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# Enhancement of the catalytic performance to methanol synthesis from $CO_2/H_2$ by gallium addition to palladium/silica catalysts

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The hydrogenation of $CO_2$ was investigated on Ga-promoted $Pd/SiO_2$ catalysts. A 500-fold turnover rate enhancement and an increase of the selectivity to methanol synthesis, up to 70%, were found under pseudo stationary state conditions (523 K and 3 MPa) using the promoted materials as compared to $Pd/SiO_2$. Based on apparent activation energy values and product distribution, a reaction pathway to $CH_3OH$ involving intermediates which are intrinsically associated to adsorbed $CO_2$ is proposed. It is concluded that the Ga-Pd interaction, proved through DRS and TPR experiments, brings the catalytic performance of these Ga-Pd/silica materials close to that of the traditional Cu/ZnO-based catalyst for methanol synthesis.

## 1. INTRODUCTION

The acceptance 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. To this purpose, both commercial and novel (poison-resistant) types, among which Pd based supported catalysts are gaining recognition, are now under scrutiny [1].

We have been investigating the promoting effect of calcium incorporation to supported palladium catalyst in the hydrogenation of CO and $CO_2$ [2]. Our strategy was to maximize the promoter-noble metal interaction. Using a $H_2/CO_2$ = 3/1 reaction mixture (523 K, 3 MPa), the catalysts where Ca was added to $Pd/SiO_2$ precursors ($[Pd(NH_3)_2]^{2+}/SiO_2$ ) showed turnover rates towards methanol up to 10-fold higher than that of the unpromoted palladium but only a modest increase of the methanol selectivity ($S_{CH3OH}$ ~15%) was observed for the promoted materials. Yet, CO hydrogenation to methanol was up to 40-fold faster over these promoted catalysts as compared to the palladium/silica catalyst ($S_{CH3OH}$ >98%).

Recently, Fujitani et al. [3] reported a significant effect of the support in the $CO_2$ hydrogenation when Pd was deposited over different metal oxides ($Al_2O_3$, $Cr_2O_3$,

ZnO, $Ga_2O_3$, $TiO_2$, $ZrO_2$) and silica. They found that Pd/$Ga_2O_3$ was the most active, with a $TOR_{MetOH}$ 20 times higher than that of their Cu/ZnO catalyst ($H_2/CO_2$ = 3, 523 K, 5 MPa), but no interpretation has been given so far.

Here, in order to contribute to the understanding of the impact of gallium promotion, we have designed an experimental program aimed to investigate the $CO_2$ hydrogenation reactions over a wide range of Ga to Pd atomic ratio (Ga/Pd = 0, 0.5, 1.0, 2.0, 4.0, y 8.0 at to at) using supported Pd on a pre-purified commercial silica.

## 2. EXPERIMENTAL

Catalysts samples were obtained via ion exchange of palladium acetate (Sigma, 99.97 % Pd) at pH=11 in $NH_4OH$(aq.) over a well-characterized silica gel (2% Pd w/w). The support, a mesoporous $SiO_2$ Davison Grade 59 (W. R. Grace & Co.), was previously crushed and sieved through an 80-mesh Tyler screen, purified, calcined at 773 K, and then characterized as described previously (specific surface = 301 $m^2\ g^{-1}$, average pore diameter = 160 Å, average particle diameter = 52 μm) [4].

After $[Pd(NH_3)_4]^{2+}$ was ion exchanged, the material was washed, dried and calcined in air (200 ml $min^{-1}$) at 423 K in a glass reactor. Then, different amounts of $Ga(NO_3)_3$ (Strem Chemicals, 99.99% Ga) in aqueous solution were added by incipient wetness impregnation to the $[Pd(NH_3)_2]^{2+}/SiO_2$ following our previous strategy of maximizing the promoter-palladium interaction [2]. Subsequently, water was removed by sublimation. Diffuse reflectance spectroscopy (DRS) and thermogravimetric analysis (TGA) were used to monitor the materials at the end of this last process. The resulting materials were then calcined in flowing air (200 ml $min^{-1}$) at 673 K (2 h) to obtain palladium and gallium oxides on the $SiO_2$ surface and, lastly, reduced in a 5%$H_2$/Ar mixture (200 ml $min^{-1}$) at 723 K (2 h) followed by passivating before storage. Blank samples of supported Ga oxide were also prepared.

