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Hydrogen spillover in Ga_2O_3–Pd/SiO_2 catalysts for methanol synthesis from CO_2/H_2

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The hydrogenation of CO_2 was investigated on Ga_2O_3-promoted Pd/SiO_2 catalyts and mechanical mixtures of Ga_2O_3/SiO_2 and Pd/SiO_2 catalysts ($H_2/CO_2 = 3$; $P = 3.0$ MPa; $T = 523$ K). By means of the latter it was possible to demonstrate that atomic hydrogen, H_s, can be generated by Pd^0 far from Ga_2O_3, and move (spill-over) there to reach the other reactive species (formates) and complete the reaction cycle. The reaction results indicate that (as also evidenced by *in situ* FTIR) the Ga_2O_3-Pd/SiO_2 catalyst works as a true bi-functional system. The metal-promoter intimacy is not decisive in terms of the catalytic chemistry of the system, but the closeness between the Pd crystallites and the Ga_2O_3 surface patches boost the activity, owing to a minimized effort in the H_s supply to the latter.

KEY WORDS: hydrogen spillover; methanol synthesis; CO_2 hydrogenation; gallia-promoted palladium.

1. Introduction

The recognition that CO_2 hydrogenation to methanol is a promising approach to the recycling of carbon dioxide as a response to global warming has prompted the interest to develop more active and selective catalysts for this reaction. In this context, supported precious metals such as palladium have been under particular scrutiny during the last decade [1], as it is well known that both the support and the (eventual use of a) promoter can appreciably modify the activity and/or the selectivity of this metal in methanol synthesis [2–4].

Among other novel candidates, gallia has emerged as an exceptional material for achieving effective conversion of carbon dioxide to methanol, either as bulk support [4,5] or promoter [6] of finely dispersed palladium. 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.* [4]: Using a stoichiometric H_2/CO_2 mixture (523 K, 5 MPa), their Pd/Ga_2O_3 preparations were 120-fold more active than Pd on SiO_2 (an inert support) and 7-fold more active than $Cu/ZnO/Al_2O_3$ [4,5]. The other reaction product was CO (selectivity close to 49%), which was obtained via the reverse water gas shift reaction over the metallic particles. Later on, Bonivardi *et al.* showed that gallium oxide addition to Pd/SiO_2 catalysts produced an equally dramatic enhancement of the catalytic performance to give oxygenated compounds from the hydrogenation of carbon dioxide [6]. It was then hypothesized that these gallia-promoted Pd/SiO_2 catalysts were excellent materials for methanol synthesis from CO_2/H_2 as a consequence of the formation of formate surface species on Ga_2O_3, which could later hydrogenate *via* the participation of Pd^0 as the main source of atomic hydrogen, H_s [7].

Iwasa and co-workers [8,9] claimed that the remarkable activity and selectivity achieved by Pd/Ga_2O_3 catalysts, either in the methanol synthesis or in the steam reforming of methanol, was as a consequence of the new metallic catalytic functions formed by Pd–Ga alloy. On our gallia-promoted Pd/SiO_2 catalysts, though, only Ga suboxides (but no Pd–Ga alloys—as detected by XRD-) were formed upon H_2 reduction at low temperature [7].

The promoting effect of metal oxides on the activity and selectivity of supported Pd^0 is usually attributed to the close intimacy between both components. Yet, the alternative concept of the remote control developed by Delmon and his school [10,11], where Pd^0 acts as the provider of atomic hydrogen via spillover, is also feasible on these systems, which therefore could actually be considered true bifunctional catalysts.

To face this issue we have studied the synthesis of methanol by means of mechanical mixtures of the active components, separately supported on silica, comparing their catalytic performance with that of the promoted catalysts, in which said intimacy was achieved [6]. Thus, it was possible to demonstrate that indeed H_s can be generated by Pd^0 far from Ga_2O_3 and move (spill-over) there to reach the other reactive species (i.e., formates) and complete the reaction cycle.

