

Synergetic Behavior of TiO_2 -Supported $\text{Pd}(z)\text{Pt}(1-z)$ Catalysts in the Green Synthesis of Methyl Formate

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Methyl formate (MF) is a valuable platform molecule, the industrial production of which is far from being green. In this contribution, TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts were found to be effective in the green synthesis of methyl formate (MF)—at $T = 323$ K and ambient pressure—through methanol (MeOH) oxidation. Two series of catalysts with similar bulk Pd/(Pd + Pt) molar ratios, z , were prepared; one by a water-in-oil microemulsion (MicE) method and the other by an incipient wetness impregnation (IWI). The MicE method led to more efficient catalysts owing to a weak influence of z on particle size

distributions and nanoparticles composition. $\text{Pd}(z)\text{Pt}(1-z)$ -MicE catalysts exhibited strong synergistic effects for MF production but weak synergistic effects for MeOH conversion. The catalytic performance of $\text{Pd}(z)\text{Pt}(1-z)$ -MicE was superior to that of $\text{Pd}(z)\text{Pt}(1-z)$ -IWI catalysts despite the latter displaying synergistic effects during the reaction. The catalytic behavior of TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts was explained from correlations between XRD, TEM, and X-ray photoelectron spectroscopy characterizations.

Introduction

Methyl formate (MF), an important chemical intermediate, is industrially produced by reacting liquid methanol (MeOH) with CO under high pressure, 2–4 MPa, and temperatures between 323–423 K over a potassium/sodium alkoxide catalyst.^[1–3] The efficiency of this process is rather poor. It requires recirculation of MeOH into the reaction system. In addition, the catalyst yields undesirable alkali methyl formates that tend to deposit on pipes and valves, thereby causing plant stops. Viable green

routes to produce MF, that is, at low temperature ($T < 473$ K) and atmospheric pressure, are the aerobic photocatalytic oxidation of MeOH^[4–6] and the aerobic gas-phase oxidation of MeOH over solid catalysts. Particularly, Kominami et al.^[4] reported a MF yield of 91 % at a MeOH conversion lower than 10 % for a TiO_2 photocatalyst working in flow mode. Other photocatalytic studies on the oxidation of MeOH to MF have been devoted to the establishment of a reaction mechanism.^[5,6] Concerning gas-phase oxidation, supported and unsupported MoO_3 , V_2O_5 , $\text{H}_{3+n}\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}$, RuO_2 , and PdO have been tested in the reaction.^[1,7–9] The challenge for an industrially green process is to operate the reaction at low temperatures and pressures while having high MeOH conversion but without sacrificing MF at the expense of the more thermodynamically favored CO_x . Except for noble-metal-based catalysts, the aforementioned oxides perform modestly in the reaction.^[1,7] The performance of noble metals has been related to their reducibility.^[8–11] Lichtenberger et al.^[9] showed that reduced palladium species perform better in the reaction than oxidized PdO. Wojcieszak et al.^[10–13] demonstrated that reduced palladium nanoparticles prepared by a microemulsion method (MicE) are promising catalysts for the green production of MF, that is, at ambient pressure and $T = 353$ K. This contribution concerns the green aerobic oxidation, at ambient pressure and $T = 323$ K, of MeOH to MF over TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts. This bimetallic system was selected to benefit from the probable synergetic effects coming from the individual properties of each metal in oxidation. On the one hand, platinum is known to be a very efficient catalyst in oxidation reactions, and, on the other hand, palladium has shown a high selectivity to MF.^[9–13] Several papers report on the synergy between Pd and Pt for diverse reactions such as the hydrogenation of aromat-

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ics^[14–19] and oxygenates,^[20–22] and the combustion of hydrocarbons.^[23] The bulk molar ratio between the metals is often critical for the catalytic performance. Therefore, the methodology adopted herein includes a study of the effect of the bulk Pd/(Pd + Pt) molar ratio (z) on the physicochemical and catalytic properties of two series of TiO₂-supported Pd(z)Pt(1– z) materials. The first series of catalysts was prepared by an incipient wetness (co-)impregnation (IWI method) and the second by the in situ reduction of metal precursors in a water-in-oil microemulsion (MicE method).^[10–13, 24, 25] Important differences between these two methods exist. The IWI method favors the formation of oxidized nanoparticles as it comprises a calcination step, whereas the MicE method leads to the direct deposition of reduced nanoparticles onto the support. Nanoparticles obtained by both methods were considered to serve as precursors for the catalytically active phase because the catalysts were always reduced under hydrogen flow before testing. In this manner, it was possible to determine what preparation is more convenient for a probable industrial application. Catalysts were characterized at different stages by inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), transmission electron microscopy–energy dispersive X-ray analysis (TEM-EDX in STEM or HRTEM modes), and X-ray photoelectron spectroscopy (XPS).

Results

Bulk metallic composition of the catalysts

Table S1 (in the Supporting Information) presents the bulk metal contents of the TiO₂-supported Pd(z)Pt(1– z) catalysts. The results show that the Pd and Pt contents of the catalysts prepared by the MicE method are closer to nominal values than those prepared by the IWI method. A maximum loss of 36% in the (Pd + Pt) loading of Pd(z)Pt(1– z)-IWI catalysts was observed for Pd(0.82)Pt(0.18)-IWI, whereas a loss of 5 wt.% was observed for Pd(0.65)Pt(0.35)-MicE.

Crystallinity of the catalysts

Table 1 summarizes the crystalline phases of palladium and platinum as identified by XRD as well as the average size of the detected crystallites (the XRD patterns are presented in the Supporting Information: Figures S1–S4).

For the TiO₂ support, the typical diffraction pattern (Figure S1) of a mixture of anatase and rutile was found, which was in agreement with a previous report.^[11] Concerning Pd(1.0)-IWI, the fresh catalyst, that is, only calcined, exhibited a diffraction peak at $2\theta = 33.85^\circ$ that corresponds to PdO(101). This was the only crystalline oxide phase identified within the whole series of analyzed materials. After reduction, the PdO(101) phase was not observed and, instead, a Pd(111) phase was detected. The size of the crystallites exhibiting this phase, 15 nm, was lower than that from the PdO(101) phase, 23 nm. For fresh Pt(1.0)-IWI, two crystalline phases, Pt(111) at 39.75° and Pt(200) at 46.18° , were identified. The crystallite size of these two phases was similar: 32 and 30 nm for Pt(111) and Pt(200), respectively. After re-

Table 1. Crystallinity of fresh and reduced Pd(z)Pt(1– z)/TiO₂ catalysts.^[a]

Catalyst	Crystallinity (XRD)			
	2θ	β	Size [nm]	Phase
<i>Fresh</i>				
Pd(1.0)-IWI	33.85	0.379	23	PdO(101)
Pd(0.82)Pt(0.18)-IWI	N.D.	–	–	–
Pd(0.65)Pt(0.35)-IWI	40.06	0.446	19	Pt(111) + Pd(111)*
	46.54	0.420	21	Pt(200) + Pd(200)*
Pd(0.48)Pt(0.52)-IWI	39.98	0.289	31	Pt(111) + Pd(111)*
	46.56	0.263	36	Pt(200) + Pd(200)*
Pt(1.0)-IWI	39.75	0.286	32	Pt(111)
	46.18	0.303	30	Pt(200)
Pd(1.0)-MicE	40.09	0.935	9	Pd(111)
Pd(0.81)Pt(0.19)-MicE	N.D.	–	–	–
Pd(0.65)Pt(0.35)-MicE	N.D.	–	–	–
Pd(0.44)Pt(0.56)-MicE	N.D.	–	–	–
Pt(1.0)-MicE	40.14	0.479	18	Pt(111)
<i>Reduced</i>				
Pd(1.0)-IWI	40.35	0.573	15	Pd(111)
Pd(0.82)Pt(0.18)-IWI	40.09	0.585	15	Pt(111) + Pd(111)*
Pd(0.65)Pt(0.35)-IWI	40.04	0.55	19	Pt(111) + Pd(111)*
Pd(0.48)Pt(0.52)-IWI	39.98	0.289	31	Pt(111) + Pd(111)*
	46.56	0.263	36	Pt(200) + Pd(200)*
Pt(1.0)-IWI	39.86	0.227	41	Pt(111)
Pd(1.0)-MicE	39.78	0.308	29	Pd(111)
Pd(0.81)Pt(0.19)-MicE	N.D.	–	–	–
Pd(0.65)Pt(0.35)-MicE	39.69	0.632	14	Pt(111) + Pd(111)*
Pd(0.44)Pt(0.56)-MicE	N.D.	–	–	–
Pt(1.0)-MicE	40.14	0.242	38	Pt(111)

