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Methanol synthesis from CO_2/H_2 using Ga_2O_3–Pd/silica catalysts: Impact of reaction products

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Abstract

The synthesis of CH_3OH from CO_2/H_2 mixtures using Ga_2O_3–Pd/SiO_2 promoted catalysts is strongly affected by the reaction products. At finite conversion, important amounts of water and carbon monoxide are also found in the system and, therefore, a comprehensive evaluation of their impact on the process is particularly relevant. An experimental program was conducted, using a plug-flow, differential reactor and a Berty-type CSTR recycle reactor, for a wide range of temperature (508–538 K), pressure (1–4 MPa), composition (H_2/CO_2 = 1, 3 and 6) and space velocity, including H_2–CO–CO_2 and H_2–He–CO_2 ternary mixtures as well.

The deleterious effect of CO is attributed to its strong chemisorptive bonding onto the metal, which hampers the generation and transfer of dissociated hydrogen, H_s, from the Pd crystallites to the Ga_2O_3; this effect alters both the activity and the selectivity of the catalyst. The detrimental impact of H_2O, which is produced in every stoichiometric reaction of the system, is related to its interference on the availability of coordinatively unsaturated sites (*cus*) on the gallia surface.
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Keywords: CO_2 recycling; Methanol synthesis; Bifunctional catalysts

1. Introduction

Catalytic recycling of carbon dioxide, the major man-made greenhouse gas, to more useful compounds is currently under consideration among the possible approaches for mitigating its emissions to the atmosphere. In this regard, the selective hydrogenation of CO_2 to methanol at point sources has emerged in the last decade as a promising and viable option [1]. Improvements on the catalyst selectivity towards methanol *versus* the competitive, concomitant reaction in the system: the reverse water gas shift (RWGS—which produces carbon monoxide and water, instead), have been long pursued because, to maximize H_2 utilization, recirculation loops are needed in realistic flow-sheets. So, any such selectivity improvement can allow a significant reduction in the recycle ratio of non-condensable gases inside the industrial reactors, thus contributing to maximize conversion.

Along this last guideline, the development of an active Pd/Ga_2O_3 catalyst for methanol synthesis from CO_2 hydrogenation, able to compete with the classical Cu/ZnO formulation, was first reported by Fujitani et al. [2]. Later on, Bonivardi et al. showed that the addition of gallium oxide to a Pd/SiO_2 catalyst produced a dramatic improvement of the catalytic performance to give oxygenated compounds from carbon dioxide hydrogenation: the turnover rate to methanol could be increased up to 500-fold (H_2/CO_2 = 3523 K and 3 MPa) upon going from clean Pd/silica to Ga_2O_3–Pd/silica (Ga-to-Pd atomic ratio = 8), and the selectivity to methanol went up, from 17 to 70%, the higher the gallium content on the Pd/SiO_2 was [3].

More recently, using mechanical mixtures of Pd/silica and Ga_2O_3/silica and combined reaction and *in situ* FTIR experiments, we were able to demonstrate that under typical process conditions the Ga_2O_3–Pd/silica catalysts are bifunctional: atomic hydrogen (H_s) is generated by the Pd crystallites, while the Ga_2O_3 patches onto the silica support are responsible for CO_2 activation (*via* formates) and complete the reaction cycle [4,5]. The metal-promoter intimacy does not seem to be decisive in terms of the catalytic chemistry of the system, but the closeness between the Pd crystallites and the Ga_2O_3 surface

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patches boost the activity, owing to a minimized effort in the H_s supply to the latter. In this catalytic system hydrogen-spillover, or hydrogen 'remote control' as per the concept coined by Delmon and co-workers [6,7], seems to be fully operational.

In addition, it is well-known that, whichever the catalyst under scrutiny, a thorough kinetic study – carried out, particularly, under the expected range of conditions of the process variables found in an industrial reactor – is of fundamental importance. Therefore, we present here a study on the impact of the reaction products on a stabilized Ga_2O_3–Pd/silica catalyst, as an integral part of our current research efforts towards the development of novel methanol synthesis catalysts.

2. Experimental

2.1. Catalyst preparation

A first stock material, with 2 wt.% Pd loading, was obtained by ion exchanging palladium acetate at pH 11 in NH_4OH (aq) onto a mesoporous silica support (Davison G59). The support was previously crushed and sieved through an 80-mesh Tyler screen, purified, calcined at 773 K and characterized (specific surface = 301 $m^2\ g^{-1}$; average pore diameter = 160 Å; average particle diameter = 52 μm). Then, $Ga(NO_3)_3$ (aq), was added by incipient wetness impregnation, so as to obtain a Ga/Pd = 3 atomic ratio. Water was eliminated by sublimation at reduced pressure and then the material was calcined in air (200 $cm^3\ min^{-1}$) at 623 K (2 h), to obtain gallia and palladium oxide on the support surface. Next, the catalyst was reduced under 5% H_2 in argon (200 $cm^3\ min^{-1}$) at 723 K (2 h) and passivated with oxygen pulses, prior to use, as already described in a previous work [3].