Temperature-programmed reduction (TPR) experiments were carried out over the calcined precursors (5% $H_2$/He, 0.17 K $s^{-1}$) and specific surfaces ($S_g$, BET-$N_2$) of the reduced samples were measured.

Catalytic performance of these materials was evaluated at 3 MPa, 493-523 K, using $H_2/CO_2$ = 3/1 in a copper-plated plug flow microreactor under two different space velocities. The reaction products were analyzed by gas chromatography.

Palladium dispersion of the reduced catalysts was measured before and after reaction by CO pulse chemisorption. A JEOL 100 CX electron microscope operating in the bright field mode was employed to perform TEM characterization.

## 3. RESULTS AND DISCUSSION

### 3.1. Evidence of Gallium-Palladium interaction

After the addition of acidic Ga(III) aqueous solutions (1<pH<2) to the diamminepalladium(II) complex, the DRS spectra of impregnated materials showed at least two convoluted bands: One peak located at 300 nm and the other/s at

wavelength higher than 340 nm. The first one is consistent with the absorption band of nitrate anion observed in aqueous solution and on the untreated blank materials, i.e., $Ga(NO_3)_3$ on silica support. The UV-vis absorption peak at higher wavelength is assigned to adsorbed $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ complexes with $n \leq 2$ [4,5]. This band widened and its maximum shifted from 330 to 368 nm as the Ga to Pd atomic ratio (Ga/Pd) increased from 0.5 to 8.0 at to at, respectively, where the average value of $n$ is between 1 and 0 in the last case. Then, an exchange of ammine by water ligands of the Pd(II) coordination sphere due to an acid-base reaction, leading to ammonium nitrate and gallium hydroxide next to palladium cations, has occurred.

A decrease in the intensity of the aquoamminepalladium(II) complexes band while increasing Ga loading (Ga/Pd $\geq$ 1) was observed, which is difficult to explain at the moment. The absorption coefficients are approximately the same for these metal complexes [6]. Then, we could anticipate no significant variation of absorption peak intensity as the content of palladium was kept constant. However, the gallium(III) nitrate surplus remaining on the surface of the precursors might: i) increase the ionic strength of the environment of palladium(II) complexes, thus modifying their absorption coefficients, or ii) transform the scattering properties through small gallium nitrate *white* particles deposited onto the deamminated palladium ions. In either case, a change of the capacity of the complexes to absorb photons more efficiently would be expected [7].

TPR results of calcined gallium nitrate/silica showed two overlapped peaks, one at 583 K and the other at 627 K, with equivalent areas. Additionally, preliminary XPS experiment showed a partial reduction of Ga(III) to Ga(I), after in situ hydrogen treatment of silica supported gallia at 723 K [8]. Therefore, these temperature programmed reduction results plausibly indicate two consecutive reduction steps involving two redox reactions, each with the same amount of exchanged electrons, rather than an inhomogeneous or bimodal distribution of $Ga_2O_3$ particles.

Nevertheless, for the calcined promoted material ($Ga_2O_3$-PdO/$SiO_2$) only one reduction peak appeared in the TPR experiments at 388 K, next to the reduction temperature of the ultradispersed PdO/$SiO_2$ (380 K). After reducing the gallium-palladium calcined precursors at 423 K under static hydrogen, the presence of Ga(III) and Ga(I) was verified again by in situ X-ray photoelectron spectroscopy [8]. It follows that under the presence of palladium, hydrogen can partially reduced gallium(III) at a much lower temperature than in the case of gallia supported on $SiO_2$.

Different types of promoted reduction of gallium trioxide have been reported [9-12]. Carli and co-workers have shown that under the presence hydrogen at 723 K HZSM-5 could reduce 50% of the gallium trioxide loaded in the catalyst [9]. Similar results were obtained by Shpiro et al. on GaZSM-5 catalysts, but a noticeably promotion for the Ga (III) reduction to Ga(I) was observed after adding Pt to the last catalytic material [10]. A more extensive gallium reduction was reported by Iwasa et al. for massive Pd/$Ga_2O_3$ and Pt/$Ga_2O_3$ catalysts using X-ray diffraction. These authors were able to detect palladium-gallium and platinum-gallium alloys by reducing at 773 K the calcined metal nitrates deposited over gallium oxide [11].