2. Experimental

Mechanical mixtures (MM) were prepared using different mass proportion of Pd/SiO_2 (2 wt% Pd) and

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Ga_2O_3/SiO_2 (9.2 wt% Ga). The support, a mesoporous SiO_2 Davison Grade 59 (W. R. Grace & Co.), was previously purified and calcined at 773 K (Specific surface = 301 $m^2\ g^{-1}$; average pore diameter = 160 Å; particle size < 170 μm −80 mesh-).

Pd/SiO_2 was obtained by ion exchange (IE) of palladium acetate (Sigma, 99.97%), at pH = 11 in $NH_4OH_{(aq)}$, onto the support. The exchanged material was washed at the same pH, and dried at 423 K. The resulting supported diammine palladium complex was calcined in air at 643 K for 2 h under flowing air (200 cm^3/min) in a glass reactor to obtain palladium oxide on the SiO_2 surface. The Pd metal dispersion of the reduced catalyst, measured by CO dynamic-pulse-chemisorption, was equal to 58%. The mean diameter of the Pd crystallites, determined by TEM, was 14 Å.

$Ga(NO_3)_3 \times H_2O$ (Strem Chemicals, 99.99% Ga), in aqueous solution, was added by incipient wetness impregnation to the SiO_2 support at 3 Torr N_2 (1 Torr = 133.3 Pa) and ambient temperature, in a rotary evaporator. Subsequently, the solid was frozen in liquid nitrogen and water was removed by sublimation at 3 Torr of N_2 to give a dry *precursor*. The resulting precursor was then calcined in flowing air (200 cm^3/min), by heating from 298 to 673 K (2 h) at 2 K/min, to obtain gallium oxide on the SiO_2 surface.

Each powder was ground (<5 μm) to maximize contact between the solid particles. To homogenize the MM, they were suspended in *n*-pentane (10 ml/g of solid), and stirred, with further evaporation of the solvent at RT. The powders were then pelletized, carefully crushed and sieved to return to the original particle size of the silica support (table 1).

2.1. Promoted catalysts (PR)

To compare the MM with equivalent Ga-promoted Pd/SiO_2 catalysts, a set of the latter was prepared to obtain the desired matching Ga/Pd ratios (table 1). Different amounts of $Ga(NO_3)_3$ in aqueous solution were added by incipient wetness impregnation to the $[Pd(NH_3)_2]^{2+}/SiO_2$ precursor prepared as before (i.e., dried at 423 K), at 3 Torr N_2 and ambient temperature in a rotary evaporator. The resulting materials were then calcined in flowing air (200 cm^3/min) by heating from 298 to 673 K (2 h) at 2 K/min, to jointly obtain palladium and gallium oxides on the SiO_2 surface.

2.2. Catalytic activity

500 mg of each catalysts were loaded into a copper-plated, tubular differential microreactor, operated under standardized plug-flow conditions ($H_2/CO_2 = 3$; $P = 3.0$ MPa; $T = 523$ K; SV = 7800 h^{-1}). The catalysts were pretreated by reducing *in-situ* with H_2(5%)/Ar from 298 to 723 K (at 2 K/min), holding then 2 h at 723 K and later cooling to 523 K. Prior to reaction, pure H_2 was flowed for 1 h. The reaction products (CO, CH_3OH, DME, H_2O and traces of CH_4 and CH_3OOCH_3) were analyzed by gas chromatography (Porapak-QS 80/100 mesh, TCD and FID).

2.3. FT–IR Studies

In situ transmission infrared spectroscopy was performed using 10 mg samples of the materials, which were pressed into self-supported wafers (dia. = 13 mm) at 5 ton/cm^2. The wafers were located in turn into a Pyrex cell with water-cooled NaCl windows, which was attached to a conventional high vacuum system (base pressure = 1.33×10^{-4} Pa) equipped with a manifold for gas flow. The cell could be heated up to 723 K, using a PID controller. The pretreatments and IR measurements on the materials were performed *in situ* at 0.1 MPa, except during evacuation.

