn supported. Because palladium is not adequate to operate H_2/CO_2 reaction mixtures with recycle of non-condensable gases, copper was chosen instead. This metal, as the only constituent of a heterogeneous catalyst is rather inactive [18], but in combination with several oxides it has a preponderant role as the producer of atomic hydrogen [6] and as the activation site of CO_2 [19]. In this work in particular, we evaluate the catalytic performance for methanol synthesis of several $Cu–Ga_2O_3–ZrO_2$ prototype materials, using always ternary mixtures as the feed.

2. Experimental

A set of Ga_2O_3/ZrO_2 supported copper catalysts was prepared, using high purity (99.00 wt%) copper nitrate. Each of the pure supports was also synthesized. Both of them were prepared by sol–gel procedures, in basic media, deliberately avoiding the use of precursor salts that might include any other cation. For the same reason, inert vessels were used instead of glass ones. Zirconia ($S_{BET} = 25\,m^2/g$) was obtained by hydrolysis of Zr(IV) n-propoxide in 1-propanol (70 wt%), at ambient temperature, and gallia ($S_{BET} = 90\,m^2/g$) was prepared by hydrolyzing gallium nitrate (99.999 wt% purity) with NH_4OH(aq.) in ethanol.

Gallium oxide was supported on an aliquot of zirconia by incipient wetness impregnation of gallium nitrate using several loadings (1, 6 and 9 wt%), without any significant decrease of the specific surface area of these materials after drying (384 K, 4 h) and calcinations (673 K, 4 h). These supports were labeled as x-Ga_2O_3/ZrO_2. In other sub-set of preparations gallia was incorporated after copper, as detailed below.

To assess the impact of the interaction between copper and the different supports several series of catalysts were prepared. In the first two series the metal was deposited either by incipient wetness (IW) impregnation: IW Cu/Ga_2O_3, IW Cu/ZrO_2 and IW Cu/x-Ga_2O_3/ZrO_2, or by ion exchange (IE) of the copper salt at pH 11: IE Cu/Ga_2O_3, IE Cu/ZrO_2 and IE Cu/x-Ga_2O_3/ZrO_2. To perform the ion exchanges, each support was put in contact with aqueous solutions of ammonia complexes of copper (mostly $[Cu(NH_3)_4]^{2+}$ at this pH), under stirring, using always the same liquid to solid ratio (200 ml/g). The suspensions were then filtered and washed (two times, 15 min/ea.) with NH_4OH(aq.), also at pH 11. All the materials

Table 1
Catalyst features.

Supports and catalysts[a]	S_{BET} (m^2/g)	Ga/Cu (at/at)	wt% Cu[c]
ZrO_2	25		
Ga_2O_3	90		
6 wt% Ga_2O_3/ZrO_2	24		
IW Cu/ZrO_2	10		
IW Cu/Ga_2O_3	71		
IE Cu/ZrO_2	15		1.77
IE Cu/Ga_2O_3	89		2.00
2 wt% Cu–1 wt% Ga_2O_3/ZrO_2[b,d]	<10	1/3	
2 wt% Cu–6 wt% Ga_2O_3/ZrO_2[b,d]	<10	2/1	
2 wt% Cu–9 wt% Ga_2O_3/ZrO_2[b,d]	<10	3/1	

[a] The metal dispersion on each catalyst was: $D_{Cu} \sim 3\%$ (by N_2O titration at 318 K [20]).
[b] All series – see text.
[c] Copper loading after the 2nd NH_4OH(aq.) wash, measured by AA.
[d] The Cu loadings after the 2nd wash ranged between 1.72 and 1.98 wt%.

were dried (323 K, 18 h, and then 383 K, 4 h) and calcined (673 K, 2 h) under the same conditions.

In another two complementary series Ga_2O_3 was incorporated by incipient wetness, in the same mass percentages indicated above (1, 6 and 9 wt%), but after the addition of copper (by ion exchange) to the circonia, with either just further drying [series x-Ga_2O_3/IE Cu/ZrO_2 (D)] or drying and calcining [series x-Ga_2O_3/IE Cu/ZrO_2] prior to the incorporation of the gallium nitrate. Afterwards, similar drying (383 K, 4 h) and final calcining (673 K, 2 h) treatments to the ones used in the previous series were applied. The dried and calcined catalysts were crushed and sieved to 60–80 mesh prior to further use.

X-ray powder diffraction patterns were obtained with a Shimadzu XD-D1 diffractometer using Cu Kα radiation, at 30 kV and 30 mA. Patterns were recorded from 10° to 75° (2θ).

XPS spectra of the catalysts, calcined at 523 K (10 min) under flowing 5%O_2/Ar and reduced at 553 K (20 min) under flowing 5%H_2/Ar, were obtained with a UNI-SPECS electron spectrometer equipped with an PHOIBOS 100/150 MCD hemispherical analyzer, using an aluminum anode. Binding energy (BE) values were referenced to the C 1s peak (285 eV) for data processing.

Table 1 indicates the specific surface area, nominal Ga/Cu atomic ratio and final Cu loading, after washing, of the prepared catalysts. The metal dispersion, about 3% in every case, was measured following the technique of Waugh and coworkers [20]. More detailed information on the preparation and characterization of the complete catalyst series will be presented in an incoming paper [21].

The catalytic activity was evaluated using a glass coated, stainless steel plug-flow microreactor (60 cm long, 0.4 cm I.D.). The reactor was placed inside an aluminum sheath (1.5 cm thick) to get uniform temperature. The assembly was placed into a (PID) temperature controlled custom-made oven. For catalytic testing, small aliquots (~0.1 g) of the finely divided catalysts were mixed (i.e., diluted) with 0.5 of crushed quartz (40/60 mesh) and positioned in the central region of the reactor tube, between quartz wool separators. The remaining portions of the tube were filled with coarser quartz particles (20/40 mesh size).