2.2. Catalyst stabilization

The stock of catalyst was stabilized by flowing consecutively mixtures of $H_2/CO_2 = 3$ (20 h) and then $H_2/CO = 3$ (12 h), followed by pure H_2 (10 h), under typical methanol synthesis process conditions: 523 K, 3 MPa. The catalyst was then cooled to room temperature (RT) under hydrogen flow and air-passivated again. This sequence ensured a constant exposed metal fraction (FE = 4%) throughout the experimental program [8]. The specific surface of the stabilized, powdered catalyst was 278 $m^2\ g^{-1}$.

2.3. Catalysts evaluation

The catalyst performance was evaluated using two different set-ups. In a first series of experiments a glass-lined, plug-flow differential microreactor was fed with different proportions of CO_2, CO and hydrogen, but keeping a constant $H_2/(CO_2 + CO) = 3$ mol ratio, at 523 K and 3 MPa total pressure. The catalyst was used in powdered form. In other experiments of the series CO was replaced by He, but still maintaining the $H_2/(CO_2 + He) = 3$ mol ratio in the feeding mixture. Prior to each run a fresh load of the catalyst was reduced *in situ* under H_2, with a heating rate of 3 K/min from RT to 523 K, then maintaining the last temperature for 1 h.

In a second series of experiments, a pressurizable internal recycle, Berty-type CSTR reactor (500 cm^3) was used, to collect activity and selectivity data at integral conversion values in the absence of extraparticle mass-transfer resistances. The inner parts of the reactor were gold plated, *via* electrolytic deposition, to ensure total inertness of the device. The stock of passivated, powdered catalyst was pelletized and crushed to make small particles of about 1 mm diameter (specific surface of the pelletized catalyst = 233 $m^2\ g^{-1}$). A wide range of temperature (508–538 K), pressure (1–4 MPa), composition (H_2/CO_2 = 1, 3 and 6) and space velocities ($W/F^0_{CO_2}$) was used, including H_2–CO–CO_2 ternary mixtures as well. To discriminate mechanistic differences and/or promoting effects, further runs were done using the base stock material Pd (2 wt.%)/silica, under similar process conditions.

Gas flows were controlled using Brooks 5850 TR mass-flow units. The exit lines from the reactors were inert (glass-lined stainless steel) and were kept between 373 and 393 K to prevent any condensation of the reaction products. The gas composition was analyzed by GLC in two Shimadzu 9A units arranged in parallel, employing Porapak QS and Carbosieve SII filled (1/8 in. i.d., 3 m long) stainless steel columns. The only compounds detected were CO, CO_2, H_2, CH_3OH, CH_3OCH_3 (DME) and CH_4 (traces).

According to this, the molecular reactions involved in the system are just the following:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (2)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (3)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (1')$$

3. Results and discussion

3.1. Differential reactor data

Fig. 1 shows the monotonic reduction of the reaction rate to methanol, R_{MeOH}, at standard process conditions (523 K, 3 MPa), using both ternary mixtures, upon decreasing the CO_2 fraction in either feed. *Vis-à-vis*, for the same p_{CO_2} in the system, this reduction became far-reaching when $H_2/(CO_2 + CO)$ was used instead of $H_2/(CO_2 + He)$. This reduction in R_{MeOH} cannot be ascribed to selectivity changes in oxygenates production, as the methanol-to-DME ratio, defined here as MeOH/(MeOH + DME), was always >80% save for the $H_2/CO = 3$ feed, where only traces of DME were detected. After running the H_2/CO binary mixture, the initial activity of the catalyst using $H_2/CO_2 = 3$ could be recovered following a reduction in flowing H_2 for 10 h at the same conditions, *i.e.*, 523 K and 3 MPa.