Table 1

Catalysts synthesized (mechanical mixtures and promoted materials)

Catalyst Code	ϕ^a	Pd^b (wt%)	Ga^c (wt%)	Ga/Pd^d (at/at)	Pd_s^e ($m^2\ g^{-1}_{cat}$)	$(Ga_2O_3)_s^f$ ($m^2\ g^{-1}_{cat}$)	$(Ga_2O_3)_s/Pd_s^g$ (m^2/m^2)
Pd20Ga00	100	2.0	0.0	0	5.2	–	0
Pd18Ga09 MM	90	1.8	0.9	0.75	4.7	0.9	0.2
Pd15Ga23 MM	75	1.5	2.3	2.3	3.9	2.2	0.6
Pd10Ga46 MM	50	1.0	4.6	7.0	2.6	4.4	1.7
Pd05Ga69 MM	25	0.5	6.9	21	1.3	6.7	5.2
Pd00Ga92	0	0.0	9.2	–	–	8.9	–
Pd00Ga49	0	0.0	4.9	–	–	4.5	–
Pd20Ga26 PR	–	2.0	2.6	2.0	4.0	2.2	0.5
Pd20Ga49 PR	–	2.0	4.9	3.7	1.1	4.5	4.1
Pd20Ga92 PR	–	2.0	9.2	7.0	0.5	8.9	18.0

[a] Percent mass fraction of Pd/SiO_2 [2 wt% Pd] in the mechanical mixture (MM).

[b] g Pd/g catalyst

[c] g Ga/g catalyst (Determined by Atomic Absorption).

[d] Gallium-to-palladium atomic ratio in the catalyst.

[e] Estimated from the exposed metal fraction (Determined by pulse CO chemisorption [7]).

[f] Estimated from infrared data (Ga–H stretching band) of H_2 chemisorption on gallia [7,12].

[g] Surface ratio between Ga_2O_3 and Pd in the catalysts.

Before any experiments were performed, each sample was exposed to the following pretreatment procedure: First, O_2 was admitted into the cell (100 cm^3/min) and then the temperature was raised from 298 to 723 K (at 5 K/min) and immediately lowered to 323 K, under vacuum. Next, the cell was heated to 723 K at 5 K/min under H_2 (100 cm^3/min). After 30 min at this last condition the cell was evacuated for 20 min, still at 723 K. Finally, the temperature was gradually decreased, under vacuum, to allow for reference IR spectra of the 'clean wafers' to be taken.

Temperature programmed reaction experiments (TPR) were performed over some of the pretreated samples (Pd00Ga49, Pd20Ga26 PR, Pd20Ga49 PR and Pd10Ga46 MM in table 1), as follows: (i) the reacting H_2/CO_2 mixture ($H_2/CO_2 = 3/1$, 140 cm^3/min, 0.1 MPa) was flowed through the cell for 15 min, at RT; (ii) the infrared cell was then heated to 723 K, at 3 K/min.

Infrared transmission spectra were acquired with a Shimadzu 8210 FT-IR spectrometer using a DLATGS detector (4 cm^{-1} resolution, 100 scans). Further processing of the spectra was carried out with the Microcal Origin® 4.1 software. Background correction of the spectra was achieved by subtracting the spectra of the 'clean wafers' at each temperature; a Lorentzian sum function was used for fitting the overlapped bands, measuring peak areas and/or intensities.

3. Results and discussion

To help in rationalizing the role of each active component in the catalytic performance of these catalysts, we firstly estimated the palladium and gallia surface dispersions on the materials. The exposed metal fraction (FE) of palladium on the Pd(2%)/SiO_2 powder used to make the MM, calculated by pulse CO chemisorption (labeled as Pd20Ga00 in table 1) was 58%. A monotonic decrease of the FE was found in the promoted materials as the gallium loading (that is, the Ga to Pd atomic ratio) was increased: Pd20Ga26 PR = 45%; Pd20Ga49 PR = 12%; Pd20Ga92 PR = 6%. However, the average diameter of the Pd crystallites, measured by TEM, was always in the range of 14–18 Å [7]. This fact has already been previously discussed by some of us in a previous work, where it was shown by XPS that, after exposing the catalysts to H_2 at 523 K almost 30% of the gallia was reduced to Ga^{δ} ($\delta \sim 1$), and it was put forward that most likely some of the Pd metal particles became covered by 'patches' of Ga_2O_x (i.e., containing reduced gallium species,) in intimate contact—thence–with the palladium crystallites [7]. Further work using EXAFS confirmed this picture [13].