Each catalyst was reduced in situ under hydrogen flow (50 ml/min), with a heating ramp of 2 K/min from room temperature to $T = 553$ K, keeping this temperature for 2 h under H_2 flow. This temperature limit was chosen to ensure a complete reduction of Cu and minimize metal sintering of the metal crystallites [6,22,23]. The reactor was then cooled, under hydrogen flow, down to the reaction temperature ($T = 523$ K) and then the set up was pressurized to the working pressure ($P = 3$ MPa). Afterwards, the flow of hydrogen was substituted by a first reaction mixture (from now on designated as **M1**): $H_2/CO_2/CO = 75/22/3$ (v/v). This feed composition is similar to the ones that would be found at the inlet

Table 2
Composition of the reaction mixtures, conversion of CO_2, and selectivity to CH_3OH, at thermodynamic equilibrium ($T = 523$ K; $P = 3$ MPa).

	Reaction mixture	
	M1: $H_2/CO_2/CO = 75/22/3$	**M2**: $H_2/CO_2/He = 75/22/3$
$(y_{H_2}\%)_{EQ}$	68.8	68.2
$(y_{CO_2}\%)_{EQ}$	19.4	17.8
$(y_{CO}\%)_{EQ}$	3.7	2.7
$(Y_{CH_3OH}\%)_{EQ}$	3.8	2.7
$(y_{H_2O}\%)_{EQ}$	4.3	5.4
$(X_{CO_2}\%)_{EQ}$	18.2	23.3
$(S_{CH_3OH}\%)_{EQ}$	88.9	50.4
$(X_C\%)_{EQ}$[a]	14.3	23.3

[a] Carbon conversion.

of industrial plants for methanol manufacture from CO_2 and H_2 operating with full recycling of non-condensable gases [1]. The chosen temperature and pressure conditions are within the typical range used in industrial processes for methanol synthesis [24]. The selected carbon-based space time, W/F_C (~90 g cat min/mol C), allowed comparative analyses of the catalysts performance under differential conditions, without hampering quantitative evaluation of the product composition. Given the geometric dimensions of the catalyst particles, the reactor was always operated inside the kinetic regime [25].

These operating conditions (523 K, 3 MPa, GHSV = 20,000 h^{-1}) were kept for 20 h, to evaluate possible changes in activity and/or selectivity. Afterwards, the feed gas composition was changed to one in which CO was substituted by helium (from now on designated as **M2**): $H_2/CO_2/He = 75/22/3$ (v/v), while the space velocity remained still the same (GHSV = 20,000 h^{-1}), to appraise the impact of the CO content in the catalysts performance. The composition of both mixtures at thermodynamic equilibrium is given in Table 2.

The process gases were U.H.P. grade or better. Hydrogen was purified through oxygen (Pd/Al_2O_3) and water (5 Å molecular sieve) traps, while the **M1** ternary mixture ($H_2/CO_2/CO$) was circulated through a carbonyl trap (finely crushed quartz kept at 523 K). On-line filters were used as well (Fig. 1).

The exit gas composition was analyzed by GLC in two Shimadzu 9A units arranged in series, employing packed stainless steel columns: Porapak QS (80/100 mesh) to quantify methanol and dimethyl ether (FID) and water (TCD) in the first unit, and Carbosieve SII (60/80 mesh) in the second one, to quantify CO and

CO_2 (TCD). The exit molar fractions (y_i) were used to calculate catalytic activity (R_i) and selectivity (S_i) to CH_3OH, CO and DME, carbon dioxide conversion ($X_{CO_2}\%$) and methanol yield (Yield$_{CH_3OH}\%$) – see Appendix A.

From the analysis of the comparative performance of the set of ternary catalysts (in particular the stability results), the synthesis was refined further, focusing only on the best of the four series: the x-Ga_2O_3/IE Cu/ZrO_2. Pure zirconia was again prepared ($S_{BET} = 35$ m^2/g), onto which copper was incorporated first, by ion exchange. The metal loading was 2.6 wt%, to preserve the former ratio of metal loading to specific surface. After drying and calcining, different amounts of Ga_2O_3 (0.96, 3.84 and 7.67 wt%) were loaded to the IE Cu/ZrO_2 by incipient wetness, so as to get atomic ratios Ga/Cu = 1/4, 1/1 and 2/1, respectively. These materials were tested using the **M2** ($H_2/CO_2/He = 75/22/3$, v/v) feed, at 3 MPa and 523 K, during 30 h: first 8 h at GHSV = 20,000 h^{-1} (this is indicated as 'condition a' in Table 4), followed by 4 h at GHSV = 10,000 h^{-1}; ('condition b'), then 10 h under static conditions, GHSV = 0 h^{-1} (exposure to the thermodynamic equilibrium mixture, 'condition c') and finally 8 h at GHSV = 20,000 h^{-1} (again 'condition a').

3. Results and discussion

The XRD patterns of representative materials, namely, IE Cu/ZrO_2, IE Cu/Ga_2O_3, 6-Ga_2O_3/IE Cu/ZrO_2, IW $Cu/6$-Ga_2O_3/ZrO_2 and IE $Cu/6$-Ga_2O_3/ZrO_2 catalysts are shown in Fig. 2. The peak positions of IE Cu/ZrO_2 and ternary catalysts showed that ZrO_2 crystallized as a mixture of the tetragonal (T) and monoclinic (M) phases, with a higher percentage of the former one. Clearly, these peak positions were unaffected by either the addition of copper, gallia or the preparation method used to incorporate copper, which suggest that the Cu^{2+} or Ga^{3+} ions were not incorporated into the structural network of ZrO_2. The IE Cu/Ga_2O_3 catalyst shows the peaks characteristic of the γ-Ga_2O_3 polymorph. None of the XRD patterns of the ternary catalysts shows peaks of Ga_2O_3 phase, illustrating the presence of highly dispersed crystallized Ga_2O_3 or amorphous. No reflections from bulk CuO were detected in the catalysts samples, which is indicative of highly dispersed domains, either crystalline particles (smaller than the detection limit of XRD technique, ≤ 3 nm), or just amorphous aggregates.