FTIR experiments [9] have shown that: (i) CO_2 is hydrogenated stepwise, into monodentate formate, methylenebisoxy, methoxy and methanol (whereas only a small

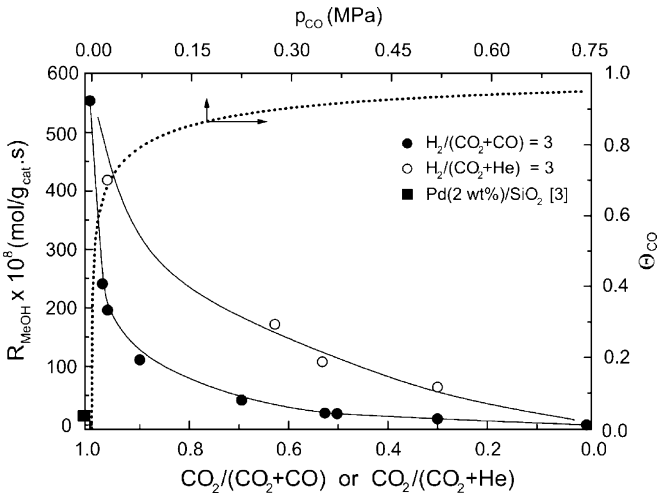

Fig. 1. Reaction rate to methanol (R_{CH_3OH}) under differential reaction conditions, using Ga_2O_3–Pd/silica and feeding different $H_2/(CO_2 + CO)$ and $H_2/(CO_2 + He)$ ternary mixtures while keeping a constant $H_2/(CO_2 + CO) = 3$ mol ratio (523 K and 3 MPa). Dotted line: carbon monoxide Temkin isotherm *vs.* p_{CO}, at 523 K [11].

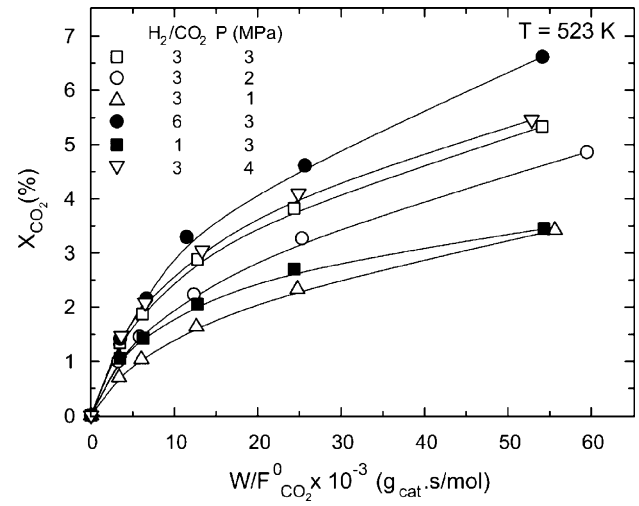

Fig. 2. Percent CO_2 conversion using the Ga_2O_3–Pd/silica catalyst as a function of space velocity ($W/F^0_{CO_2}$) in the CSTR Berty-type reactor at 523 K.

quantity of monodentate formate was detected using CO in the feed); (ii) all these species are bonded to gallia; (iii) CO_2 hydrogenation on Ga_2O_3/SiO_2 gave only traces of methanol, due its modest capability to dissociate H_2 [10], while this hydrogenation was far more effective when the Ga_2O_3–Pd/SiO_2 catalyst was used (in this case, the temperature for the maximum concentration for each species experienced a downshift of about 100 K); (iv) CO production, *via* the RWGS reaction, was observed *only* in the presence of Pd. These combined findings further support postulating the bifunctional mechanism for methanol synthesis on Ga_2O_3–Pd/SiO_2 catalysts, namely: CO_2 chemisorbs onto Ga_2O_3 and hydrogenates there, stepwise, to methanol, using atomic hydrogen spillovered from the Pd crystallites.

FTIR results can offer a direct proof that the decrease in R_{MeOH} cannot be ascribed to competitive chemisorption of CO onto gallia but, rather, that CO is strongly chemisorbed on Pd at process conditions, which hampers the ability of the metal to dissociate H_2 and, consequently, decreases the rate of hydrogenation of CO_2 (*via* H-spillover) on gallia. So, direct evidence to sustain this hypothesis was produced by analyzing the impact of CO coverage on Pd (θ_{CO}) as a function of p_{CO} [11]. A Temkin isotherm at reaction temperature (523 K) was generated using the initial heat of adsorption of CO, $Qad^{O}_{(CO)}$, measured on Pd/SiO_2. Fig. 1 shows that, in fact, there is a direct correspondence between θ_{CO} increases and R_{MeOH} diminution when p_{CO} in the reaction mixture is made higher.

3.2. Integral reactor data

These results will be mostly analyzed taking the usual process temperature (523 K) as a reference value, and adding further remarks whenever needed. Table 1 gives the full set of experimental data obtained at such temperature as well as most of the relevant data regarding exit composition and percent carbon conversion, while Fig. 2 synthesizes the observed trends, namely: (i) as expected, the higher the space velocity, $W/F^0_{CO_2}$, was set the higher the carbon conversion became, (ii) for a given H_2/CO_2 ratio, the conversion was higher the higher the reactor pressure was set, as befits any reaction – in our case the methanol synthesis reaction – in which the number of moles decreases (*e.g.*, see open symbols in Fig. 2 for $H_2/CO_2 = 3$), and (iii) for a given total pressure the higher the hydrogen to CO_2 mol ratio was set the higher the conversion was.

