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Remarkable CO₂ hydrogenation to ethanol on Pd/Fe₃O₄ single-atom catalyst

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Abstract: CO₂ hydrogenation into value-added chemicals is one of the most investigated methods to reduce CO₂ emissions into the atmosphere and thereby contribute to a sustainable chemical industry. While the catalytic hydrogenation of CO₂ into methanol and synthetic hydrocarbons is well established, the effective and selective transformation of CO₂ into higher alcohols is still challenging. Here we show that Pd single atoms anchored on the surface of Fe₃O₄ are very active for the hydrogenation of CO₂ into ethanol at 300 °C, even at atmospheric pressure. By comparing various Pd/MO_x catalysts we conclude that the metal/oxide interface has a strong influence on the catalytic behavior.

The conversion of carbon dioxide by hydrogen not only mitigates its emission into the Earth's atmosphere but also produces commodity chemicals that can be used either as fuels or as precursors in many industrial chemical processes.^[1] The catalytic transformation of CO₂ is often carried out at elevated pressure and moderate temperature in the range of 200–400 °C. The CO₂ hydrogenation to CO through the reverse water gas shift (RWGS) reaction occurs on various precious metals (Pt, Pd, Rh and Au) and non-precious metals (Cu, Fe and Ni) supported on inorganic oxides.^[2] In addition to the classical Fischer-Tropsch (FT) process over Co- and Fe-based catalysts for the synthesis of long-chain hydrocarbons, the CO₂ hydrogenation to CH₄ (Sabatier reaction) is nowadays widely studied in the framework of the power-to-gas technologies to produce synthetic natural gas and it is usually performed on Ni, Ru and Rh catalysts supported on various oxides.^[2] Besides, the CO₂ hydrogenation to CH₃OH (methanol) has gained tremendous

interest in recent years and it is mainly performed on oxide-supported Cu, Pd and Au catalysts, being Cu/ZnO/Al₂O₃ the catalyst used in industry.^[3] However, limited success has been achieved in the selective CO₂ hydrogenation to ethanol and higher alcohols, which are preferable in many industrial processes. Additionally, ethanol holds potential as a hydrogen carrier in fuel cell technologies.^[4] The direct synthesis of ethanol and higher alcohols from CO₂ and H₂ in heterogeneous catalysis is usually regarded as a combination of the RWGS reaction and the subsequent reaction of syngas using a catalyst incorporating C-C coupling and CO hydrogenation functionalities.^[5] Therefore, catalysts combining FT synthesis and methanol synthesis capabilities have been investigated.^[6] Alternatively, supported catalysts based on Rh^[7] or Pt,^[8] as well as CoMoS,^[9] have also shown ability to convert syngas into ethanol. Recently, small Au nanoparticles supported on TiO₂ capable of activating simultaneously H₂ and CO₂,^[10] as well as bimetallic Pd-Cu nanoparticles supported on TiO₂ active for C-C coupling,^[11] have shown high selectivity toward ethanol in the hydrogenation of CO₂ in batch operation mode. Motivated by recent advances in single-atom catalysis (SAC),^[12] here we report on a Pd/Fe₃O₄ catalyst containing Pd single atoms which exhibits outstanding selectivity and yield toward ethanol in CO₂ hydrogenation under mild conditions.

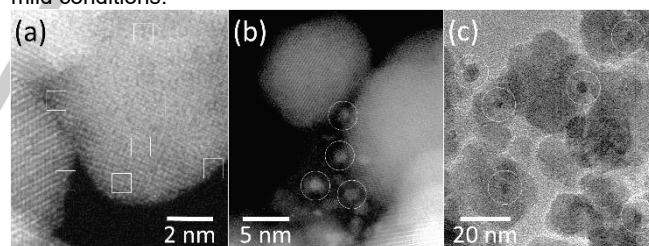


Figure 1. Representative aberration-corrected HAADF-STEM images of 0.1Pd/Fe₃O₄ showing Pd single atoms (a) and 0.4Pd/Fe₃O₄ showing Pd clusters of 1.2±0.2 nm (b). Representative TEM image of 3Pd/Fe₃O₄ containing Pd nanoparticles of 4.3±0.4 nm (c). Pd nanoparticles and single metal atoms are enclosed in circles and squares, respectively.