Fig. 3 shows the Cu 2p XPS spectra obtained from the calcined and hydrogen-reduced samples of these representative catalysts. The satellite peak at 942.7–941.5 eV, which is characteristic of Cu^{2+},
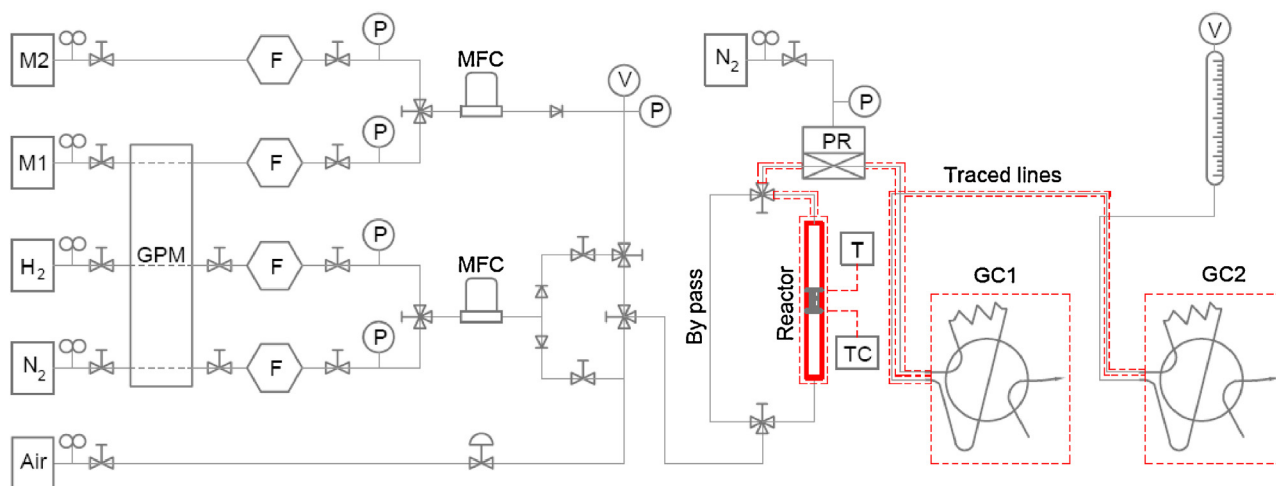

Fig. 1. Reaction set up. F: filter; MFC: mass flow controller; PR: back-pressure regulator; V: vent; P: pressure gauge; T: temperature reader; TC: temperature controller; GPM: gas purification module.
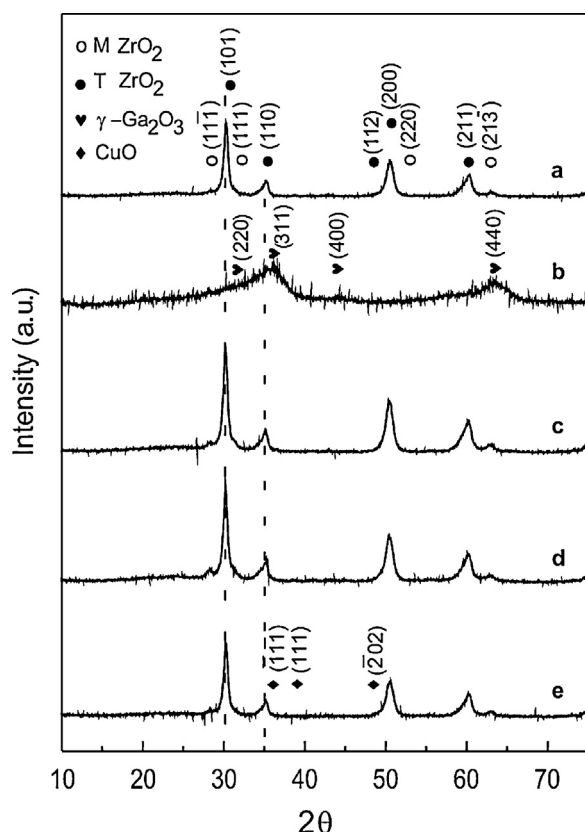
Fig. 2. Representative XRD patterns of the prepared catalysts: (a) IE Cu/ZrO$_2$, (b) IE Cu/Ga$_2$O$_3$, (c) IW Cu/6-Ga$_2$O$_3$/ZrO$_2$, (d) IE Cu/6-Ga$_2$O$_3$/ZrO$_2$, and (e) 6-Ga$_2$O$_3$/IE Cu/ZrO$_2$.
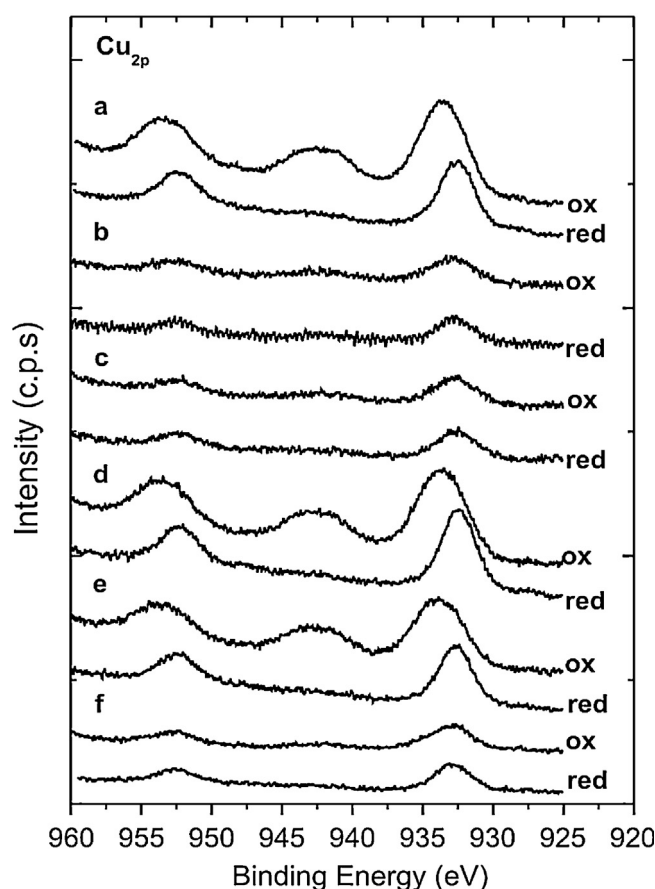