To estimate the surface dispersion of gallium oxide we have used experimental data of the H_2 chemisorption on gallia, obtained by in situ FTIR. We recently reported that H_2 adsorbs dissociatively on the different crystallographic phases of pure gallium oxides, giving Ga–H surface species with an infrared stretching mode around 2000 cm^{-1}. The IR intensity of this signal was found to be proportional to the specific surface of gallia [13]. We have also shown, by combined use of FTIR and XPS, that on Ga–Pd/SiO_2 and Ga/SiO_2 catalysts the concentration of $Ga^{\delta+}$ sites is proportional to the percent weight loading of gallia [7]. Thus, the estimated surface amount of gallia—using the IR absorbance of the Ga–H bond stretching frequency—of the Ga_2O_3/SiO_2 (9.2 wt% Ga) powder employed to make MM samples was found to be 8.9 $m^2\ g^{-1}{}_{cat}$ (table 1).

Table 2 shows the activity and the selectivity to CH_3OH for the whole set of catalysts. It can readily be appreciated that these values are much higher than on Pd/SiO_2, both in the promoted materials and in the mechanical mixtures. The blank sample of Ga_2O_3/SiO_2 (9.2 wt% Ga) only produced traces of dimethylether.

A closer inspection of the data shows that the R_{MetOH} is maximal in the MM with $\phi = 50\%$ but, also, that the selectivity to DME increases monotonically the higher the amount of Ga is. However, the promoted catalysts always exceed the performance of the mechanical mixtures.

The activity results of the MMs show that it is necessary to provide an optimal proportion of both

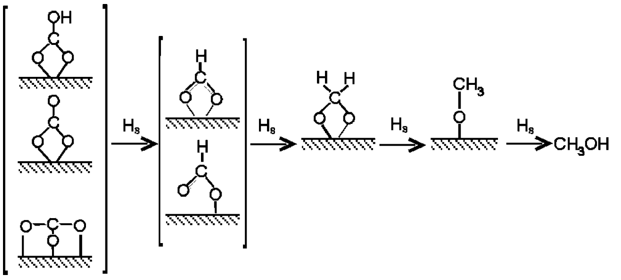
Table 2
Reactivity and selectivities to products ($H_2/CO_2 = 3$; $P = 3$ MPa, $T = 523$ K; SV = 7800 h^{-1})

Catalyst Code	$R_i \times 10^8$ (mole g_{cat}^{-1} s^{-1})			Selectivity (%)[a]		
	CH_3OH	CO	DME	CH_3OH	CO	DME
Pd20Ga00	24.1	63.7	0.02	27.3	72.3	0.04
Pd18Ga09 MM	39.8	46.9	1.18	44.5	52.5	2.4
Pd15Ga23 MM	60.4	81.1	1.8	41.3	55.4	2.5
Pd10Ga46 MM	63.2	76.4	3.4	42.9	51.7	4.6
Pd05Ga69 MM	26.9	55.4	2.9	30.3	62.3	6.6
Pd00Ga92	0	0	0.2	0.0	0.0	100
Pd00Ga49	0	0	$\asymp 0$	0.0	0.0	100
Pd20Ga26 PR	221	89	2.4	70.0	28.2	1.5
Pd20Ga49 PR	167	67	3.7	68.9	27.6	3.1
Pd20Ga92 PR	127	85	4.5	57.2	38.3	4.1

[a] Balance is closed with traces of methane and methyl formate.