Three Pd/Fe₃O₄ catalysts were prepared containing 0.11, 0.38 and 3.0 wt% Pd as measured by inductively coupled plasma (ICP) spectroscopy. They are referred to as 0.1Pd/Fe₃O₄, 0.4Pd/Fe₃O₄ and 3Pd/Fe₃O₄, respectively. The different Pd loading values were selected according to ref.^[13] to obtain catalysts containing different Pd particle sizes. In particular, 0.1Pd/Fe₃O₄ contains exclusively Pd single atoms (Figure 1a and S1), 0.4Pd/Fe₃O₄ contains small Pd clusters of 1.2±0.2 nm (Figure 1b), and 3Pd/Fe₃O₄ contains Pd nanoparticles of 4.3±0.4 nm (Figure 1c).

The series of Pd/Fe₃O₄ samples was first investigated as prepared for the hydrogenation of CO₂ at 300–400 °C and

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Supporting information for this article is given via a link at the end of the document.

atmospheric pressure under dynamic conditions in a packed bed reactor with a feed gas composition of 10% CO₂ + 40% H₂ + 50% N₂ and a weight hourly space velocity (F/W) of 60 L g_{cat}⁻¹ h⁻¹. The conversion of CO₂, selectivity values of all the products present, and activity values normalized on the basis of Pd weight or on the basis of calculated Pd surface area are compiled in Table 1, entries 1-9. Remarkably, Pd/Fe₃O₄ catalysts showed, in addition to CO, an outstanding selectivity towards the formation of alcohols, particularly ethanol. For the 0.1Pd/Fe₃O₄ catalyst, the selectivity towards ethanol was 97.5% at 300 °C and the activity was 413 mmol_{EIOH} g_{Pd}⁻¹ h⁻¹ (entry 1). This result is among the highest catalytic activities ever reported for the synthesis of ethanol from CO₂ hydrogenation.^[10,11] At increasing temperature the selectivity towards ethanol decreased at the expense of CO, but propanol and traces of butanol were produced, in particular at 400 °C (entries 2 and 3). This was accompanied by an increase in CO₂ conversion. The high selectivity toward ethanol and the total absence of hydrocarbon production on 0.1Pd/Fe₃O₄ is remarkable. Taking into account that a blank run over the bare Fe₃O₄ support yielded only CO at high temperatures (entries 10-12), it is likely that the first step in the reaction is the transformation of CO₂ into CO over the Fe₃O₄ support through the RWGS reaction, and then Pd assists in the C-C coupling. This scheme is reinforced by the fact that higher partial pressures of CO at high temperature favour the formation of propanol, possibly through a CO insertion-type mechanism.^[7c] This reaction mechanism was supported by studying the CO hydrogenation over 0.1Pd/Fe₃O₄ under the same reaction conditions (Table 2). The catalyst was 100 % selective to ethanol at 300 °C (entry 1) and at higher temperatures the yield toward propanol (accompanied by traces of butanol) increased progressively (entries 2-3). Moreover, at high temperature ethane was also formed. The capacity of the

catalyst for C-C coupling merits to be highlighted since no methane or methanol were observed in any case.

The selectivity values of the catalysts with higher Pd loading, 0.4Pd/Fe₃O₄ and 3Pd/Fe₃O₄, were similar to that of 0.1Pd/Fe₃O₄ at high temperatures (350 and 400 °C), except that CH₄ was also formed over 3Pd/Fe₃O₄ at 400 °C. Also, the CO₂ conversion was higher at increasing Pd loading (entries 5-6 and 8-9). However, at 300 °C both samples exhibited a poor selectivity toward ethanol, with activities of only 51 and 6 mmol_{EIOH} g_{Pd}⁻¹ h⁻¹ (entries 4 and 7). The difference in ethanol yield is even more pronounced on the basis of the calculated Pd surface area: 279, 17 and 2 mmol_{EIOH} m_{Pd}⁻² h⁻¹ for 0.1Pd/Fe₃O₄, 0.4Pd/Fe₃O₄ and 3Pd/Fe₃O₄, respectively. There is a clear relationship between ethanol yield and Pd particle size, which is directly correlated with the metal exposed; the smaller the Pd particle size the higher the ethanol yield, being the ethanol selectivity boosted by the presence of Pd single atoms.