Fig. 3. XPS spectra of selected binary and ternary catalysts, calcined at 523 K (10 min) under flowing 5%O$_2$/Ar (upper traces) and reduced at 553 K (20 min) under flowing 5%H$_2$/Ar (lower traces): (a) IW Cu/ZrO$_2$, (b) IE Cu/Ga$_2$O$_3$, (c) IW Cu/Ga$_2$O$_3$, (d) IW Cu/6-Ga$_2$O$_3$/ZrO$_2$, (e) 6-Ga$_2$O$_3$/IE Cu/ZrO$_2$, and (f) 6-Ga$_2$O$_3$/IE Cu/ZrO$_2$ (D).

was observed in all the oxidized materials. This signal disappeared in the reduced samples, implying that, after the H$_2$ reduction (at 553 K), the copper in all these catalysts was reduced to Cu$^+$/Cu$^\circ$. This was confirmed by checking the Cu LMM Auger spectra (not shown). Nevertheless, no significant BE shift was observed in the Cu 2p peaks of the oxidized vs. the reduced samples of the catalysts where the highest copper–gallia intimacy was expected, namely: IW Cu/Ga$_2$O$_3$, IE Cu/Ga$_2$O$_3$ and 6-Ga$_2$O$_3$/IE Cu/ZrO$_2$ (D), unlike the other materials, which strongly suggests the formation of a CuGa$_2$O$_4$ spinel on the former [26].

The catalytic activities of the complete set of prepared catalysts after 20 h on stream (pseudo steady-state values), obtained in the microtubular reactor at 3 MPa and 523 K using the ternary mixtures **M1** (H$_2$/CO$_2$/CO) and **M2** (H$_2$/CO$_2$/He) under differential conversion conditions, are shown in Fig. 4. The reaction rates to methanol (R_{MeOH}) were between 60 and 130 × 10^{-8} mol/s g cat. Per mass of catalyst, these performances represent just about 50% of the activity of commercial Cu–Zn–Al catalysts operating under the same conditions. However, per mass of copper, the activity of these novel materials is far higher.

Fig. 4 shows that the rate to methanol decreases upon replacing CO (mixture **M1**) by He (mixture **M2**) in all the catalysts of the set, which might suggest that CO does participate in the CH$_3$OH synthesis, via (R$_3$). In other words, it could be inferred *prima facie* that both CO$_2$ and CO can be considered as carbon sources of methanol using these copper-based materials. Nevertheless, the catalytic activity normalized with respect to the moles of carbon fed to reactor was slightly higher (5–10%) when the **M2** mixture was employed. Under identical operating conditions the catalytic performance of the pure oxide supports (ZrO$_2$ and Ga$_2$O$_3$) was negligible, using any of the feed mixtures.

The reaction rate values displayed in Fig. 4 showed no correlation with the specific surface (S_{BET}) of the catalysts (Table 1). Likewise, considering that the metal dispersion of copper of the fresh materials was about 3% in every case (Table 1), the initial activity values (R_{MeOH}) measured during the first hour on-stream did not show any simple (e.g., linear) dependence with the exposed metal fraction either. Rather, these different catalytic activities are mostly associated to the diverse metal/support interactions produced by the intentional modifications of the Cu–gallia vs. Cu–zirconia intimacy achieved with the different catalyst preparation protocols (i.e., addition of Cu by IE or IW, sequence of addition of the different components, thermal pretreatments, etc.), as discussed below.

Table 3 displays the percent conversion of carbon dioxide (X_{CO_2}%) and the percent selectivity to methanol (S_{MeOH}%) of the set of copper-based ternary catalysts for both reacting mixtures, at 3 MPa and 523 K. Under these operating conditions, DME was produced only on the binary, gallia-supported catalysts, while traces of methane were formed by all of them ($S_{CH_4} \approx 1.5\%$, about constant, in every case). Most of the catalysts showed higher selectivity to methanol with the **M1** (H$_2$/CO$_2$/CO) mixture. This finding might be primarily related to a (kinetically) unfavored progress of the RWGS (R$_2$) in the presence of CO, because an alternative hypothesis (attributable to the assumption that the direct synthesis of methanol, via (R$_3$), were able to enhance the S_{MeOH}% when the **M1** mixture was used) would be in contradiction with the experimental results shown in Fig. 4 (namely, that there was a higher reactivity to methanol per carbon atom when the **M2** mixture was fed to the reactor).
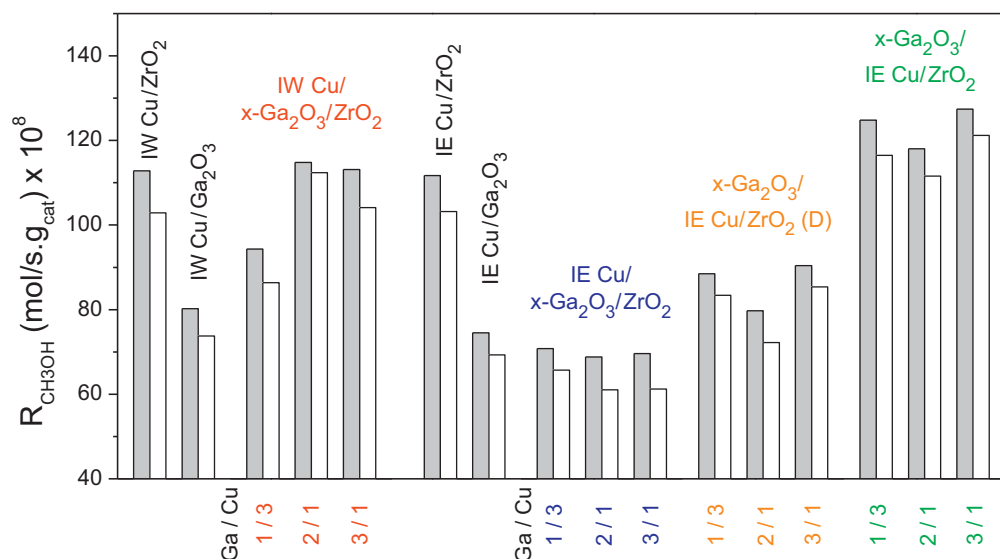
Fig. 4. Activity to methanol (R_{CH_3OH}) of the set of examined catalysts. Process conditions: $P = 3$ MPa; $T = 523$ K; GHSV = 20,000 h^{-1}. Gray bars: Reacting mixture **M1** ($H_2/CO_2/CO = 75/22/3$), after 20 h on stream. White bars: Reacting mixture **M2** ($H_2/CO_2/He = 75/22/3$), after 4 h on stream.