As shown in Table 1 and Fig. 2, the maximum CO_2 conversion reached in our experimental program was around 7%, which indicates upon comparison with the equilibrium conversion under these experimental conditions (≈32%), that the entire set of data was not tainted by thermodynamic constraints. Moreover, the experimental mass-law action partial pressure relationships (J) of products *versus* reactants for reactions (1) and (2) were always less than their corresponding equilibrium constant (K_{eq}) values, 13 and 7.5%, respectively (these maximum values were reached at $T = 538$ K), which further support the following analyses.

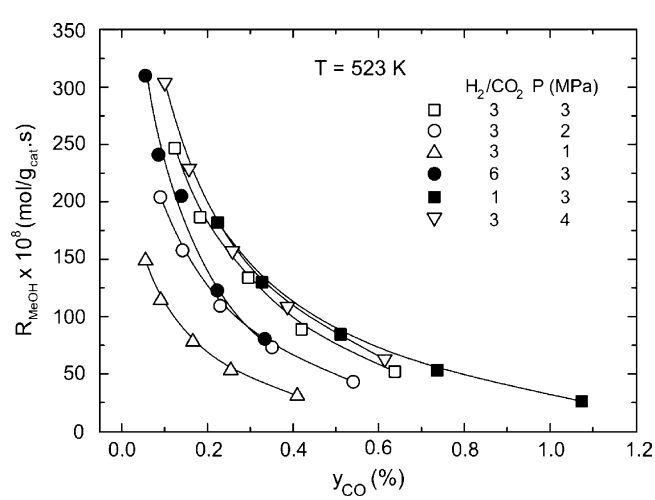

Fig. 3. Reaction rate to methanol (R_{MeOH}) using the Ga_2O_3–Pd/silica catalyst *vs.* the CO mol fraction in the CSTR Berty-type reactor (523 K).

Table 1
Comparative reaction rates, CO_2 conversion and approach to thermodynamic equilibrium, for different values of the reactants ratio, total pressure and space velocity, using the Ga_2O_3–Pd/SiO_2 catalyst in the Berty-type CSTR reactor (T = 523 K)

H_2/CO_2	P_{TOTAL} (MPa)	$W/F^0_{CO_2} \times 10^{-3}$ (g_{cat} s mol^{-1})	$R_{MeOH} \times 10^8$ mol g^{-1}_{cat} s^{-1}	y_{H_2O} (%)[a]	y_{CO} (%)[a]	X_C (%)		$(X^{EXP}_C/X^{EQ}_C) \times 100$
						EXP	EQ	
3	3	3.48	246.6	0.40	0.12	1.34	21.96	6.10
		6.19	186.4	0.57	0.18	1.87		8.51
		12.8	133.7	0.86	0.29	2.88		13.1
		24.4	88.7	1.14	0.42	3.82		17.4
		54.1	52.0	1.50	0.64	5.33		24.2
3	2	3.32	204.0	0.30	0.09	1.00	19.32	5.20
		5.84	157.6	0.42	0.14	1.46		7.54
		12.3	109.3	0.64	0.23	2.24		11.6
		25.3	73.2	0.91	0.35	3.27		16.9
		59.5	43.1	1.33	0.54	4.86		17.7
3	1	3.35	148.8	0.14	0.06	0.70	17.36	4.05
		6.01	114.1	0.25	0.09	1.04		5.97
		12.6	77.8	0.40	0.17	1.64		9.44
		24.8	52.9	0.59	0.25	2.33		13.4
		55.6	30.9	0.87	0.41	3.42		19.7
6	3	3.52	309.9	0.18	0.06	1.41	32.12	4.42
		6.67	240.9	0.28	0.09	2.16		6.71
		11.5	205.1	0.43	0.14	3.29		10.2
		25.7	122.6	0.63	0.22	4.61		14.3
		54.1	80.3	0.91	0.33	6.62		20.6
3	3	3.53	265.2	0.31	0.10	1.31	21.96	5.96
1	3	3.50	181.8	0.60	0.22	1.05	11.18	9.41
		6.28	129.7	0.76	0.33	1.42		12.8
		12.8	84.3	1.08	0.51	2.05		18.3
		24.4	53.1	1.50	0.74	2.70		24.1
		54.3	26.0	1.63	1.07	3.44		30.8
3	3	3.46	253.5	0.30	0.09	1.19	21.96	5.42
3	4	3.63	303.8	0.34	0.10	1.47	24.84	5.92
		6.48	229.0	0.48	0.16	2.08		8.37
		13.3	157.1	0.74	0.26	3.04		12.3
		24.9	108.5	1.05	0.39	4.09		16.5
		52.9	62.9	1.16	0.61	5.46		21.9

[a] Percent mol fraction at the reactor exit.