[a] β = Full width at half maximum. N.D. = Not detected. *Ambiguous attribution.

duction, only the Pt(111) phase was detected, along with an increase in crystallite size. For Pd(z)Pt(1– z)-IWI diffraction peaks at angles close to those of fresh Pt(1.0)-IWI were identified. However, these peaks cannot be unambiguously ascribed to Pt(111) and Pt(200) as they are not sufficiently separated from the peaks of Pd(111) and Pd(200). Comparing the fresh and reduced samples, for Pd(0.82)Pt(0.18)-IWI a peak corresponding to Pt(111) + Pd(111) evolved after reduction, whereas for Pd(0.65)Pt(0.35)-IWI the peak ascribed to Pt(200) + Pd(200) was no longer observed. For Pd(0.48)Pt(0.52)-IWI, no changes in the XRD pattern were observed. These trends indicate an evolution of the metallic crystallites during reduction as a function of z . Considering that the Scherrer equation mostly provides information on the size of nanoparticles bigger than approximately 10 nm,^[11, 25] and supported by TEM measurements (see the next section), the detection of the Pt(111) + Pd(111) phase after reduction of Pd(0.82)Pt(0.18)-IWI can be ascribed to the growth of nanoparticles smaller than 10 nm. These trends indicate an evolution of the size of the metallic crystallites during reduction as a function of z .

Morphology and composition of the metallic phases of the catalysts

TEM measurements in HRTEM and STEM-EDX modes were performed on selected samples. First, fresh Pd(1.0)-IWI, Pd(1.0)-MicE, Pt(1.0)-IWI, Pt(1.0)-MicE, and spent Pd(1.0)-IWI and

Pt(1.0)-IWI were studied. Afterwards, samples of all spent Pd(z)Pt(1-z)-IWI and Pd(z)Pt(1-z)-MicE were analyzed. It must be mentioned that for Pd(z)Pt(1-z)-IWI, the amount of nanoparticles observed per grain of TiO₂ were observed, whereas a high concentration of small nanoparticles was also observed in a TiO₂ single grain.

Figure 1 shows selected images for fresh Pd(1.0)-IWI (Figure 1a), Pd(1.0)-MicE (Figure 1b), Pt(1.0)-IWI (Figure 1c), and Pt(1.0)-MicE (Figure 1d). Mostly, rounded particles were observed for fresh Pd(1.0)-IWI, Pd(1.0)-MicE, and Pt(1.0)-MicE, in which only a few edged particles were identified (Figure 1a, b, d, respectively). Fresh Pt(1.0)-IWI displayed a series of faceted and cornered particles with a polyhedral and tetrahedral geometry typical of sintered Pt supported catalysts (Figure 1c).^[32,33] Such particles are normally enclosed by (111) facets.^[33,34] Some of the platinum nanoparticles appeared rounded or exhibited a truncated tetrahedral or cubic-like shape (Figure 1c). These truncated particles normally comprise (200) facets.^[33]

In general, TEM results for the monometallic catalysts (Figure S5 in the Supporting Information) showed that the IW

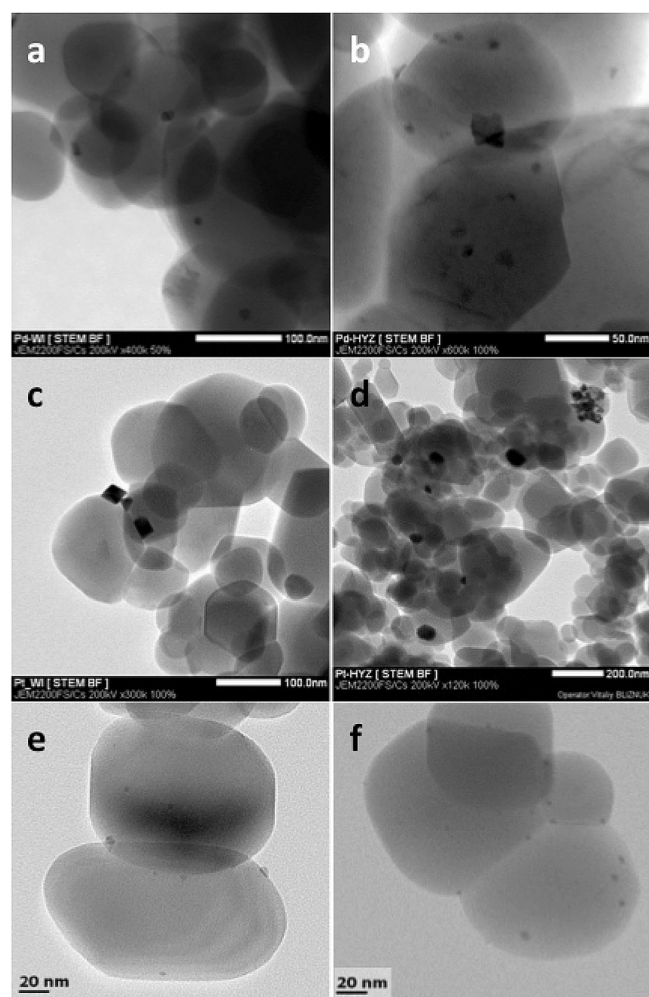


Figure 1. Selected TEM images of the fresh monometallic samples of TiO₂-supported Pd(z)Pt(1-z) as acquired in STEM mode.

method leads to highly heterogeneous particle size distributions (PSDs) with statistical coefficients of variation, CV, higher than 60 %. In contrast, the MicE method led to more homogeneous PSD with CV ≈ 35 %. Comparing fresh catalysts, the Pd catalysts displayed much lower average particle size ($\langle D_p \rangle$) than the Pt catalysts, regardless of the preparation method. Finally, spent monometallic catalysts prepared by the IW method displayed a decrease in $\langle D_p \rangle$ compared with the fresh catalysts.