It can be concluded, then, that in our catalysts palladium has a promoting effect over the reduction of Ga(III) cations adjacent to Pd. This finding together with the acid-base reaction between gallium nitrate and diamminepalladium(II) complexes, could be the result of our expected Pd-Ga interaction, which might explain new catalytic functions such as those reported vide infra, as well as for the steam reforming and the dehydrogenation of methanol on the Pd-Ga catalytic system [11].

### 3.2. Enhancement of the catalytic performance to methanol

Table 1 sums up representative results of Pd dispersion (CO chemisorption) and catalytic performance at t = 0 h as a function of the Ga content (523 K, 3 MPa, $H_2/CO_2 = 3$). The main products of the $CO_2$ hydrogenation were $CH_3OH$ and CO.

A remarkable enhancement of the catalytic activity towards methanol synthesis was obtained with every increase of gallium loaded on the catalysts. Thus, the PdGa-80 catalyst was approximately 240-fold more active than $Pd/SiO_2$ (PdGa-00) for similar low methanol conversions, where rates can be considered as *true* initial rates. As the pseudo stationary state (*pss*) was reached, this trend not only remained but also notoriously improved: the activity to methanol on promoted samples grew up more than 500-fold compared to unpromoted Pd. Besides, a major raise of the selectivity towards methanol (up to 70%, as opposed to the thermodynamic equilibrium value: ~ 50%) was achieved with PdGa-20 under *pss* and for the lowest

Table 1
Dispersion, catalytic performance and activation energy to methanol vs. Ga/Pd ratio

| Code | Ga/Pd (at/at) | $D_{CO}$[a] (%) | $X_{MetOH}$[b] (%) | Selectivities at t = 0h (%) | | | | | TOR[c] ($10^{-3}$ $s^{-1}$) | $E_{act}$[d] (kJ/mol) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $CH_4$ | CO | MetOH | DME | MF | | |
| PdGa-00 | 0.0 | 58 | 0.3[e] | 2.2 | 80.7 | 17.1 | 0.0 | 0.0 | 0.002 | 60 |
| PdGa-20 | 2.0 | 45 | 1.9[e] | 0.2 | 30.9 | 65.0 | 1.5 | 0.3 | 0.018 | - |
| | | | 0.7[f] | 0.2 | 37.2 | 62.0 | 0.8 | 0.6 | 0.048 | 39 |
| PdGa-40 | 4.0 | 12 | 1.8[e] | 0.1 | 33.4 | 59.4 | 2.8 | 0.2 | 0.067 | - |
| | | | 0.8[f] | 0.0 | 35.4 | 63.3 | 0.8 | 0.4 | 0.233 | 37 |
| | | | 0.7[f,g] | 0.1 | 43.9 | 53.7 | 1.6 | 0.5 | 0.179 | 38 |
| PdGa-80 | 8.0 | 6 | 1.6[e] | 0.1 | 45.8 | 47.9 | 4.3 | 0.4 | 0.111 | - |
| | | | 0.7[f] | 0.1 | 38.7 | 59.3 | 1.2 | 0.7 | 0.448 | 39 |

[a]Initial Pd dispersion, [b]Conversion at t = 0 h (equilibrium conversion = 10.6%),[c]TOR to MetOH at t = 0h, [d]Under *pss* conditions, [e]SV = 7800 $h^{-1}$, [f]SV = 78000 $h^{-1}$, [g]Average particle catalyst diameter = 5 μm.

space velocity employed (see Fig. 1a).