3.1. Comparison among the different catalysts

3.1.1. Copper added by incipient wetness

From the results shown in Fig. 4 and Table 3, it is apparent that the best performing catalyst among those prepared by IW of copper nitrate onto the Ga_2O_3/ZrO_2 support is the one with 6 wt% gallia [IW Cu/6-Ga_2O_3/ZrO_2].

The equivalent binary catalyst IW Cu/ZrO$_2$, though, was just about as active and considerably more selective to methanol – but unstable (vide infra), both in presence and absence of CO in the feed stream. Conversely, the binary IW Cu/Ga$_2$O$_3$ catalyst was far

worse. Overall, the combined R_{MeOH} and S_{MeOH} performance of the ternary Cu–Ga–Zr catalyst was consistently better, which strongly points out to the convenience of putting together the metal with both "supports".

It was also noticeable that a further increase of the Ga_2O_3 content from 6 to 9 wt% (that is, Ga/Cu ratios equal to 2/1 and 3/1, respectively) did not contribute to any improvements in activity or selectivity to methanol. Due to the moderate surface area of our high purity zirconia, though, we believe that this aspect deserves further research, using higher surface area ZrO_2.

Table 3
Carbon dioxide conversion and selectivity to methanol of the Cu–Ga–Zr catalysts (first set).[a]

Catalyst[b]	Reaction mixture			
	M1: $H_2/CO_2/CO = 75/22/3$ (1)		**M2**: $H_2/CO_2/He = 75/22/3$ (2)	
	X_{CO_2}%	S_{CH_3OH}% (3)	X_{CO_2}%	S_{CH_3OH}% (4)
IW Cu/ZrO$_2$	1.1	69.0	1.0	69.0
IW Cu/Ga$_2$O$_3$	0.9	69.5[c,d]	1.1	57.5[c,e]
IW Cu/1-Ga$_2$O$_3$/ZrO$_2$	0.81	70.5	0.7	78.0
IW Cu/6-Ga$_2$O$_3$/ZrO$_2$	0.84	90.3	0.96	77.7
IW Cu/9-Ga$_2$O$_3$/ZrO$_2$	0.98	77.5	0.94	76.5
IE Cu/ZrO$_2$	1.1	64.9	1.2	58.0
IE Cu/Ga$_2$O$_3$	1.17	50.5[c,f]	1.0	55.4[c,g]
IE Cu/1-Ga$_2$O$_3$/ZrO$_2$	0.68	67.8	0.67	65.4
IE Cu/6-Ga$_2$O$_3$/ZrO$_2$	0.65	75.6	0.69	65.0
IE Cu/9-Ga$_2$O$_3$/ZrO$_2$	0.59	78.5	0.63	67.6
1-Ga$_2$O$_3$/IE Cu/ZrO$_2$ (D)	0.72	80.5	0.75	75.6
6-Ga$_2$O$_3$/IE Cu/ZrO$_2$ (D)	0.73	72.1	0.66	74.7
9-Ga$_2$O$_3$/IE Cu/ZrO$_2$ (D)	0.77	77.3	0.78	75.5
1-Ga$_2$O$_3$/IE Cu/ZrO$_2$	1.33	65.8	1.14	72.9
6-Ga$_2$O$_3$/IE Cu/ZrO$_2$	1.07	73.2	1.05	72.2
9-Ga$_2$O$_3$/IE Cu/ZrO$_2$	1.28	66.7	1.16	72.0

(1) After 20 h on stream.
(2) After 4 h on stream.
(3) Precision of calculated values = ±7%.
(4) Precision of calculated values = ±2%.
[a] Operating conditions: $P = 3$ MPa; $T = 523$ K; GHSV = 20,000 h^{-1}.
[b] Nominal copper loading: 2 wt%.
[c] S_{CH_3OH} in the column heading stands for "total selectivity to methanol".
[d] Partial values were: $S_{CH_3OH} = 56.5\%$; $S_{DME} = 13\%$.
[e] Partial values were: $S_{CH_3OH} = 46.5\%$; $S_{DME} = 11\%$.
[f] Partial values were: $S_{CH_3OH} = 41.0\%$; $S_{DME} = 9.5\%$.
[g] Partial values were: $S_{CH_3OH} = 44.7\%$; $S_{DME} = 10.7\%$.

Table 4
Performance of the Cu–Ga–Zn catalysts (second set).