Figure 2 presents TEM particle size distributions for the spent bimetallic catalysts. The trends in particle size distribution for spent Pd(z)Pt(1-z)-IWI and Pd(z)Pt(1-z)-MicE were different. Spent catalysts prepared with the IW method showed average $\langle D_p \rangle$ values smaller than the spent catalysts prepared with the MicE method. Moreover, PSDs for Pd(z)Pt(1-z)-IWI were skewed to D_p values lower than 11.8 nm. Furthermore, the IW method led to catalysts with more heterogeneous PSDs compared with the MicE method. This fact is evident from the high variability of the coefficients of variation in Figure 2a. It is apparent that PSDs for both groups of TiO₂-supported Pd(z)Pt(1-z) catalysts are affected by z. To be sure that

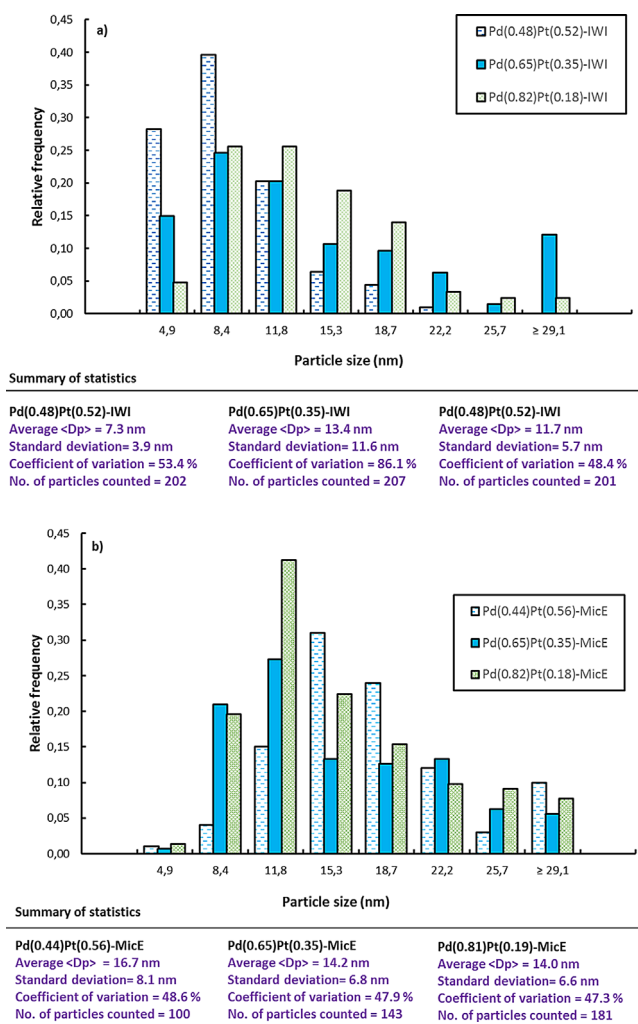


Figure 2. Particle size distributions for spent a) Pd(z)Pt(1-z)-IWI and b) Pd(z)Pt(1-z)-MicE catalysts and summary of statistics as derived from TEM measurements.

such an effect was statistically meaningful, we performed a single factor ANOVA test for both series of prepared catalysts. Results of this test showed a p -value = 9.97×10^{-15} for Pd(z)Pt(1-z)-IWI and a p -value = 7.12×10^{-3} for Pd(z)Pt(1-z)-MicE. These p -values allow us to ascertain that indeed PSDs depend on z to a confidence level of 95 %. On the other hand, by comparing both p -values, it can be said that the effect of z on PSDs is stronger for catalysts prepared with the IWl method.

Figures 3 and 4 show the statistical distribution of the molar Pd/(Pd+Pt) ratio of the metallic nanoparticles analyzed by HRTEM-EDX (z_{EDX}) for the spent Pd(z)Pt(1-z)-IWI and Pd(z)Pt(1-z)-MicE catalysts. Regardless of the bulk metallic molar ratio and the preparation method, a mixture of mono- and bimetallic nanoparticles was observed (HRTEM images enclosed in Figures 3 and 4). To determine if the bulk metallic molar ratio of the catalysts had a statistically meaningful effect on the composition of the nanoparticles, a single factor ANOVA test was also performed, in this case giving a confidence level of 95 %.

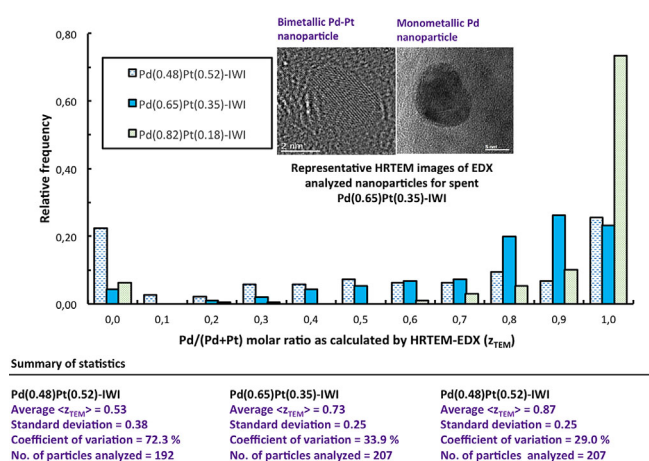


Figure 3. Distribution of the composition of metallic nanoparticles for spent TiO_2 -supported Pd(z)Pt(1-z)-IWI catalysts as calculated from HRTEM-EDX. Probe diameter = 0.5–1.0 nm.

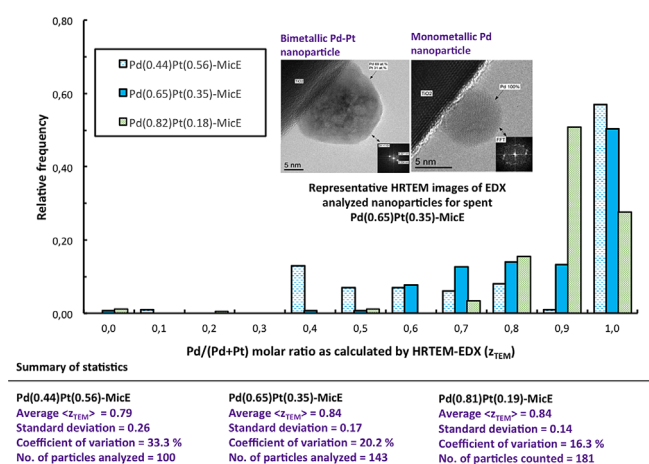


Figure 4. Distribution of the composition of metallic nanoparticles for spent TiO_2 -supported Pd(z)Pt(1-z)-MicE catalysts as calculated from HRTEM-EDX. Probe diameter = 0.5–1.0 nm.

For the spent Pd(z)Pt(1-z)-IWI catalysts, a p -value = 1.85×10^{-27} was obtained, which implies that the Pd/(Pd+Pt) molar ratio employed for catalyst preparation has a strong effect on the composition of the metallic nanoparticles formed on the catalysts. In the case of the MicE series of catalysts, a p -value = 2.7×10^{-3} was obtained. Such a value is very close to the α value of the ANOVA test ($\alpha = 0.05$), which implies that although the molar ratio of the metals used for preparing the catalysts has an effect on the final composition of its metallic nanoparticles, such an effect is rather weak. Therefore, although for the IWl method, z has a deep impact on the final composition of the metallic nanoparticles of the catalysts, this is not the case for the MicE preparation method.

On the other hand, it is important to notice that the MicE method led to a higher relative fraction of Pd-enriched nanoparticles, $z_{\text{TEM}} = 0.8$ –0.9, and monometallic Pd nanoparticles compared with the IWl method. In addition to the above observations, both the mono- and bimetallic nanoparticles belonging to spent Pd(0.65)Pt(0.35)-IWI (Figure 3) exhibited typical lattice fringes in the orientations (111) and (200). However, the nanoparticles belonging to spent Pd(0.65)Pt(0.35)-MicE showed lattice fringes only in the (111) orientation. In any case, the acquired HRTEM images did not show the existence of core-shell Pd–Pt bimetallic nanoparticles.