components (Pd and Ga_2O_3) to maximize the production of methanol. These results are congruent with our infrared data: By means of TPR-IR (H_2/CO_2) experiments on Pd/β-Ga_2O_3 and β-Ga_2O_3, we have shown the following reaction pathway for the CO_2 hydrogenation on the gallia surface: where carbon dioxide chemisorbs to form carbonate species, which are hydrogenated stepwise to formates (mono and bidentate), methylene-bisoxy, methoxy and—finally—methanol [14]. This entire process can occur on the support alone (via the H_2 dissociative adsorption on gallia [7]), but is greatly accelerated in the presence of Pd metal, since it easily provides H_s *via* a spillover mechanism. In this reaction pathway, formate ($HCOO_s$) species bounded to gallium sites are, as shown in the following paragraphs, the key intermediate in the methanol synthesis. Hence, to further investigate the methanol synthesis reaction on the mechanical mixtures and promoted catalysts, we have now performed temperature programmed reaction experiments ($H_2/CO_2 = 3$), following the HCOO surface concentration by *in situ* FTIR.

At this time it is worth mentioning that methanol synthesis from carbon dioxide over the clean Pd/SiO_2 catalyst occurs through a different mechanism, which involves the formation of CO [through the reverse water gas shift reaction (RWGS)] and its subsequent hydrogenation [15]. A distinctive character of the latter reaction is the higher apparent activation energy of 60 kJ mol^{-1}, versus 38 kJ mol^{-1} in gallium-promoted materials [6]. Accordingly, no formate species were detected by FTIR on the unpromoted material.



Scheme 1.

The evolution of the formate IR intensity [$\nu_{as}(COO) = 1592$ cm^{-1}] as a function of the temperature of reaction for some of the selected catalysts is plotted in figure 1; the characteristic IR spectra, at T_{max}, are shown in figure 2. The onset of the formate signal in the reference material, without Pd (Pd00Ga49), is around 450 K, a temperature above which H_2 begins to dissociate on $Ga^{\delta+}$ sites [7]; the highest formate concentration is reached at 600 K. However, in the presence of palladium the highest concentration of formate is shifted down by more than 100 K for both the promoted (Pd20Ga49 PR) and mechanical mixture (Pd10Ga46 MM) catalysts with the same loading of Ga. In addition, on the promoted sample a concentration of HCOO higher than on the MM counterpart is observed, even though their Ga superficial concentrations are identical (table 1). Finally, the more active catalyst of the set (Pd20Ga26 PR, table 2) shows the lowest onset temperature for formate formation and, also, the lower temperature for the concentration maximum. No new signals were observed by FTIR regardless of the type of catalytic system used (viz., MM or PR samples).

The infrared evidence clearly shows that: (i) the key carbonaceous intermediate is the same, whether or not Pd is present on the catalyst; (ii) the closer the two active phases are, the better the catalytic performance result (i.e., supported materials are more efficient than physical admixtures).

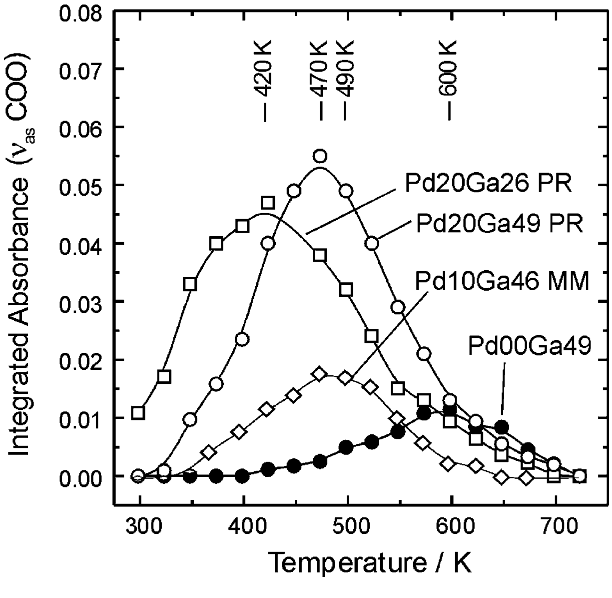


Figure 1. Evidence of formate formation by in situ FTIR [$\nu_{as}(COO) = 1592$ cm^{-1}] in temperature-programmed reaction experiments ($H_2/CO_2 = 3/1$; 140 cm^3/min; 0.1 MPa).