Figure 2a shows the yield of products other than CO of 0.1Pd/Fe₃O₄ over time on stream at different temperatures. It is seen that the catalyst suffers deactivation, being the decay particularly severe at 400 °C. At this temperature, the drop in ethanol and propanol yields occurs simultaneously to the appearance of methane and ethane. To gain insight into the processes associated to the deactivation phenomenon, additional experiments were carried out and quenched at different conditions, as indicated in Figure 2a. The corresponding aberration-corrected HAADF-STEM images are reported in Figure 2b-d. The sample operating at 300 °C (Figure 2b) shows exclusively Pd single atoms, which reinforces the observation that these species are responsible for the selective formation of

Table 1. Initial catalytic performances of Pd/Fe₃O₄ catalysts at 1 bar, CO₂:H₂=1:4 (molar) and F/W=60 L g_{cat}⁻¹ h⁻¹.

#	catalyst	T (°C)	χ _{CO2} (%)	Selectivity (%)					mmol _{EIOH} ·g _{Pd} ⁻¹ ·h ⁻¹	mmol _{EIOH} ·m _{Pd} ⁻² ·h ⁻¹
				CO	CH ₄	MeOH	EtOH	PrOH		
1	0.1Pd/Fe ₃ O ₄	300	0.3	-	-	2.5	97.5	-	413	279
2		350	2.4	83.3	-	-	16.0	0.7	459	310
3		400	3.9	77.5	-	-	17.8	4.7	846	571
4	0.4Pd/Fe ₃ O ₄	300	1.0	84.9	-	-	13.9	1.1	51	17
5		350	2.8	81.1	-	-	14.6	4.2	144	47
6		400	5.6	97.4	-	-	1.3	1.3	26	9
7	3Pd/Fe ₃ O ₄	300	1.2	85.1	-	-	11.8	3.1	6	2
8		350	3.6	80.1	-	0.1	15.1	4.7	24	8
9		400	8.8	94.6	2.8	-	1.3	1.2	5	2
10	Fe ₃ O ₄	300	-	-	-	-	-	-	-	-
11		350	0.4	100	-	-	-	-	-	-
12		400	1.1	100	-	-	-	-	-	-

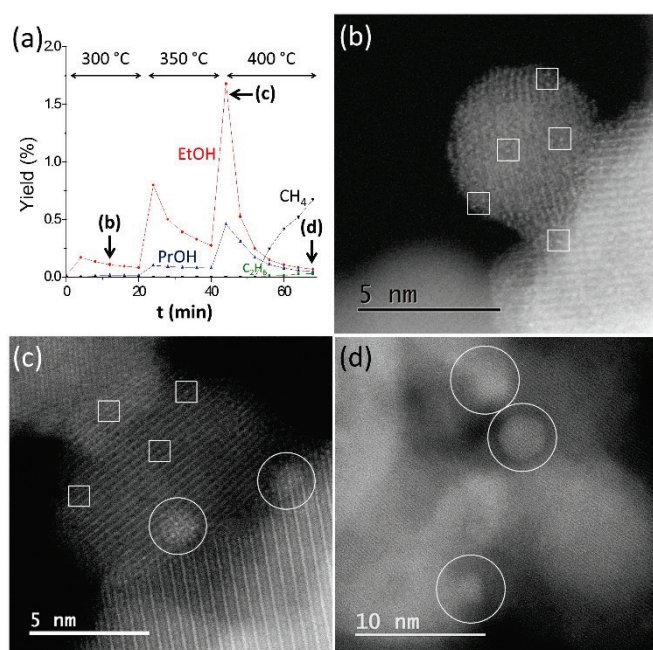


Figure 2. (a) Yield of products other than CO obtained on 0.1Pd/Fe₃O₄ over time on stream at 1 bar, CO₂:H₂=1:4 (molar) and F/W=60 L g_{cat}⁻¹ h⁻¹. (b-d) Representative aberration-corrected HAADF-STEM images recorded at different stages, as indicated in (a). Pd nanoparticles and single metal atoms are enclosed in circles and squares, respectively.