Composition and chemical state of the surface of the catalysts

The surface XPS composition for both the fresh and spent catalysts is presented in Table S2 (in the Supporting Information) in reference to the element/Ti molar ratios. The presence of several impurities belonging to the commercial TiO_2 support was unexpectedly revealed; namely, potassium, phosphorus, and calcium. Of these impurities, only potassium was not found on Pd(z)Pt(1-z)-MicE, whereas phosphorous and calcium remained at similar concentration levels for all of the catalysts.

Comparing the C/Ti ratios, two trends can be remarked upon: first, Pd(z)Pt(1-z)-MicE catalysts presented more surface carbon, which can be ascribed to carbonaceous residua from the preparation method; second, C/Ti ratios did not increase in the spent catalysts, which suggests that no coke deposition occurred during the catalytic tests.

XPS results showed that the relative concentration of palladium on the surface is higher than the relative concentration of platinum, regardless of the preparation method and whether the catalysts were fresh or spent. This is in good agreement with the TEM results mentioned earlier.

Table S3 (in the Supporting Information) presents the results obtained for the decomposition of the Pd3d core level for the prepared catalysts. The following general observations can be made: (i) regardless of the preparation method, there was always a combination of Pd^0 and $\text{Pd}^{\delta+}$ before and after the catalytic tests; (ii) the relative percentages of $\text{Pd}^{\delta+}$ or Pd^0 remained more or less constant with z ; (iii) Pd(z)Pt(1-z)-MicE catalysts clearly distinguished themselves from Pd(z)Pt(1-z)-IWI because a majority of Pd^0 species was always present on their

surface; (iv) a high fraction of palladium present in fresh Pd(z)Pt(1-z)-IWI was Pd^{δ+}, but almost 80% of palladium in spent Pd(z)Pt(1-z)-IWI was Pd⁰. This percentage was similar to the one determined for Pd(z)Pt(1-z)-MicE. Concerning platinum, Table S4 (in the Supporting Information) shows the identified binding energies (BE) for the Pt4f_{7/2} core level as well as the FWHM values of the peaks. The results allow us to ascertain that a high fraction of platinum was present in fresh Pd(z)Pt(1-z)-IWI as Pt^{δ+} and then further reduced to Pt⁰ during the catalytic tests. Conversely, in Pd(z)Pt(1-z)-MicE a higher fraction of platinum was always as Pt⁰.

Catalytic performance

As reported previously,^[11,13] the TiO₂ support was not active under the reaction conditions employed herein. Table 2 presents the results for the performance of the catalysts in the reaction.

Pd(z)Pt(1-z)-MicE displayed the best catalytic performance and bimetallic Pd(z)Pt(1-z)-MicE were always more effective in the reaction than the monometallic catalysts.

A maximum in MF selectivity, $S_{MF}=0.67$, was obtained for Pd(0.65)Pd(0.35)-MicE at $X_{MeOH}=0.78$. Pt(1.0)-MicE displayed the highest MeOH conversion for the series ($X_{MeOH}=0.87$), but with a S_{MF} value about three times lower, $S_{MF}=0.23$, than Pd(0.65)Pd(0.35)-MicE. Pd(1.0)-MicE displayed lower MeOH conversion ($X_{MeOH}=0.68$), but a slightly better S_{MF} value, $S_{MF}=0.29$, than Pt(1.0)-MicE. The best Pd(z)Pt(1-z)-IWI catalyst was Pd(0.65)Pd(0.35)-IWI. It is important to note that this is indeed the same z value as for the best catalyst in the reaction. The conversion for Pd(0.65)Pd(0.35)-IWI was $X_{MeOH}=0.56$ with a corresponding selectivity $S_{MF}=0.48$. Pt(1.0)-IWI displayed higher methanol conversion and selectivity, $X_{MeOH}=0.38$ and $S_{MF}=0.44$, than Pd(1.0)-IWI ($X_{MeOH}=0.16$, $S_{MF}=0.13$). One fact worth noticing is that Pd(1.0)-IWI produced much less MF than Pt(1.0)-IWI, whereas the contrary was true for Pd(1.0)-MicE. Finally, a comparison between the two series of catalysts leads to the general conclusion that the MicE method is of much more interest for a probable industrial application (STY_{MF} values in Table 1).

Table 2. Catalytic performance of TiO₂-supported Pd(z)Pt(1-z) catalysts in methanol partial oxidation.^[a]

Catalyst	X_{MeOH} [%]	Y_{MF} [%]	S_{MF} [%]	S_{CO_2} [%]	STY_{MF} [kg _{MF} × kg _{cat} ⁻¹ h ⁻¹]
Pd(1.0)-IWI	0.16	0.02	0.13	0.87	29.4
Pd(0.82)Pt(0.18)-IWI	0.29	0.08	0.28	0.72	117.6
Pd(0.65)Pt(0.35)-IWI	0.56	0.29	0.48	0.52	426.3
Pd(0.48)Pt(0.52)-IWI	0.32	0.06	0.19	0.81	88.2
Pt(1.0)-IWI	0.38	0.16	0.44	0.56	235.2
Pd(1.0)-MicE	0.68	0.25	0.29	0.71	367.5
Pd(0.81)Pt(0.19)-MicE	0.72	0.27	0.37	0.63	396.9
Pd(0.65)Pt(0.35)-MicE	0.78	0.52	0.67	0.33	764.4
Pd(0.44)Pt(0.56)-MicE	0.85	0.45	0.53	0.47	661.5
Pt(1.0)-MicE	0.87	0.20	0.23	0.77	294.0

[a] Conditions: $T=323$ K, ambient pressure, total feed flow = 100 cm³ min⁻¹ with 5 vol.% MeOH and 2.5 vol.% O₂.

Stability test

Considering the superior performance of Pd(0.65)Pd(0.35)-MicE in the reaction, a stability test was conducted for this catalyst. Figure 5 shows the evolution of the catalytic performance with time on stream. After 1800 min, the catalyst lost 7% of its initial MeOH conversion and 25% of its initial MF production. These results demonstrate that even though the catalyst does not rapidly deactivate, its selectivity can be affected in the long term.

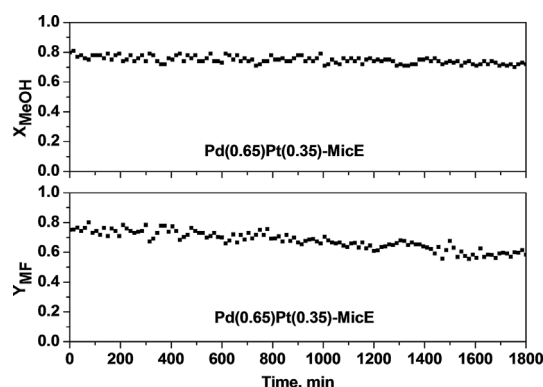


Figure 5. Evolution of the catalytic performance, methanol conversion, and methyl formate yield for Pd(0.65)Pt(0.35)-MicE during a stability test at 323 K, p_{atm} , 100 cm³ min⁻¹ of 5 vol.% MeOH and 2.5 vol.% of O₂ in He.

Discussion

Establishment of synergetic effects in TiO₂-supported Pd(z)Pt(1-z)

To establish the existence of synergetic effects between palladium and platinum, we prepared the plots presented in Figure 6 according to the definitions given in the Supporting Information. The figure shows the observed X_{MeOH} and yield of MF (Y_{MF}) by bulk mmol of (Pd + Pt) as a function of the corresponding calculated X_{MeOH} and Y_{MF} by bulk mmol of (Pd + Pt) for all of the TiO₂-supported Pd(z)Pt(1-z) catalysts. For the sake of clarity, a 45° line representing the absence of synergetic effects was traced. The behaviors of monometallic catalysts naturally fall within this line. For bimetallic catalysts, points above the 45° line imply synergy. The farther the values above this line are, the stronger the apparent synergetic effect is. Accordingly, Pd(z)Pt(1-z)-IWI catalysts exhibited synergetic effects for both the conversion of MeOH and for the production of MF, Figure 6a and c, respectively. For Pd(z)Pt(1-z)-MicE the synergetic effects were very strong for MF production but very weak for the conversion of MeOH, Figure 6b and d, respectively. The bottom line is, thus, that the preparation method plays a central role on the synergetic behavior of platinum and palladium.