Fig. 3 depicts the evolution of the reaction rate to methanol *versus* the exit CO mol fraction in the Berty-type reactor at 523 K (R_{MeOH} *vs.* y_{CO}). The data, which explicitly identify the amount of carbon monoxide produced in the CSTR reactor, show a decrease in reactivity towards the methanol synthesis of about fourfold between the high space velocity conditions (*i.e.*, 'almost CO free') and the high conversion (*i.e.*, maximum CO produced), for the whole set of experimental data. Indeed, Fig. 3 shows that for the same y_{CO} in the exit stream (that is, whenever the Pd crystallites are covered by chemisorbed carbon monoxide in about the same proportion) the R_{MeOH} was much more affected when the high H_2/CO_2 ratios were used. For instance, at 523 K and 3 MPa the percent *decrease* of R_{MeOH} for y_{CO} = 0.22% *versus* y_{CO} = 0.33% were 35 and 29% (H_2/CO_2 = 6 resp. H_2/CO_2 = 1). For any given y_{CO}, this observation can be fully explained by just considering the corresponding partial pressures of H_2 and CO_2 in the reactor mixtures, because in the first case (H_2/CO_2 = 6) the partial pressure of carbon dioxide was about 0.43 MPa, whereas it was close to 1.5 MPa when the substoichiometric ratio (H_2/CO_2 = 1) was used.

The extrapolation of the R_{MeOH} *versus* y_{CO} ratio to differential conditions gives far higher initial rates. Indeed, performing such extrapolation for P = 3 MPa and H_2/CO_2 = 3, the following values were obtained: $R_{MeOH} = 402 \times 10^{-8}$ mol g^{-1} s^{-1} and $R_{CO} = 210 \times 10^{-8}$ mol g^{-1} s^{-1} (taken from a plot of R_{CO} *versus* y_{CO} similar to Fig. 3, not shown here). They were in fairly good agreement with the experimental values obtained under differential conditions (GHSV = 300,000 h^{-1}, or $W/F^0_{CO_2} = 424$ g s mol^{-1}) in the plug-flow microreactor: 530×10^{-8} and 220×10^{-8} mol g^{-1} s^{-1}, respectively.

The presence of reaction products also affected R_{CO}, which significantly decreased the higher $W/F^0_{CO_2}$ was made, but much less than the main reaction (Table 2). Consequently, the selectivity to methanol (S_{MeOH}) decreased the higher the residence time in the reactor was (see Fig. 4a).

At first sight, it would seem that the S_{CH_3OH} worsened the higher the process temperature was set, which could then be straightforwardly attributed to the differences in the activation energies of reactions (1) and (2). Yet, upon a more careful examination it was established that for the same levels of

Table 2
CO_2 conversion and comparative catalytic activity of the Ga_2O_3–Pd/SiO_2 and unpromoted Pd/SiO_2, at $T = 523$ K, $P = 3$ MPa ($H_2/CO_2 = 3$)

Catalyst	X_{CO_2} (%)	$R_{MeOH} \times 10^8$ (mol g^{-1} s^{-1})	$R_{CO} \times 10^8$ (mol g^{-1} s^{-1})	$R_{DME} \times 10^8$ (mol g^{-1} s^{-1})
Ga_2O_3–Pd/SiO_2[a]	1.34	246	163	4.4
	1.87	186	138	4.0
	2.80	134	108	3.8
	3.82	89	78	3.6
	5.30	52	53	3.5
Pd/SiO_2[b]	0.78	5.9	24.2	–
	1.08	5.4	16.8	–
	1.57	5.1	11.5	–
	2.11	4.1	8.3	–
	2.70	2.9	4.9	–

[a] Ga/Pd mol ratio = 3; 2 wt.% palladium loading.
[b] Metal loading: 2 wt.%.