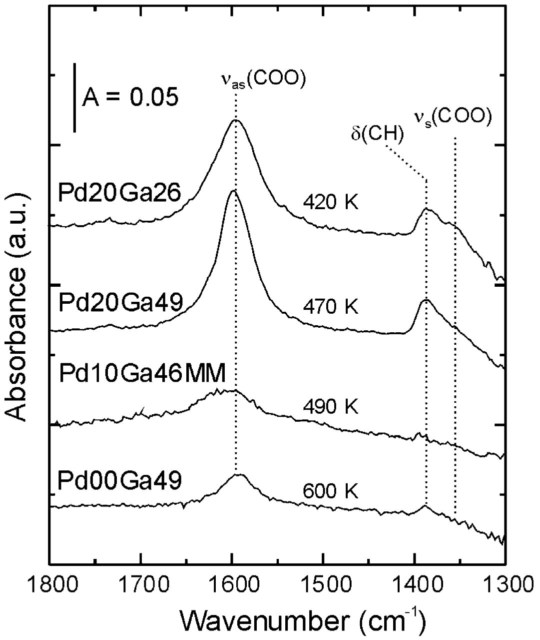


Figure 2. Infrared spectra of the formate species, at the temperature of their highest superficial concentration, T_{max}, during the TPR experiments ($H_2/CO_2 = 3/1$; 140 cm^3/min; 0.1 MPa).

Yet, the reaction data suggest that, in order to maximize the catalysts' performance it is necessary to provide an optimal proportion of *both* components (Pd and Ga_2O_3) on the surface. Figure 3a presents the activity of each catalyst type as a function of the available specific surface area of palladium on the solid. The shapes of the 'tendency lines' for both, the PR and MM catalysts, are very similar and they reach a maximum at ca. 3.0 m^2 Pd$_s$ g$^{-1}_{cat}$.

In the case of the mechanical mixtures, this finding is entirely consistent with a classical 'spill-over' situation, as dissociated hydrogen (H_s) spilt-over from the Pd/SiO_2 grains can only reach the Ga_2O_3/silica grains in the powdered catalyst composite via the intergranular contact (which is optimum when $\phi = 50\%$). If the amount of Pd/SiO_2 is smaller, the metal cannot keep equilibrated the formate/H_2 ratio, which leads to less CH_3OH and more DME. In accordance, a higher selectivity towards CO (RWGS) is observed in the MMs when the Pd/Ga ratio is too low, as a consequence of the diminished hydrogenating capability of the system. Too much Pd/SiO_2 in the mechanical mixture is equally deleterious, though: not only the intergranular contact area becomes smaller but, also, the amount of active Ga_2O_3/SiO_2 phase is also insufficient for achieving a good specific activity.

In the case of the PR catalysts, where the Pd is always 'decorated' or very close to Ga_2O_3, the R_{CH_3OH} and S_{CH_3OH} are higher the higher is the Pd *surface* loading, Pd$_s$. This trend, however, is only sustainable as long as sufficient gallia is available: in a supplementary experiment, additional preparations of two promoted Ga_2O_3–Pd/SiO_2 catalysts were made, with lower Ga/Pd ratios: 1.0 and 0.5. Under identical operating conditions, their catalytic activity was 61 and 45 mole$_{MetOH}$ g$_{cat}^{-1}$ s^{-1}, respectively.