Particle size effects on the catalytic performance

The preparation method clearly influenced the particle size distribution of the TiO₂-supported Pd(z)Pt(1-z) catalysts. Particle

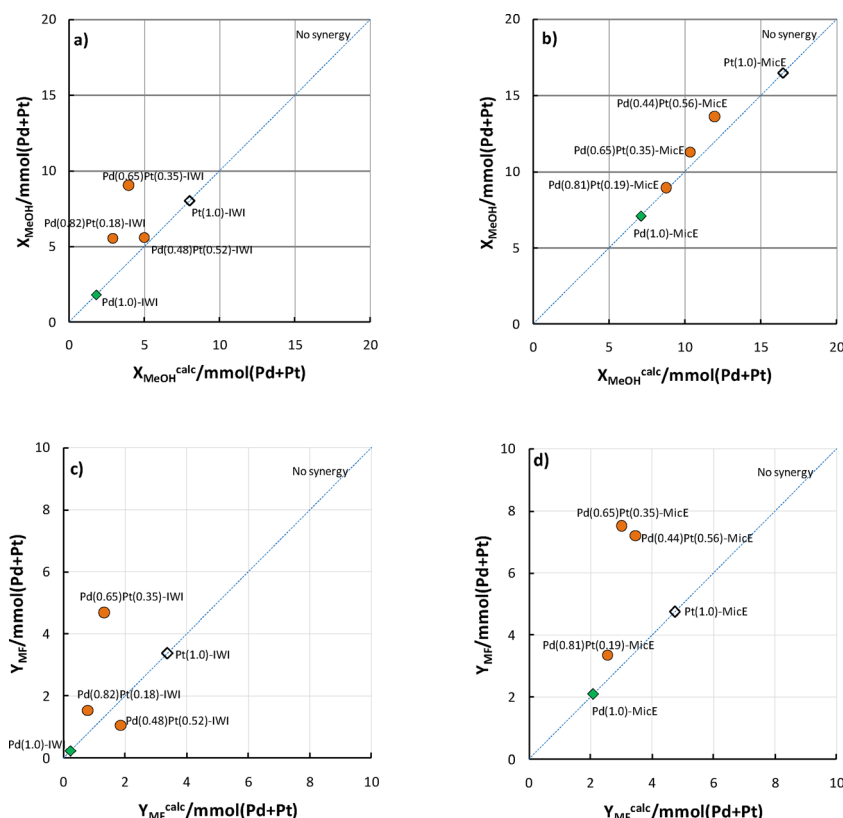


Figure 6. Synergy curves for TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts in the methanol oxidation to methyl formate. a) and b) MeOH conversion for $\text{Pd}(z)\text{Pt}(1-z)$ -IWI and $\text{Pd}(z)\text{Pt}(1-z)$ -MicE, respectively; c) and d) MF production for $\text{Pd}(z)\text{Pt}(1-z)$ -IWI and $\text{Pd}(z)\text{Pt}(1-z)$ -MicE, respectively. $T = 323$ K and atmospheric pressure, methanol to oxygen molar ratio = 2.

size distributions of $\text{Pd}(z)\text{Pt}(1-z)$ -IWI were strongly influenced by the molar ratio of the metals employed for catalyst preparation, whereas those for $\text{Pd}(z)\text{Pt}(1-z)$ -MicE were weakly affected by z . At the same time, $\text{Pd}(z)\text{Pt}(1-z)$ -IWI showed stronger synergetic effects regarding X_{MeOH} than $\text{Pd}(z)\text{Pt}(1-z)$ -IWI. This suggests that synergetic effects between palladium and platinum in the oxidation of methanol to methyl formate are influenced by the degree of heterogeneity in particle size distributions.

As early as 1975, Gómez et al.^[14] reported no synergetic effects on benzene hydrogenation over $\text{Pd}(z)\text{Pt}(1-z)/\text{Al}_2\text{O}_3$ catalysts, which exhibited a narrow, almost homogeneous, particle size distribution. Rousset et al.^[27,28] prepared $\text{Pd}(z)\text{Pt}(1-z)/\alpha\text{-Al}_2\text{O}_3$ catalysts with homogeneous particle size distributions, which did not exhibit synergetic effects in aromatic hydrogenation.

It is important to notice that despite the weak synergetic effects in MeOH conversion displayed by $\text{Pd}(z)\text{Pt}(1-z)$ -MicE, these catalysts were more active in the reaction than $\text{Pd}(z)\text{Pt}(1-z)$ -IWI and that synergetic effects for the production of MF were indeed present for both series of catalysts. The literature also indicates that one of the characteristics that make Pd nanoparticles very active and selective in the reaction is a narrow particle size distribution.^[10,11] This characteristic is present for $\text{Pd}(z)\text{Pt}(1-z)$ -MicE.

Concerning the effect of the preparation method, despite its wide use, impregnation methods for catalyst preparation yield particle size distributions that strongly depend on metal load-

ing,^[52–54] because, as Miller et al. puts it,^[54] the method depends on many different variables at the same time: “support composition, metal salt, method of metal addition, pH, metal loading, calcination temperature, etc.” On the other hand, the literature shows that MeOH oxidation is strongly influenced by particle size effects. Louis et al.^[52] prepared a series of $\text{MoO}_3/\text{SiO}_2$ catalysts with different molybdenum loadings by impregnation and grafting for this reaction. They found a strong effect of the Mo loading on the particle size distribution of the impregnated catalysts. Because of this fact, it was not possible to establish a correlation between the dispersion of MoO_3 and the catalytic performance. Conversely, a straight correlation between MeOH turnover numbers and MoO_3 dispersion for the grafted catalysts, the dispersion of which did not depend on the Mo loading, was established. A similar correlation was not found for S_{MF} however. One may notice the resemblance between these results and the ones presented herein. Regarding an explanation for this effect, the relationship between the synergy in the catalytic activity and the heterogeneity in particle size distribution of $\text{Pd}(z)\text{Pt}(1-z)$ -IWI could be associated with some sort of cooperative effect between small and bigger nanoparticles. For example, very recently, Fernández et al.^[55] evoked hydrogen spillover from big to small nanoparticles in mechanical mixtures to explain the catalytic behavior of $\text{Ru}/\text{Al}_2\text{O}_3$ in ammonia synthesis.

Effect of nanoparticles composition and structure on the catalytic performance

Regardless of the preparation method, the strongest synergetic effect was observed for catalysts prepared with $z=0.65$. TEM-EDX results showed that preparing bimetallic catalysts with a given bulk molar composition, z , does not imply that the composition of the nanoparticles of the synthesized catalyst will have such a composition. Furthermore, a mixture of monometallic and bimetallic nanoparticles of different compositions is present in the TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts studied herein. For catalysts prepared with $z=0.65$, as already mentioned, most of the analyzed bimetallic nanoparticles had a $\text{Pd}/(\text{Pd}+\text{Pt})$ molar ratio within the range $0.7 < z_{\text{TEM}} < 1.0$. Figure 7 plots the apparent rates of reaction as a function of the composition of the metallic nanoparticles as measured by HRTEM-EDX.