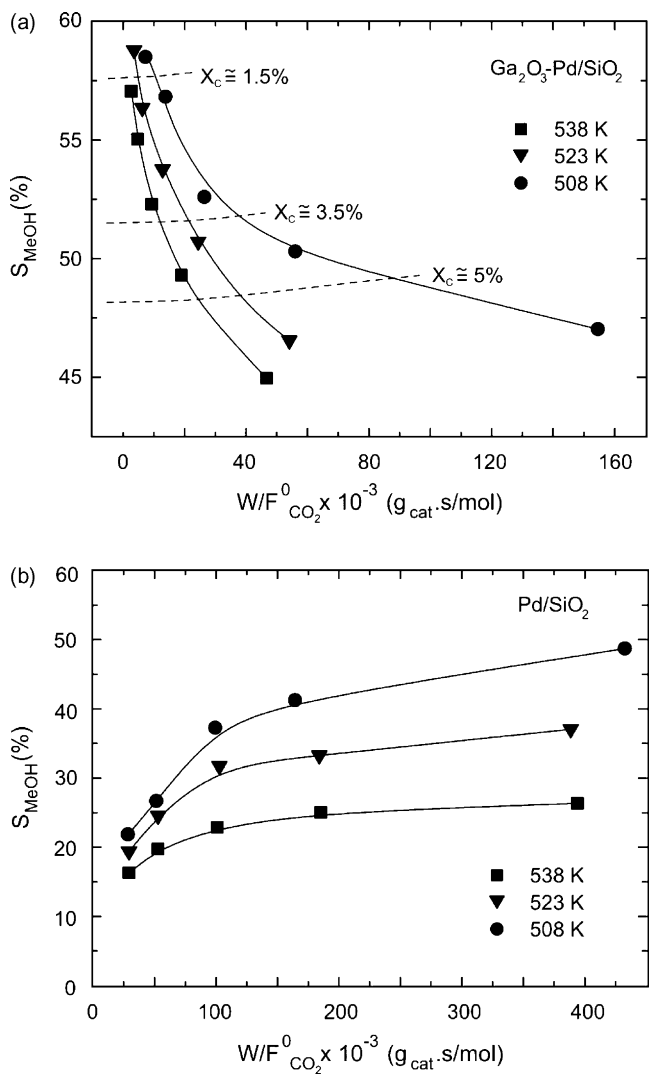

Fig. 4. Comparative selectivities to methanol (S_{MeOH}) *vs*. space velocity ($W/F^0_{CO_2}$) using the gallia-promoted and the unpromoted Pd/silica in the CSTR Berty-type reactor, at different temperatures: (a) Ga_2O_3–Pd/SiO_2 and (b) Pd/SiO_2 (3 MPa; $H_2/CO_2 = 3$).

conversion the selectivity was about the same (see dashed lines in Fig. 4a). Indeed, our preliminary results obtained under differential conditions where the CO mol fraction was <0.038%, gave activation energies values equal to $E_1 = 88$ and $E_2 = 82$ kJ/mol, for reactions (1) and (2), respectively. This implies a low sensitivity in the reaction selectivity of the direct (*i.e.*, forward) reactions with temperature, a trend which is also shown in Fig. 4a when the conversion is low. Then, estimating again the activation energies from the CSTR reactor data in the low-conversion region, $E_1 = 80$ and $E_2 = 83$ kJ/mol values were obtained. These values, entirely similar to those calculated under differential conditions, verify the absence of mass-transport limitations in the Berty reactor and validate them.

At this point, it is convenient to compare the performance of this gallia-promoted catalyst with that of the unpromoted Pd/silica. Using the latter, the selectivity to methanol also decreased with temperature, but S_{CH_3OH} *increased* the longer the residence time was (Fig. 4b). This is due to the existence of different reaction pathways for CH_3OH synthesis on each material, because Pd activates CO_2 without formates formation, which certainly Ga_2O_3 does [12]. The Ga_2O_3–Pd/silica produces sizable amounts of CO (probably from formates, *via* a reductive pathway), whereas Pd/SiO_2 produces less amount of CO, given its low capacity for carbon dioxide dissociation, but at the expense of much lower reactivity, as shown in Table 2.

To further analyze the impact of the presence of carbon monoxide in the reaction system, increasing amounts of CO were added to the mixture fed to the Berty-type CSTR reactor, while always keeping a constant hydrogen-to-carbon oxides ratio [$H_2/(CO + CO_2) = 3$]. Fresh loadings of the Ga_2O_3–Pd/silica and Pd/SiO_2 catalysts were used each time, and the reactor was operated under similar conversion conditions (up to 4%) in both cases, as illustrated in Fig. 5a and b. The comparison between both figures shows that the increase in the CO mol fraction affect quite differently the performance of each material: when CO is added to the reaction mixture, the activity of Pd/SiO_2 towards methanol synthesis decays much less, at higher $W/F^0_{CO_2}$, than upon using H_2/CO_2, in complete agreement with previous work by our group, which shows that CO is the main reactant for CH_3OH synthesis on unpromoted palladium [reaction (1′) in the scheme].