Catalyst[a]	Condition[b]	GHSV (h^{-1})	X_{CO_2}%	S_{MeOH}%	R_{MeOH}[c]
IE Cu/ZrO$_2$	a	20,000	1.8	51	131
	b	10,200	2.9	45	94
	c	0	–	–	–
	a	20,000	1.3	58	108
0.96-Ga$_2$O$_3$/IE Cu/ZrO$_2$	a	20,000	1.55	63	137
(Ga/Cu = 1/4)	b	18,000	1.7	62	130
	c	0	–	–	–
	a	20,000	1.1	64	100
3.8-Ga$_2$O$_3$/IE Cu/ZrO$_2$	a	20,000	1.4	70	135
(Ga/Cu = 1/1)	b	13,300	1.8	69	113
	c	0	–	–	–
	a	20,000	1.0	73	100
7.7-Ga$_2$O$_3$/IE Cu/ZrO$_2$	a	20,000	1.3	74	141
(Ga/Cu = 2/1)	b	12,000	1.85	70	110
	c	0	–	–	–
	a	20,000	0.9	72	98

[a] Copper loading: 2.6 wt%. Specific surface of the zirconia support: $S_g = 35$ m^2/g.
[b] $T = 523$ K, $P = 3$ MPa. See text for details.
[c] R_{MeOH} [=] (mol/s g cat) $\times 10^{-8}$.

3.1.2. Copper added by ion exchange

The relative activity of the binary preparations, IE Cu/ZrO$_2$ and IE Cu/Ga$_2$O$_3$ clearly indicates (Fig. 4) that the former support gives a better catalyst, as was the case with the IW preparations. The poor performance of the binary, gallia-supported catalysts (IE Cu/Ga$_2$O$_3$ and IW Cu/Ga$_2$O$_3$) might be due to the increased interaction between copper and gallia, with formation of the spinel-type CuGa$_2$O$_4$ that was identified by XPS, thus decreasing the amount of superficial copper available to react. Zirconia rather than gallia emerges, then, as the support of choice between them.

A comparison among the different ternary materials in which copper was added by IE shows that, within the same series, the catalytic activity to methanol did not improve substantially with the progressive addition of gallia (1–9 wt%), regardless of whether Cu was incorporated after or before gallia, or whether the IE Cu/ZrO$_2$ base materials were just dried (D) or dried/calcined prior to the addition of gallium nitrate. This is certainly at variance with the catalysts in which copper was incorporated by incipient wetness.

Also, within the same series the selectivity to methanol, S_{MeOH}%, was found to be quite dependent on the gallium loading when the H$_2$/CO$_2$/CO ternary mixture (**M1**) was used (Table 3), whereas upon using the **M2** mixture (H$_2$/CO$_2$/He), the S_{MeOH}% was indifferent to the gallia loading (this issue will be analyzed in detail below). Interestingly, these trends were consistently similar regardless of whether the addition of copper was by incipient wetness or ion exchange, which could signal that the dry synthesis of methanol (via (R$_3$)) requires an optimum amount of gallia on the surface. Nonetheless, as compared with the binary Cu/ZrO$_2$ or Cu/Ga$_2$O$_3$ catalysts, the S_{MeOH}% of the ternary materials was always better, using the **M1** or the **M2** feeds.

It merits noticing that the ternary catalysts in which copper was added by IE on the mixed oxides [IE Cu/x-Ga$_2$O$_3$/ZrO$_2$] were substantially less active than the binary IE Cu/ZrO$_2$ catalyst, albeit the selectivity to methanol of the former was better. These activity values were similar – indeed, slightly worse – than the one of the binary IE Cu/Ga$_2$O$_3$ catalyst, which strongly suggested us that the gallia domains on the Ga$_2$O$_3$/ZrO$_2$ support surface were preferred by copper during the ion exchange preparation step [21]. This led us to incorporate gallium after copper had been previously added to the zirconia.

Indeed, in the series where gallium nitrate was impregnated onto the dried IE Cu/ZrO$_2$ base stock [series x-Ga$_2$O$_3$/IE Cu/ZrO$_2$(D)] the reaction rates to methanol were higher (70–90 10^{-8} mol/s g cat) than those of the previous one. These rates were somewhat smaller

than the R_{MeOH} of the binary IE Cu/ZrO$_2$ but, nevertheless, the selectivity to methanol of the complete series was above 70% for both reaction mixtures, **M1** or **M2**.

Furthermore, on the catalysts of the last series, where the gallium salt was impregnated onto the dried and calcined IE Cu/ZrO$_2$ base stock [series x-Ga$_2$O$_3$/IE Cu/ZrO$_2$] the reaction rates to methanol were the highest of the set: 110–130 × 10^{-8} mol/s g cat), with selectivities to methanol also close to 70%. This last observation prompted us to select this type of preparation of the ternary Cu–Ga–Zr catalysts, focusing on the amount of gallia needed to maximize the catalyst performance.

It is quite suggesting that the XPS results showed a clear BE shift in the dried and calcined ternary catalyst [x-Ga$_2$O$_3$/IE Cu/ZrO$_2$] upon reduction (Fig. 3), whereas no BE shift could be observed in the sample where the gallium salt was impregnated onto the just dried IE Cu/ZrO$_2$ base stock [x-Ga$_2$O$_3$/IE Cu/ZrO$_2$(D)]. Again, an 'excessive interaction' between copper and gallia does not seem to be favorable for the synthesis of methanol.

3.2. Impact of the gallia loading (Ga/Cu atomic ratio) on the selectivity to methanol

Table 4 shows the performance (CO$_2$ conversion, reaction rate and selectivity to methanol) of the new set of ternary catalysts prepared according to the x-Ga$_2$O$_3$/IE Cu/ZrO$_2$ protocol, evaluated at 3 MPa and 523 K using the **M2** reaction mixture, for different values of space velocity, including a 'dwelling time' of several hours in static (no-flow) conditions, so as to reach full exposure of the catalysts to the reaction products under the maximum conversion attainable under these process conditions (i.e., exposing the catalysts to the thermodynamic equilibrium mixture). For comparison purposes, the binary IE Cu/ZrO$_2$ was also included in the testing.