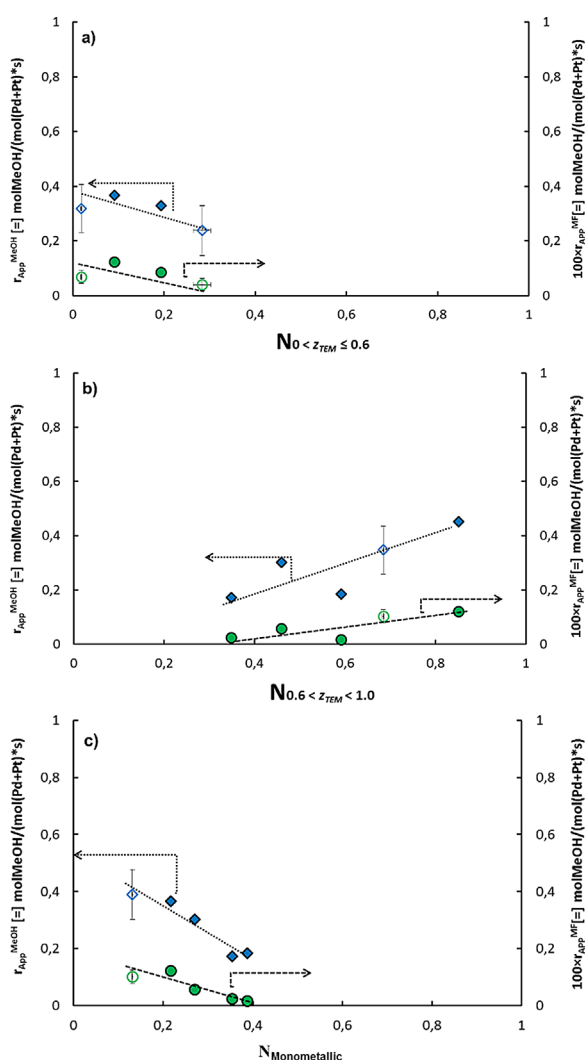


Figure 7. Steady-state apparent reaction rates as a function of the relative fraction of nanoparticles (N), the composition (z_{TEM}) of which was determined by HRTEM-EDX measurements performed on the spent catalysts. a) Bimetallic nanoparticles with $0 < z_{\text{TEM}} \leq 0.6$; b) bimetallic nanoparticles with $0.6 < z_{\text{TEM}} < 1.0$; c) monometallic Pd ($z_{\text{TEM}} = 1$) and Pt ($z_{\text{TEM}} = 0$) nanoparticles ($N_{\text{Monometallic}}$). Unfilled marks correspond to average values.

The figure shows a correlation between the composition of the nanoparticles and the catalytic performance. The trend observed in Figure 7b demonstrates that the increase in the concentration of bimetallic nanoparticles whose molar $\text{Pd}/(\text{Pd}+\text{Pt})$ ratio is above 0.6 promotes the catalytic performance of TiO_2 supported $\text{Pd}(z)\text{Pt}(1-z)$.

One may notice that the presence of monometallic nanoparticles and bimetallic nanoparticles whose composition is within the range $0 < z_{\text{TEM}} \leq 0.6$ has a negative impact on the catalytic performance (Figure 7a and b). Most literature works report synergetic effects for $\text{Pd}(z)\text{Pt}(1-z)$ catalysts with $z=0.6-0.8$.^[16,56,57] At present, there is not a satisfactory explanation for why such a composition leads to these effects. In the case of hydrotreatment reactions, Jiang et al.^[57] found that a substitution of Pd atoms on Pt(111) crystallites changes the dynamics of the competitive adsorption and dissociation of sulfur, H_2 , and H_2S . The geometric structure of the Pd-replaced bimetallic surface is more favorable for the adsorption of H_2 compared with H_2S and S atoms and this, in addition, increases the adsorption energy of H_2 on the surface. One may speculate that a similar structural configuration of the bimetallic Pd–Pt nanoparticles could be behind the trends in catalytic performance for TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$. By considering that Pauling's electronegativity for oxygen (3.44) is higher than that for sulfur (2.58),^[31] one may postulate that if a given surface has a lower affinity for sulfur it would likely also have a lower affinity for oxygen. In this sense, a weakening of the oxygen–metal bond during the oxidation reaction could be expected. Such weakening would facilitate the surface reaction of adsorbed methoxy species ($\text{CH}_3\text{O}_{\text{ads}}$), which are responsible for methyl formate production,^[58–60] and would inhibit the oxidation of these intermediates to CO_{ads} and therefore to gaseous CO_x . However, testing the above hypothesis is out of the scope of this work.

Role of palladium and platinum on the catalytic performance

The XPS results showed that metallic Pd^0 and Pt^0 species should be prevalent on the active phase of TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$. On the other hand, the XRD and TEM results demonstrated that the crystalline structure of the nanoparticles of the reduced catalysts corresponds to $\text{Pd}(111)$ and/or $\text{Pt}(111)$. As previously mentioned, the resolution of the XRD peaks obtained during these tests was not enough as to clearly distinguish $\text{Pd}(111)$ from $\text{Pt}(111)$ in the bimetallic catalysts (Figure S1). Therefore, a fully satisfactory explanation of the role of these phases in the reaction cannot be obtained from the present work. From the literature, one might analyze some key factors on the subject and thus try to correlate them with the behavior of the TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts nonetheless. Particularly, DFT calculations have shown that the energy of adsorption of CH_3O over $\text{Pt}(111)$ is lower, -1.80 eV, compared with that over $\text{Pd}(111)$, -1.99 eV.^[61] This implies that platinum is more effective than palladium for $\text{CH}_3\text{O}_{\text{ads}}$ decomposition; a fact that is in agreement with the catalytic trends presented herein. In addition, Ren et al.^[61] also showed that CH_3O is preferentially adsorbed on a face-centered cubic (fcc)- $\eta^2(\text{C},\text{O})$ configuration on $\text{Pt}(111)$, that is, with the oxygen

bound to one Pt atom, whereas an $\eta^1(\text{O})$ configuration, in which the oxygen atom of CH_3O is triply bound to the surface and at shorter distance compared with the $\text{fcc-}\eta^2(\text{C},\text{O})$ configuration, is favored for CH_3O adsorption on $\text{Pd}(111)$. The reactivity of methanol over the bimetallic catalysts would be given by a competition between both mechanisms and by a competitive adsorption and transformation of the reaction intermediates over the available surface palladium and platinum atoms. Lichtenberger et al.^[9] described three possible mechanisms for MF formation: (i) condensation of $\text{CH}_3\text{O}_{\text{ads}}$ with $\eta^2(\text{C},\text{O})$ -formaldehyde species to form $\text{CH}_3\text{OCH}_2\text{OH}$ (methoxymethanol) intermediates, which then dehydrogenate to methyl formate; (ii) esterification of formic acid (HCOOH) intermediates formed by CH_2O oxidation; or (iii) CH_2O dimerization through a Tischenko-type reaction. In addition, Levis et al.^[58–60] proposed that stable $\text{CH}_{3\text{ads}}$ species from the scission of $\text{CH}_3\text{OH}_{\text{ads}}$ could also be important for oxidation mechanism by their reaction with O_{ads} . Tentatively, the behavior of $\text{Pd}(z)\text{Pt}(1-z)$ in the reaction can be explained by considering a mechanism in which platinum atoms would rapidly activate MeOH molecules in an $\text{fcc-}\eta^2(\text{C},\text{O})$ mode whereas palladium would play the role of a stabilizer for the corresponding reaction intermediates by adsorbing them in the $\eta^1(\text{O})$ configuration. Moreover, the MeOH molecules activated by palladium atoms would also present a more stable surface configuration. This hypothesis is in better agreement with mechanism (i). Therefore, the synergetic effects observed in the production of methyl formate with $\text{Pd}(z)\text{Pt}(1-z)$ could be ascribed to the stabilization of different species: $\text{CH}_3\text{O}_{\text{ads}}$, $\eta^2(\text{C},\text{O})$ -formaldehyde, $\text{CH}_2\text{O}_{\text{ads}}$ or HCOOH , on the metallic active phase and further condensation to form MF. Finally, if, as proposed by Levis et al.,^[58–60] stable $\text{CH}_{3\text{ads}}$ species are participating in the mechanism of reaction, the surface oxidative dehydrogenation of such species could promote C_{ads} species, which are known coke precursors. The relationship between the latter phenomenon and the slight deactivation observed for $\text{Pd}(0.65)\text{Pt}(0.35)\text{-MicE}$ during the long duration test deserves future studies. In addition, a correlation between the XRD, TEM, and XPS results indicated that both the small and big nanoparticles of the catalysts grew during the catalytic tests. The losses in catalytic activity and MF productivity during the stability test could be associated with particle size growth. Although some pieces of evidence are still lacking to gain further insight into these phenomena, it can be concluded with certainty that particle size distribution is a central player in the existence of synergetic effects in the reaction. As MeOH oxidation is a surface sensitive reaction,^[11] the explanation behind this trend should be related to the structure and to the chemical state of the active phase of the catalysts.