ethanol. The sample just reaching 400 °C (Figure 2c and S2) contains both Pd single atoms and Pd nanoparticles of about 1.1±0.3 nm. These Pd nanoparticles are likely produced at 300–350 °C and are responsible for the partial deactivation of the catalyst. In contrast, the sample deactivated strongly at 400 °C (Figure 2d and S3) only contains Pd nanoparticles of 2.2±1.2 nm; they are no longer selective to the production of alcohols and methanation is the main reaction occurring over this sample. These observations are also consistent with the fact that the ethanol selectivity recorded over 0.4Pd/Fe₃O₄ and 3Pd/Fe₃O₄ at 300 °C are much lower than that obtained over 0.1Pd/Fe₃O₄ (13.9 and 11.8 vs. 97.5 %, respectively; entries 4, 8 and 1 in Table 1), but similar at 350–400 °C (16.0 and 17.8 %, entries 2–3 in Table 1). Hence, the 0.1Pd/Fe₃O₄ catalyst suffers a progressive loss of ethanol selectivity due to agglomeration of Pd single atoms into small Pd nanoparticles at increasing reaction temperature, whereas 0.4Pd/Fe₃O₄ and 3Pd/Fe₃O₄ initially contain Pd nanoparticles and are less selective to ethanol at low temperature. Recently, the sintering of Pd atoms supported on a model Fe₃O₄ (001) surface under a CO atmosphere has been observed by STM.^[14] Taking into account that CO is an intermediate in the CO₂ hydrogenation on Pd/Fe₃O₄, the rapid deactivation observed could be related to the mobility of Pd atoms under a CO-rich atmosphere. As an additional proof of the role of Pd single atoms in the formation of ethanol, in a separate experiment the 0.1Pd/Fe₃O₄ catalyst was heated under N₂ at 400 °C to transform the Pd single atoms into nanoparticles (Figure S4) and then tested under the same

reaction conditions for CO₂ hydrogenation. The sample was inactive at 300 °C and at higher temperature the main product was CO, with only minor amounts of ethanol (selectivity of only 2.4–5.1% at 350–400 °C).

Table 2. Initial catalytic performance of 0.1Pd/Fe₃O₄ catalyst at 1 bar, CO:H₂=1:4 (molar) and F/W=60 L g_{cat}⁻¹ h⁻¹.

#	T (°C)	χ _{CO₂} (%)	Selectivity (%)				mmol _{EIOH} · g _{Pd} ⁻¹ h ⁻¹
			C ₂	MeOH	EtOH	PrOH	
1	300	0.2	-	-	100	-	244
2	350	0.4	12.6	-	79.3	8.1	379
3	400	1.5	9.6	-	71.5	18.9	1317

Since the selective hydrogenation of CO₂ into ethanol is favoured at low temperature over 0.1Pd/Fe₃O₄ and pressure has a positive effect on CO₂ hydrogenation reactions, this catalyst was tested at 250–300 °C and 3–30 bar total pressure with a stoichiometric CO₂:H₂ ratio for alcohol formation of 1:3 (Table 3). An increase of pressure resulted in higher CO₂ conversion rates and the maximum selectivity toward ethanol was obtained at 250 °C, being the highest ethanol activity 440 mmol_{EIOH} g_{Pd}⁻¹ h⁻¹ at 250 °C and 30 bar (entry 5). It is remarkable that under these conditions the only products of the reaction are ethanol (98.0 % selectivity) and methanol (2.0 % selectivity). The increase of temperature from 250 to 300 °C had a positive effect on CO₂ conversion and propanol selectivity at 3 and 30 bar, but the selectivity toward ethanol decreased considerably at the expense of CO (entries 4 and 6). A blank run was conducted over the bare Fe₃O₄ support at 3 bar and 250–300 °C, and no CO₂ transformation was recorded.

Table 3. Initial catalytic performance of 0.1Pd/Fe₃O₄ catalyst at 250–300 °C and 1–30 bar under CO₂:H₂=1:3 (molar) and F/W=60 L g_{cat}⁻¹ h⁻¹.

#	P (bar)	T (°C)	χ _{CO₂} (%)	Selectivity (%)				mmol _{EIOH} · g _{Pd} ⁻¹ h ⁻¹
				CO	MeOH	EtOH	PrOH	
1	1	250	0.1	-	17.4	82.6	-	101
2		300	0.3	-	2.6	97.4	-	413
3	3	250	0.3	-	20.4	79.6	-	291
4		300	0.8	71.0	2.1	25.5	1.4	235
5	30 ^[a]	250	1.4	-	2.0	98.0	-	440
6		300	2.9	46.8	5.0	46.1	2.1	429

[a] F/W=8 L g_{cat}⁻¹ h⁻¹.