After the first 8 h under the maximum space velocity employed in the runs (operating condition a, GHSV = 20,000 h^{-1}), the four catalysts showed similar activity to methanol (R_{CH_3OH}). However, their selectivities to methanol (S_{CH_3OH}) were substantially different. So, during the following 4 h on stream, the space velocity employed with each ternary catalyst was adjusted ('condition b') so as to get values of the selectivity to methanol under iso-conversion conditions (X_{CO_2} ~1.8%). As it is shown in Fig. 5, the selectivity to methanol (or, similarly, the yield to methanol) was higher at higher gallia loading or, likewise, higher Ga/Cu atomic ratio. This finding distinctly indicates that although a progressive addition of gallia
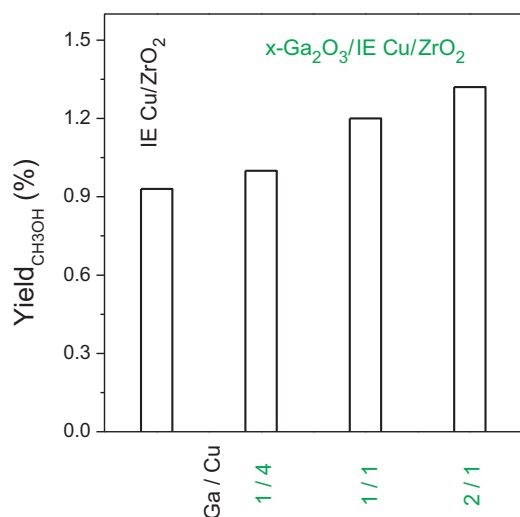
Fig. 5. Yield to methanol (Y_{CH_3OH}%) of the binary and ternary catalysts (second set) evaluated under iso-conversion conditions (X_{CO_2} = 1.8%). P = 3 MPa; T = 523 K; **M2** mixture ($H_2/CO_2/He$ = 75/22/3); GHSV: variable (see Table 4).

does not improve the activity of these ternary Cu–Ga–Zr catalysts, it surely improves the selectivity to methanol.

3.3. Stability of the different catalysts

After 20 h on stream at 3 MPa and 523 K, using the reaction mixture **M2** ($H_2/CO_2/He$) under differential reaction conditions, the deactivation degree of the catalysts of the first set (as measured by CO_2 conversion decay) was about 30% for the binary Cu/ZrO$_2$ catalysts (prepared either by IW or IE) and of about 12%, on average, for the binary Cu/Ga$_2$O$_3$ catalysts. The most stable preparations were those where gallium nitrate had been added by IW onto the dried/calcined copper–zirconia [x-Ga$_2$O$_3$/IE Cu/ZrO$_2$], for which the X_{CO_2}% was practically constant with time. The other ternary catalysts, featuring different loading of gallia, deactivated by 10–20%.

Yet, the percent selectivity to methanol remained about constant for all of them. Moreover, the S_{CH_3OH}% improved slightly (by about 2.5–7%) in the x-Ga$_2$O$_3$/IE Cu/ZrO$_2$(D) series after the 20 h test duration. Likewise, on the binary copper–gallia catalysts (i.e., IW Cu/Ga$_2$O$_3$ and IE Cu/Ga$_2$O$_3$) the selectivity also improved with time, by approximately 6%. This finding is a strong indication that the Cu(ox)/Cu° couples are changing with time on these catalysts, a fact that can be plausibly attributed to the promoting effect of Ga [27].

These precedents led us to analyze with more detail the stability issues, using the second set of catalyst preparations. Fig. 6a and b shows comparative plots of the conversion of carbon dioxide with time (X_{CO_2}%) on two of these catalysts, synthesized by incorporating copper to zirconia by ion exchange, using the reaction mixture **M2** ($H_2/CO_2/He$) at 3 MPa and 523 K, with GHSV = 20,000 h^{-1} (operating condition a, Table 4). It readily follows that the stability of the ternary catalyst, containing gallia [3.8-Ga$_2$O$_3$/IE Cu/ZrO$_2$] is far better that the stability of the binary one, IE Cu/ZrO$_2$. The other ternary catalysts of the series behaved similarly. This behavior agrees fairly well with the observations of Toyir et al. [27], who reported on the higher stability of Cu–Zn–Ga/SiO$_2$ catalysts as compared to their counterpart without gallia, Cu–Zn/SiO$_2$.

Fig. 6a and b also shows X_{CO_2}% for the binary and the ternary catalysts after they were exposed to a 'simulated plant shutdown' situation by discontinuing the flow of the reaction mixture for several hours (thus allowing the reaction mixture to reach thermodynamic equilibrium), and then reestablishing again the gas flow. After the exposure to a high concentration of the reaction products
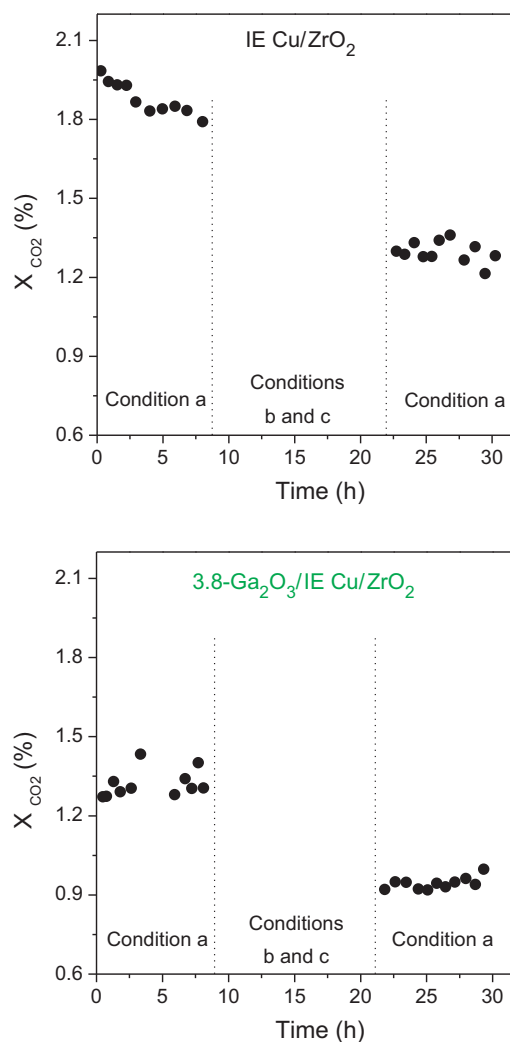