Conclusions

The green production of methyl formate through methanol oxidation at industrially relevant reaction rates was achieved over TiO_2 -supported $\text{Pd}(z)\text{Pt}(1-z)$ catalysts. It was determined that the water-in-oil microemulsion preparation method, MicE, leads to highly efficient catalysts that exhibit strong synergetic effects for the production of methyl formate. Conversely, cata-

lysts prepared by incipient wetness (co)-impregnation, IWI, were less efficient in the reaction despite also displaying synergy between palladium and platinum. The key factors behind such trends were found to be: first, narrower particle size distributions and less dependence on the metallic palladium to platinum molar ratio used for catalysts preparation in the water-in-oil microemulsion method compared with incipient wetness (co)-impregnation; second, the presence of an important amount of bimetallic nanoparticles with a palladium to platinum molar higher than 0.6; third, the constitution of an active phase composed of palladium and platinum species of metallic character, particularly, zerovalent palladium and platinum with crystalline phases corresponding to $\text{Pd}(111)$ and $\text{Pt}(111)$. It was postulated that the role of platinum in the bimetallic species would be to promote the activation of the reactants whereas palladium would act a selectivity modifier that promotes MF formation. The ensemble of the results presented in this paper contribute to the development of green synthesis processes for methyl formate production.

Experimental Section

Catalysts preparation

Commercial grade TiO_2 (Merck) was employed as the support without further treatment. The Brunauer–Emmett–Teller (BET) surface area of this material is $8 \text{ m}^2 \text{ g}^{-1}$.^[10,11,24,25] The selection of such a low area support was based on previous works, where their advantages for partial oxidation reactions were demonstrated owing to the deposition of the catalytic active phase on the external surface of the support.^[10–13,24,25] For both series of catalysts, a nominal $\text{Pd}+\text{Pt}$ metallic content of 1 wt.% was fixed. Appropriate amounts of ammonium tetrachloroplatinate(II) $[(\text{NH}_4)_2\text{PtCl}_6]$, Johnson Matthey and ammonium tetrachloropalladate(II) $[(\text{NH}_4)_2\text{PdCl}_6]$, 97%, Sigma–Aldrich were used as the metallic precursors. For the IWI method, aqueous solutions of these precursors were poured drop by drop onto the TiO_2 support. As the support became progressively wetted, a slurry was formed. This slurry was left to dry at ambient conditions and then calcined for 4 h at 773 K in a static oven. The MicE method was adapted from previous works.^[10–13,24,25] Briefly, it consists on the in situ reduction of an aqueous phase of the metallic precursors, which form a microemulsion with an oil phase by means of an amphiphile surfactant. Herein, cyclohexane (commercial grade, Sigma–Aldrich) was the oil phase, AOT [sodium bis(2-ethylhexyl)sulfosuccinate, 96%, Sigma–Aldrich] was the surfactant, and hydrazine (80 wt.% in water, Fluka) was the reducing agent. An appropriate amount of TiO_2 was added to the reactant flask containing the microemulsion at 323 K and under magnetic stirring. After 30 min, hydrazine (3 mL) was injected into the reactant flask while keeping the temperature constant. Reduction, under an inert N_2 atmosphere, was allowed to proceed until the suspension in the flask turned black. Upon reduction completion, a slurry was recovered from the suspension by filtering and washing with acetone (99%, VWR) and hot distilled water. The catalysts thus synthesized were afterwards dried at 373 K for 1 h and used as such.

Bulk Pd and Pt contents and catalyst nomenclature

Bulk Pd and Pt contents were determined by ICP-AES with a Thermo Jarrell ASH IRIS Advantage apparatus. Bulk metallic contents (reported in Table S1) were converted to bulk molar ratios, z

for Pd, [Eq. (1)], and $(1-z)$ for Pt, and these values were employed in the catalyst nomenclature: Pd(z)Pt($1-z$). The suffixes -MicE, and -IWl indicate the preparation method. For example, Pd(1.0)-MicE stands for monometallic palladium prepared by the MicE method.

$$z = \frac{\text{molPd}}{\text{mol(Pd + Pt)}} \quad (1)$$

Crystallinity by XRD

An X-ray diffraction study was carried out with a Siemens D5000 diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The 2θ range was scanned between 2 and 70° at a rate of $0.01^\circ \text{ s}^{-1}$. The identification of the crystalline phases was made with the ICDD-JCPDS database after analyzing the recorded spectra with CasaXPS (Casa Software Ltd.) where the position of the peaks and their full width at half maximum (FWHM) was determined. A Gaussian/Lorentzian (70/30) product function and a linear background were employed for peak fitting. Catalysts were examined after preparation and after reduction under the same conditions as the reaction tests. XRD spectra were recorded at least twice to confirm the presence of the identified crystalline phases. The Scherrer equation^[26] was employed for estimating the crystallite size of the detected phases.

Nanoparticle identification, morphology, size, and composition by TEM

TEM measurements were performed with a JEOL JEM-2200FS/Cs-corrected FEG TEM instrument operated at 200 kV and provided with an in-column omega filter. Two modes or measurement were employed: namely, high resolution (HRTEM) and scanning (STEM) mode. The probe diameter was 0.5–1.0 nm. By combining STEM with energy dispersive X-ray analysis (EDX), we performed a systematic measurement of the composition of the observed individual metallic nanoparticles. On the basis of these measurements, Pd/(Pd + Pt) molar ratios (z_{TEM}) for the individual nanoparticles were defined in the same fashion as in Equation (1). Similar approaches have been previously presented in the literature.^[23,27,28]