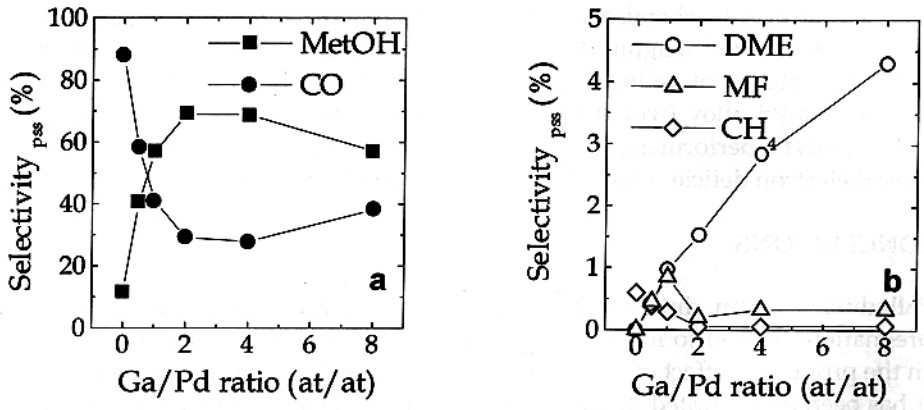


Fig. 1. Product distribution under *pss* vs. gallium content on promoted $Pd/SiO_2$ catalysts. Reaction conditions: 523 K, 3 MPa, $H_2/CO_2$= 3/1, SV= 7800 $h^{-1}$.

Apparent activation energy for methanol synthesis ($E_{act}$) are reported in Table 1. These values were measured under *pss* conditions and for methanol conversions lower than 7% of the equilibrium value, running experiments at different space velocities and average particle catalysts diameters. The $E_{act}$ is at least 20 kJ/mol lower for gallium-promoted materials than for palladium/silica which suggests the existence of two different rate determining steps, or independent pathways to methanol formation over Pd-Ga and Pd catalysts.

In a previous work using calcium-palladium/silica catalysts, we have proposed that methanol synthesis from a $H_2/CO_2$ mixture is produced through the CO formation and its consecutive hydrogenation, on the basis of product distribution and apparent activation energies values which were close to 65 kJ/mol [2]. This appears not to be the case when Pd is promoted with Ga. A mechanism involving carbonate to formate reaction intermediates from adsorbed $CO_2$, similar to those sustained for Cu/ZnO catalysts [13,14], plausibly accounts for the methanol production on our Pd-Ga system, since almost no methanol was synthesized when the reactor was fed with a $H_2/CO$ = 2.5/1 mixture (523 K and 3 MPa) over these gallium promoted $Pd/SiO_2$ materials.

The other products of the reaction were dimethyl ether (DME), and traces of methane as well as methyl formate (MF), as it is shown in Fig. 1b. A modest amount of DME which increased steadily with the Ga content in spite of the almost constant methanol production (mol $g_{cat}$ $s^{-1}$) was observed *only* on promoted materials. Bearing in mind that gallia has amphoteric properties and resembles alumina as a catalysts for the conversion of alcohols, the previous observation implies that DME is produced by methanol dehydration over the acidic sites of gallium oxide spots [15].

Another significant feature is the decrease in the metal dispersion as the Ga to Pd ratio goes up (Table 1). For PdGa-80 catalyst, the estimated average diameter of the Pd crystallites by CO chemisorption is 19 nm. Yet, the value measured by TEM is 2 nm, i.e. one order of magnitude lower. We believe that Pd metal particles, mostly covered by patches of reduced gallium species (probably $Ga_2O$), or by a small fraction of Ga-Pd alloy over the metal crystallite surfaces, are responsible for the singular catalytic performance of our Ga-Pd/$SiO_2$ catalysts rather than a previously proposed electron deficient palladium for a Pd/$Ga_2O_3$ catalyst [3].

## 4. CONCLUSIONS

Palladium-gallium interaction achieved by gallium(III) incipient wetness impregnation method to ion exchanged palladium(II) on silica, has become evident from the promoting effect of Pd on the surrounding gallium oxide reduction.

It has been demostrated that this Pd-Ga system is able to improve remarkably the performance toward methanol synthesis via carbon dioxide hydrogenation by increasing the specific activity and, also, by reversing the methanol to carbon monoxide selectivity. A reaction pathway involving the hydrogenation of intermediates originating directly from adsorbed $CO_2$ -as it is the case for Cu/ZnO catalyst, seems to account for this unusual catalytic behavior of Pd-Ga.

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