In comparison with the MM it is also apparent that, for similar $(Ga_2O_3)_s/Pd_s$ ratios, the selectivities to by-products of the promoted catalytic materials (S_{DME} and S_{CO}) are always lower, which emphasizes the beneficial role of the metal-promoter intimacy, which the MMs do not provide. As already stated, a higher R_{MetOH} in the

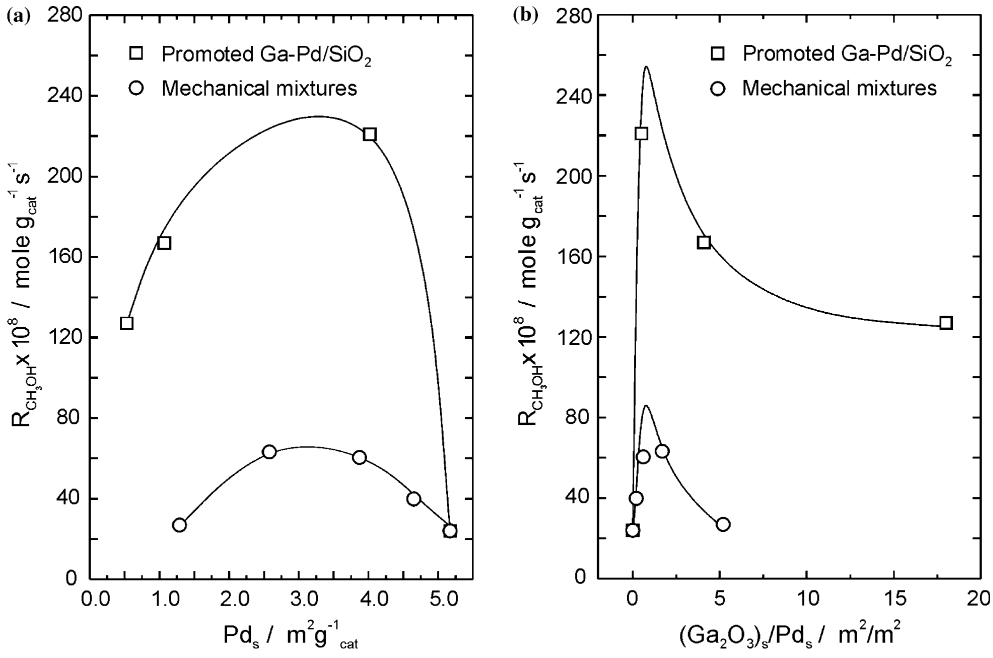


Figure 3. Comparative catalytic performance of the mechanical mixtures (MM) and promoted (PR) gallia–Pd/silica catalysts ($H_2/CO_2 = 3$; $P = 3.0$ MPa; $T = 523$ K; SV = 7800 h^{-1}): (a) As a function of the available surface area of Pd; (b) as a function of the surface ratio of Ga_2O_3 to Pd.

PR catalysts with respect to the MM ones can be directly related to the higher HCOO-Ga superficial concentration as seen by FTIR.

Since the metallic and active oxide functions on the catalyst seem to 'need to be balanced', we plot the catalytic activity of both series of materials as a function of the Ga-to-Pd *surface* ratio, $(Ga_2O_3)_s/Pd_s$ (figure 3b). Again, the shapes of the curves for the PR and MM catalysts are almost identical, and a peak in the R_{MetOH} is reached when $(Ga_2O_3)_s/Pd_s = 1.3$. This result indicate that (as also evidenced by the FTIR spectra) the Ga_2O_3–Pd/SiO_2 catalyst works as a true bi-functional system. The metal-promoter intimacy is not decisive in terms of the catalytic chemistry of the system, but certainly the closeness between the Pd crystallites and the 'Ga_2O_x surface patches' boosts the activity, owing to an improved supply of H_s to the latter and, in doing so, also improves the selectivity towards methanol versus DME.

4. Conclusions

By means of mechanical mixtures of the active components, separately supported on silica, it was possible to study and demonstrate that dissociated hydrogen, H_s, can be generated by Pd^0 far from Ga_2O_3 and move (spillover) there, to reach the other reactive species (formates) and complete the reaction cycle. The successful promotion by gallia on the Pd/silica catalysts seems to be due to the complementary impact of: (a) closeness of the Ga_2O_3–Pd functions and (b) H-spillover onto the silica support. The observed activity and selectivity are the result of the balance between both effects.

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