Chemical composition and oxidation state by XPS

XPS measurements were carried out with an SSI-X-probe spectrometer (SSX-100/206, Surface Science Instruments) equipped with a monochromatic microfocused AlK_α (1486.6 eV) X-ray source (10 kV; 22 mA). Both the fresh and spent catalysts were analyzed. At least three samples of the fresh catalysts were analyzed to test the reproducibility of the measurements. Catalyst particles were pressed into small stainless steel troughs mounted on a multi-specimen ceramic sample holder. The analysis chamber was operated under ultrahigh vacuum with a pressure close to $5 \times 10^{-7} \text{ Pa}$. Charge stabilization was achieved by using an electron flood gun adjusted at 8 eV and by placing a nickel grid 3 mm above the samples. The following sequence of spectra was recorded: general spectrum, O 1s, C 1s + K2p, Ti 2p, P 2p, Ca 2p, Pd 3d, Pt 4f, and C 1s + K2p again to check the stability of charge compensation as a function of time. General spectra were recorded at a pass energy of 150 eV whereas the elements spectra were recorded at a pass energy of 50 eV. The analyzed area was approximately 1.4 mm^2 as estimated from an elliptic spot of $1000 \mu\text{m} \times 1700 \mu\text{m}$. Surface molar concentrations were calculated by correcting peak intensities with theoretical sensitivity factors based on Scofield cross sections^[29] and the mean free path varying according to 0.7 power of

the photoelectron kinetic energy. The spectra were decomposed with CasaXPS employing a Gaussian/Lorentzian (85/15) product function after subtraction of a Shirley nonlinear sigmoid-type baseline. The binding energy (BE) scale was corrected by using the C-[C,H] component of the adventitious carbon peak at 284.8 eV as a reference.^[30] To determine the surface chemical state of palladium, a contribution from metallic palladium (Pd^0), $\text{Pd} 3d_{5/2}$ BE $\leq 335.0 \text{ eV}$,^[25,37,40] and another from oxidized palladium ($\text{Pd}^{\delta+}$), $\text{Pd} 3d_{5/2}$ BE $> 335 \text{ eV}$,^[18,25,36–37,40] were considered (Table S3). Peak decomposition was performed with the following constraints: a) The FWHM of all Pd components was fixed within the range 1.2–2.0 eV; b) FWHM of $\text{Pd} 3d_{3/2}$ peaks = FWHM of $\text{Pd} 3d_{5/2}$ peaks, for the same considered species; c) area of $\text{Pd} 3d_{3/2} = 2/3 \times \text{Pd} 3d_{5/2}$; d) a separation of 5.25 eV between the peaks $\text{Pd} 3d_{5/2}$ and $\text{Pd} 3d_{3/2}$.^[36] In addition, an asymmetry factor for Pd^0 was introduced in the mathematical decomposition so as to reflect the asymmetry of the peak of this species as observed in palladium foil samples.^[25] Such a factor corresponded to a modified Gaussian/Lorentzian line shape: A(0.25,0.25,0)GL(15) in CasaXPS. Finally, the contribution of electrons coming from the $\text{Pt} 4d_{3/2}$ core level, BE = 330–335 eV,^[37] to the Pd 3d signal was not taken into account owing the very low intensity of $\text{Pt} 4d_{3/2}$. Concerning platinum, the following constraints were imposed for peak decomposition: a) the FWHM of the main $\text{Pt} 4f_{7/2}$ peak was fixed within the range 1.5–2.0 eV; b) the FWHM of the $\text{Pt} 4f_{5/2}$ peaks = FWHM of the $\text{Pt} 4f_{7/2}$ peaks; c) the area of the $\text{Pt} 4f_{5/2}$ peaks = $0.75 \times$ area of the $\text{Pt} 4f_{7/2}$ peaks; d) a separation of 3.35 eV between $\text{Pt} 4f_{5/2}$ and $\text{Pt} 4f_{7/2}$.^[25] Although, as, in the case of palladium, two species of platinum could be present on the surface of the catalysts; namely, one corresponding to Pt^0 with BE for $\text{Pt} 4f_{7/2} < 71 \text{ eV}$,^[36,40] and another corresponding to $\text{Pt}^{\delta+}$ with BE for $\text{Pt} 4f_{7/2} > 72$,^[36,40] it was considered reasonable to use only one component owing to the low intensity of the signal and to peak overlapping with the Ti 3s plasmon loss peak for the TiO_2 support. In the case of Pd(0.82)Pt(0.18)-IWl, it was not possible to add components corresponding to platinum into the peak because the signal from platinum was completely masked by the Ti 3s plasmon loss peak. Selected XPS spectra of the Pd 3d and Pt 4f core levels are presented in the Supporting Information (Figures S6–S9).

Catalytic tests

The aerobic gas-phase oxidation of methanol was performed at atmospheric pressure in a metallic fixed-bed microreactor made of an inconel tube of 1 cm internal diameter (PID ENG&Tech). The catalytic bed ($\approx 0.5 \text{ cm}^3$) was composed of 100 mg of catalyst powder selected within the granular fraction 200–315 μm and diluted in 600 mg glass spheres that were previously confirmed inactive. Before testing, all catalysts were treated under a $50 \text{ cm}^3 \text{ min}^{-1}$ flow of pure hydrogen (99.999%, Praxair) at 573 K (heating ramp = $10 \text{ K} \times \text{min}^{-1}$) for 1 h, to reduce them under the same conditions. After this treatment, the reactor was cooled down to the reaction temperature: 323 K. The reactor feed consisted in $100 \text{ cm}^3 \text{ min}^{-1}$ of a gas mixture of 5 vol.% MeOH (anhydrous, 99.995%, Sigma-Aldrich) and 2.5 vol.% O_2 (99.999%, Praxair) diluted in He (99.999%, Praxair). The gas mixture was prepared by passing the stream of He through a container with liquid methanol, which was, in turn, placed in a saturator maintained at 278 K. Once the flows of MeOH and O_2 were stable, as verified by carrying out several injections of this stream into the online GC system, the reactants were allowed into the reactor and the catalytic test was begun. Reaction products were analyzed each 30 min by using a CP3800 Varian GC provided with TCD detector. CP-Pora-PLOT Q (25 m; 0.53 mm) and CP-Molsieve 5 $\text{\AA}$ (25 m; 0.53 mm) columns were used for the separa-

tion of the reaction products. The concentrations of the following molecules were monitored during the reaction: H_2 , O_2 , CH_4 , CO , CO_2 , $MeOH$, MF , formaldehyde, formic acid, and H_2O . Only O_2 , $MeOH$, MF , H_2O , and CO_2 were detected at the reactor exit. The catalytic performance was expressed in terms of the methanol molar conversion (X_{MeOH}), the molar yield to methyl formate (Y_{MF}), the selectivities to MF (S_{MF}) and to CO_2 (S_{CO_2}), and of the space time yield to methyl formate (STY_{MF}), which were calculated as shown in the Supporting Information. A stability test was performed under the same reaction conditions of a conventional reaction test and after 1800 min.

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Keywords: green chemistry • methanol oxidation • methyl formate • supported catalysts • synergy

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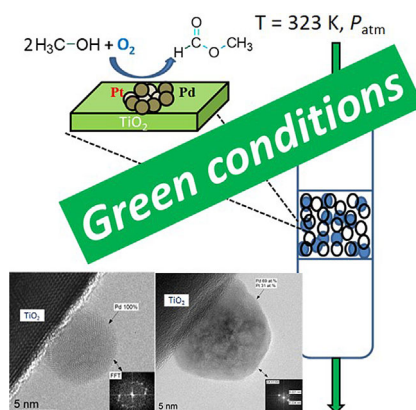
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FULL PAPERS

Microemulsion or incipient wetness impregnation?

TiO_2 -supported Pd(z)Pt(1-z) catalysts were found to be effective in the green synthesis of methyl formate (MF) by methanol oxidation. It was determined that the water-in-oil microemulsion preparation method leads to highly efficient catalysts that exhibit strong synergetic effects for the production of MF. Comparison with catalysts prepared by incipient wetness (co)-impregnation allowed the cause of such synergetic effects to be established.



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Synergetic Behavior of TiO_2 -Supported
 Pd(z)Pt(1-z) Catalysts in the Green
Synthesis of Methyl Formate