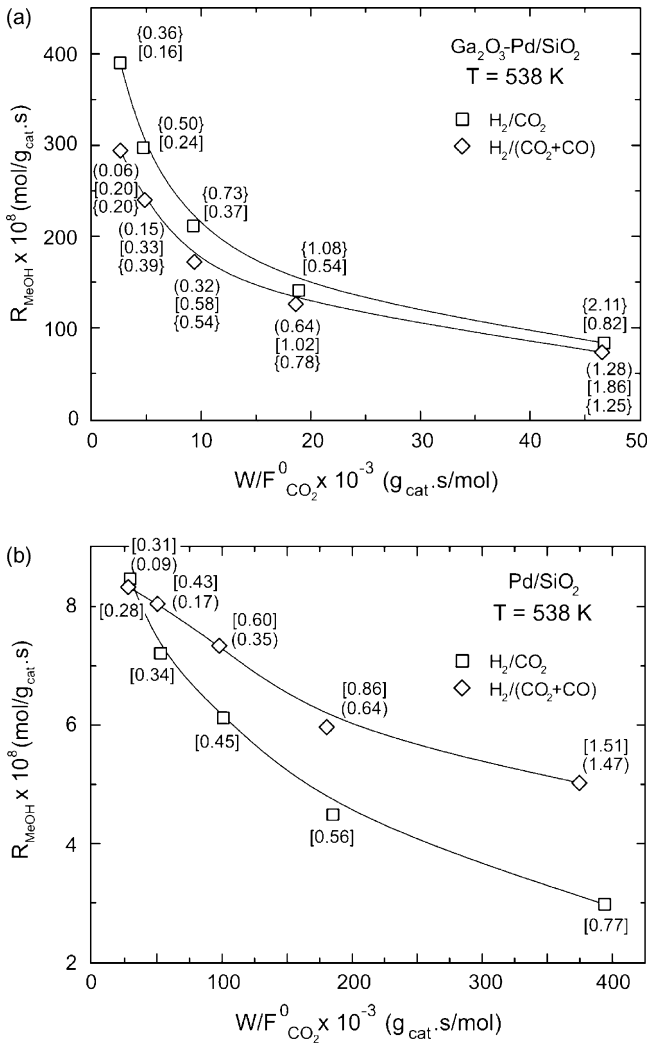

Fig. 5. Comparative reaction rates to methanol (R_{MeOH}) *vs.* space velocity ($W/F^0_{CO_2}$) using the gallia-promoted and the unpromoted Pd/silica in the CSTR Berty-type reactor: (a) Ga_2O_3–Pd/SiO_2 and (b) Pd/SiO_2 [538 K; 3 MPa; H_2/($CO + CO_2$) = 3]. Keys: ( ) CO mol% in the feed; [ ] and { } mol% of CO and H_2O, respectively, at the reactor exit.

The promoted Ga_2O_3–Pd/silica catalyst behaved in just the opposite fashion, its activity for methanol synthesis decayed – greatly at low $W/F^0_{CO_2}$ – when CO was purposely added. This feature is related with the progressive coverage of the Pd crystallites with chemisorbed CO at higher p_{CO}, which reduces an efficient supply of H_s required to attend the successive hydrogenation steps of the oxygenate intermediates (formate, methylenebisoxy, methoxy) chemisorbed onto the gallia [12]. Even though the activity of the unpromoted catalyst is *ca.* 50 times lower than the Ga_2O_3–Pd/silica (Table 2), Fig. 5a and b undoubtedly shows that on Pd/SiO_2 the most important carbon source for the methanol synthesis is CO.

Fig. 5a also shows that the behaviour of the gallia-promoted catalyst is complex. In the low-conversion (or low $W/F^0_{CO_2}$) region, when the percent of water formed is minimum, the activity decrease can be attributed almost exclusively to the CO added. However, at higher conversion (higher $W/F^0_{CO_2}$ values) the mol fractions of both, H_2O and CO, become higher in the reaction mixture. Thus, upon comparing the composition values inside the CSTR reactor for both situations, it can be observed that for higher space velocity the upper line (runs without CO added, where the percentages of H_2O are higher) gets closer to the lower one (runs with deliberate addition of CO, where the percentages of CO are higher). This suggests that the presence of water must be taken into consideration as a possible detrimental factor in the performance of Ga_2O_3–Pd/silica, either because it eliminates coordinatively unsaturated sites (*cus*) or that, given the amphoteric character of gallia, higher proportions of H_2O in the gas phase lead to a modification of its surface structure and, hence, to its reactivity. A similar inhibitory effect of the water formed as a by-product during the reaction has also been observed in Cu-based methanol synthesis catalysts [13–15].