The results reported so far demonstrate the potential of Pd single atoms supported on Fe₃O₄ for the selective hydrogenation of CO₂ to ethanol. But are Pd single atoms self-sufficient for the production of ethanol? We prepared a 0.1Pd/Al₂O₃ catalyst

containing Pd single atoms following the same procedure as for the preparation of 0.1Pd/Fe₃O₄ and tested it under the same reaction conditions. The results are reported in Table 4 and it is clearly seen that the sample is quite active in the transformation of CO₂ to CO but poorly selective to the formation of ethanol. Since bare Fe₃O₄ is active in the RWGS reaction, we can conclude that a particular interaction is established between Pd single atoms and Fe₃O₄ to construct specific active sites for C-C coupling, similarly to the specific architectures discussed in Fe₃O₄-based multifunctional catalysts for FT synthesis.^[15] This could be related to the abundant vacancies and interstitial sites observed in Fe₃O₄ in response to reducing environments.^[16] In a similar way, we also prepared 0.1Pd/ZrO₂ and 0.1Pd/CeO₂, which appeared inactive in the hydrogenation of CO₂, even at 30 bar.

Table 4. Initial catalytic performance of 0.1Pd/Al₂O₃ catalyst at 1 bar, CO₂:H₂=1:4 (molar) and F/W=60 L g_{cat}⁻¹ h⁻¹.

#	T (°C)	χ _{CO2} (%)	Selectivity (%)							mmol _{EtOH} · g _{Pd} ⁻¹ h ⁻¹
			CO	CH ₄	C ₂	MeOH	EtOH	PrOH		
1	300	2.3	92.9	-	-	-	4.2	3.0	117	
2	350	6.2	91.9	4.0	0.2	-	2.6	1.4	196	
3	400	12.2	91.2	7.9	0.1	-	0.5	0.4	77	

In this work, we have used for the first time single atoms dispersed over an inorganic oxide support to conduct the hydrogenation of CO₂ into value-added products. We have shown an outstanding selectivity toward ethanol and a high yield when the reaction is carried out over Pd single atoms anchored onto Fe₃O₄ at 250–300 °C. At higher temperature the Pd single atoms evolve progressively into Pd nanoparticles, which are poorly active in the formation of ethanol. By comparing with other inorganic oxide supports, a specific interaction between Pd single atoms and Fe₃O₄ exists, which originates a particular architecture for C-C coupling. These findings can make a significant contribution, not only to provide a new catalyst formulation for the production of ethanol, but also to add a new and important example of supported single-atom catalysis.

Experimental Section

Three Pd/Fe₃O₄ catalysts were prepared following the preparation method described in detail in the Supplementary Information. Briefly, magnetite nanoparticles were first functionalized with dopPPh₂ (N-(3,4-dihydroxyphenethyl)-4-(diphenylphosphino)benzamide) linker by sonication in methanol for 2 h. Then Pd was loaded from K₂[PdCl₄] to Fe₃O₄dopPPh₂ in water, followed by reduction with NaBH₄. The resulting nanoparticles were extracted with a magnet, washed thoroughly with water and acetone and dried under reduced pressure. The samples were characterized by ICP-OES, BET and Aberration-corrected HAADF-STEM. Catalytic tests at 1–30 bar total pressure were carried out in fixed bed reactors placed inside tube furnaces. A full description of the methodology is given in the Supporting Information.

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Keywords: carbon dioxide • heterogeneous catalysis • ethanol • palladium • single-atom catalysis

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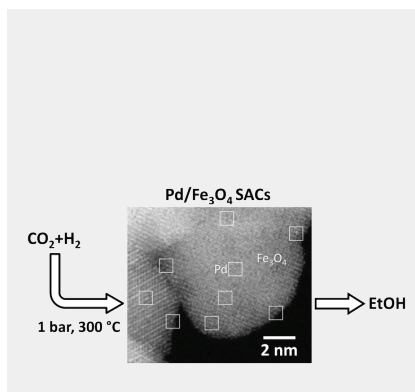
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Entry for the Table of Contents

COMMUNICATION

Pd single atoms anchored on the surface of Fe_3O_4 are very active for the hydrogenation of CO_2 into ethanol



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