Fig. 6. Percent conversion of CO_2 (X_{CO_2}%) vs. elapsed time for the: (a) IE Cu/ZrO$_2$ and (b) 3.8-Ga$_2$O$_3$/IE Cu/ZrO$_2$ catalysts, respectively. P = 3 MPa; T = 523 K; **M2** mixture ($H_2/CO_2/He$ = 75/22/3). Operating condition a: GHSV = 20,000 h^{-1}.

(water, in particular) the conversion of carbon dioxide was affected in both cases. The ternary catalyst, though, showed a stable (yet less active) performance, whereas the binary one, IE Cu/ZrO$_2$ showed a steady decrease of activity, exposing again the advantage of gallia addition.

Along these lines, in a recent study by Schüth and coworkers [28] with a large set of CuO/ZnO/Al$_2$O$_3$ catalysts for methanol synthesis, it was remarked that: (i) the addition of Al^{3+} helped to increase the specific surface area of the catalysts *and* the Cu dispersion and, also (ii) reduced the metal sintering under reaction conditions. This last observation, which is in agreement with findings of Kurtz et al. [29], seems to bear close resemblance with our findings, as we also observed higher stability – smaller sintering? – whenever gallia was present.

4. Conclusions

These novel Cu–Ga$_2$O$_3$–ZrO$_2$ catalysts show a fair performance for the synthesis of methanol from ternary H$_2$/CO$_2$/CO mixtures such as those that would be found in 'CO$_2$ capture modules' with recycle of non-condensable gases. Some of them are remarkably more active and selective to methanol than the binary Cu/ZrO$_2$ or Cu/Ga$_2$O$_3$ counterparts. To obtain active materials, zirconia must be the base-support; highly selective and stable preparations need the

three components (Cu–Ga–Zr). The best performances are achieved when gallia is added to a dried and calcined Cu/ZrO_2 precursor, where copper has been incorporated by ion exchange to the zirconia. High Ga/Cu ratios do not improve substantially the catalytic activity to methanol but lead to better yields, as the selectivity to methanol increases with higher gallium to copper ratios.

Under similar reaction conditions, commercial $Cu/ZnO/Al_2O_3$ (~45 wt% Cu) catalysts are twice as active (300 g CH_3OH/kg cat h [27]) as the best catalyst of our set, $6\text{-}Ga_2O_3$/IE Cu/ZrO_2. However, per mass of copper this last preparation was 22-fold more active. These results, together with the encouraging findings with regards to selectivity to methanol and stability of these novel $Cu\text{-}Ga_2O_3\text{-}ZrO_2$ catalysts suggest them as possible, promising alternatives to conventional commercial methanol synthesis catalysts for carbon dioxide recycling.

Acknowledgments

Appendix A. Data reduction equations

$$R_i = \frac{y_i \cdot F_{\text{TOTAL NTP}} \quad (\text{cm}^3_{\text{NTP}}/\text{min})}{24,463 \quad (\text{cm}^3_{\text{NTP}}/\text{mol}) \cdot 60 \quad (\text{s}/\text{min}) \cdot w_{\text{cat}} \quad (g)}$$
$$= \left(\frac{\text{mol}_i}{g_{\text{cat}} \text{s}} \right) \tag{A.1}$$

where

$$F_{\text{TOTAL NTP}} = \frac{F_{\text{TOTAL}} \quad (\text{cm}^3/\text{min}) \cdot P_{\text{amb}} \quad (\text{mbar}) \cdot 298.15 \quad (K)}{1013.33 \quad (\text{mbar}) \cdot (273.15 + T_{\text{amb}} \quad (^\circ C))}$$
$$= \left(\frac{\text{cm}^3}{\text{min}} \right)_{\text{NTP}} \tag{A.2}$$

$$S_i = \frac{R_i \cdot 100}{(R_{\text{CH}_3\text{OH}} + R_{\text{CO}} + 2R_{\text{DME}})} \quad i = \text{CH}_3\text{OH or}$$

$$\text{CO}, \quad S_{\text{DME}} = \frac{2 \cdot R_{\text{DME}} \cdot 100}{(R_{\text{CH}_3\text{OH}} + R_{\text{CO}} + 2R_{\text{DME}})} \tag{A.3}$$

$$X_{\text{CO}_2}\% = \frac{(R_{\text{CH}_3\text{OH}} + R_{\text{CO}} + 2R_{\text{DME}}) \quad (\text{mol}/g_{\text{cat}} \text{s}) \cdot w_{\text{cat}} \quad (g) \cdot 100}{\left(\left(F^0_{\text{CO}_2} \quad (\text{cm}^3_{\text{NTP}}/\text{min}) \right) / \left(24,463 \quad (\text{cm}^3_{\text{NTP}}/\text{mol}) \cdot 60 \quad (\text{s}/\text{min}) \right) \right)} \tag{A.4}$$

$$\text{Yield}_{\text{CH}_3\text{OH}}\% = \frac{R_{\text{CH}_3\text{OH}} \quad (\text{mol}/g_{\text{cat}} \text{s}) \cdot w_{\text{cat}}(g) \cdot 100}{\left(F^0_{\text{CO}_2} \quad (\text{cm}^3_{\text{NTP}}/\text{min}) \right) / \left(24,463 \quad (\text{cm}^3_{\text{NTP}}/\text{mol}) \cdot 60 \quad (\text{s}/\text{min}) \right)} \tag{A.5}$$

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