As it was shown in the former section using a differential plug-flow reactor under similar reaction conditions, employing ternary $H_2/(CO_2 + CO)$ and $H_2/(CO_2 + He)$ mixtures and comparing these reaction data with CO chemisorption measurements, the lower activity of the promoted Ga_2O_3–Pd/silica catalyst when y_{CO} is high can be associated with the higher Pd coverage of the Pd crystallites by chemisorbed carbon monoxide. The activity results at finite CO_2 conversions (Fig. 6) show an analogous trend for similar, comparable CO mol fractions in the gas phase both in quasi-absence (differential reactor) *versus* presence (integral CSTR reactor) of water in the system. Yet, the reactivity of the catalyst in the second case, that is, in the presence of water as reaction product *for equal amount of available CO*, is notoriously different.

It seems apparent, then, that the presence of molecular H_2O in the gas phase plays a regulating (or 'modulating') role between the amount of surface Ga–O and Ga–OH sites on the gallia. Nevertheless, the similar water stoichiometry in the methanol synthesis from CO_2/H_2 and the RWGS reaction suggests that the presence of water is more influential on the catalyst activity than upon its selectivity. On the other hand,

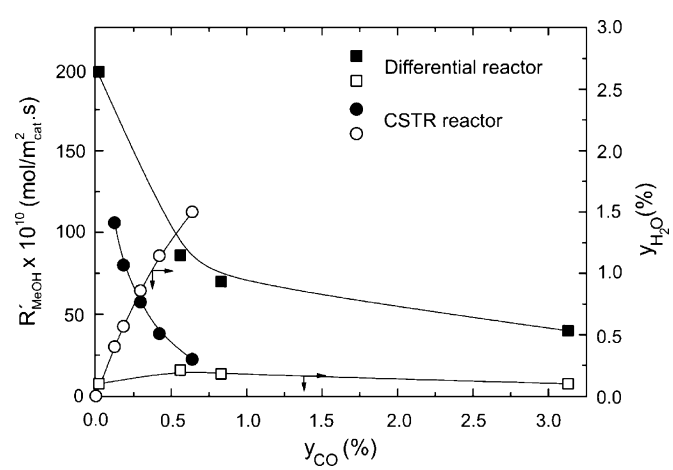

Fig. 6. Comparative reaction rates to methanol (R'_{MeOH}—normalized per specific surface of the support) and percent mol fraction of water in the exit stream (y_{H_2O}) *vs.* the percent mol fraction of CO in the exit stream, in the differential plug-flow microreactor [feed composition: $H_2/(CO_2 + CO) = 3$] and the CSTR reactor [feed composition: $H_2/CO_2 = 3$] using Ga_2O_3–Pd/silica, at 523 K and 3 MPa.

having established already that in the reaction mechanism hydrogen is dissociated by the Pd crystallites and then migrates towards the Ga_2O_3 patches supported onto the silica, by ''spillover'', to hydrogenate consecutively the formate, methylenebisoxy and methoxy surface groups (HCO_2, H_2CO, H_3CO), to finally give methanol, the impact of CO on the hydrogenating capabilities of the gallia-promoted catalyst reflects more accentuatedly on the observed changes in selectivity.

The production of DME on the Ga_2O_3–Pd/silica shows an interesting aspect: it increased patently with temperature (which is characteristic of dehydration reactions [16–19]), but the R_{DME} varied much less with $W/F^0_{CO_2}$ than what the other reactions did (see Table 2). In truth, it was hardly affected by the different conversion levels. This is, of course, concurrent with the absence of direct participation of adsorbed atomic hydrogen on its synthesis (although, indirectly, in the reactor atmosphere about 30% of the gallia surface is reduced [10]). The small reduction in R_{DME} that was found the higher the CO_2 can be assigned, unambiguously, to the increasing levels of H_2O in the reactor when both CH_3OH and CO are produced by reactions (1) and (2).

4. Conclusions

The synthesis of methanol from CO_2/H_2 using gallia-promoted Pd/SiO_2 is strongly influenced by the reaction products. The effect of carbon monoxide, considered the most significant, is associated to the interference caused by CO chemisorbed onto the Pd crystallites, with the generation and/or transference of dissociated hydrogen (H_s) from the metal to the gallia, which primarily affects the catalyst activity and – indirectly – its selectivity. The detrimental impact of H_2O is associated with its capacity to hinder the availability of *cus* on the Ga_2O_3, which affects directly the activity of the material, as water is the common product of all the molecular reactions present in the system.

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