Catalytic oxidation of methanol on Pd metal and oxide clusters at near-ambient temperatures

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Supported Pd clusters catalyze methanol oxidation to methyl formate with high turnover rates and >90% selectivity at near ambient temperatures (313 K). Metal clusters are much more reactive than PdO clusters and rates are inhibited by the reactant O2. These data suggest that ensembles of Pd metal atoms on surfaces nearly saturated with chemisorbed oxygen are required for kinetically-relevant C–H bond activation in chemisorbed methoxide intermediates. Pd metal surfaces become more reactive with increasing metal particle size. The higher coordination of surface atoms on larger clusters leads to more weakly-bound chemisorbed species and to a larger number of Pd metal ensembles available during steady-state catalysis. Chemisorbed oxygen removes H-atoms formed in C–H bond activation steps and inhibits methoxide decomposition and CO2 formation, two functions essential for the high turnover rates and methyl formate selectivities reported here.

Introduction

Methanol (CH3OH) reactions with O2 lead to formaldehyde (HCHO), methyl formate (MF) and dimethoxymethane (DMM) products, useful as chemical intermediates,1 on MoO3,2 V2O5,3,4 and Mo–Sn oxides.5,6 Ru oxides7 catalyze CH3OH oxidation to MF with extraordinary rates and selectivities at near-ambient temperatures (300–400 K). Pd-based catalysts are widely used for oxidation of higher alcohols to aldehydes at low temperatures in liquid8–13 and supercritical14 media, but they have seldom been used to oxidize smaller and less reactive alcohols (C4). The oxidation of C1–C4 alcohols was reported to occur on “giant palladium clusters” with Pd561Phen60(Oac)180 and Pd560Phen60O60(PF6)60 composition15–18 (phen = 1,10-phenanthroline) with the formation of MF as the main product. MF and HCHO were also reported as undesired incomplete oxidation products during methanol combustion on Pd.19 and Pt-based20,21 catalysts at low temperatures (<400 K).

Here we report the highest turnover rates observed for CH3OH oxidation (up to 2.6 mol CH3OH s−1 (surface Pd atom)−1) with very high MF selectivities (~90%) at near-ambient temperatures (313 K). These materials also catalyzed ethanol oxidation with high turnover rates (0.21 s−1) and acetaldehyde selectivities (~85%) at low temperatures (353 K). CH3OH oxidation rates on these catalysts were strongly influenced by the oxidation state of supported Pd clusters. Methanol oxidation turnover rates decreased markedly with decreasing Pd cluster size, as a result of a concomitant increase in the binding energy of chemisorbed oxygen species, which leads to lower concentrations of vacancies in chemisorbed oxygen monolayers during steady-state catalysis.

This remarkable reactivity of Pd-based clusters in the oxidative dehydrogenation of methanol and ethanol provides significant opportunities for the efficient use of these products as precursors to more useful chemicals; specifically, they provide direct routes from biomass-derived alcohols to methyl formate and acetaldehyde. Methyl formate is used to produce formamide via aminolysis and formic acid via acid-catalyzed hydrolysis.22 It also leads to precursors to ethylene glycol (HCOOCH2 + HCHO→HOCOCH2OOH) via HCHO-coupling and to acetic acid via intramolecular isomerization (HCOOCH3=CH2COOH) on metal complexes (Rh, Ir, Co, Ni, Ru, Pd) with iodide co-catalysts or promoters.22,23

Results and discussion

Pd-containing catalysts were exposed to methanol–O2 reactants either immediately after treatment in 20% O2–He flow at 373 K (denoted as “PdO” sample) or after subsequent treatment of these samples in H2 at 373 K (denoted as “Pd” sample). These two treatments led to markedly different CH3OH oxidation rates, indicating that the Pd oxidation state strongly influences kinetically-relevant steps.

Turnover rates on PdO/Al2O3 (treated in 20% O2–He at 673 K for 2 h) increased gradually with time on stream (Fig. 1; 333 K). Reaction products were not detectable on these catalysts at 313 K, even after contact with CH3OH–O2 reactant mixtures for 12 h, due to a very slow reaction rate. The gradual increase in CH3OH oxidation rates on PdO samples at 333 K may indicate that PdO clusters reduce slowly during CH3OH–O2 reactions and that Pd metal surfaces catalyze kinetically-relevant CH3OH oxidation steps much more efficiently than PdO surfaces, a conclusion confirmed by the marked increase in reactivity observed when these catalysts were treated in H2 to form Pd metal clusters, as described below.

Pd metal centers were proposed to act as active sites in liquid-phase oxidation of cinnamyl8 and benzyl24 alcohols on Pd/Al2O3. Cordi and Falconer22 reported that PdO/Al2O3 was less reactive than Pd/Al2O3 samples for the decomposition (in He) and oxidation (in O2) of methoxide species formed via methanol dissociation. These reactivity differences were attributed to the
Methanol conversion rates with time on stream over a 1 wt% Pd/Al₂O₃ catalyst (dispersion 0.24) treated in 20% O₂–He at 675 K prior to reaction (conditions: 4 kPa CH₃OH, 9 kPa O₂, 1 kPa N₂, balance He, 1 cm³ s⁻¹ total flow, 333 K, 3.7 mg Pd/Al₂O₃, conversion: 0.02 to 1.9%, (the catalyst bed was diluted with 1 g of quartz)). (b) Methanol conversion rates with time on stream over a 1 wt% Pd/Al₂O₃ catalyst (dispersion 0.43) treated in 20% O₂–He at 675 K followed by treatment in H₂ at 373 K prior to reaction (conditions: 4 kPa CH₃OH, 9 kPa O₂, 1 kPa N₂, balance He, 1 cm³ s⁻¹ total flow, 313 K, conversion: 6.6%, (catalyst dilution: 150 mg of a 1 : 150 Pd/Al₂O₃ : Al₂O₃ internally-diluted sample and 350 mg additional Al₂O₃)).

Selectivities with time on stream over 4 wt% PdO/Al₂O₃ treated in 20% O₂–He at 675 K prior to reaction (conditions: 4 kPa CH₃OH, 9 kPa O₂, 1 kPa N₂, balance He, 1 cm³ s⁻¹ total flow, 333 K, 3.7 mg PdO/Al₂O₃, conversion: 0.02 to 1.9%, (the catalyst bed was diluted with 1 g of quartz)). (b) Selectivities with time on stream over a 1 wt% PdO/Al₂O₃ catalyst treated in 20% O₂–He at 675 K followed by treatment in H₂ at 373 K prior to reaction (conditions: 4 kPa CH₃OH, 9 kPa O₂, 1 kPa N₂, balance He, 1 cm³ s⁻¹ total flow, 313 K, conversion: 6.6%, (catalyst dilution: 150 mg of a 1 : 150 Pd/Al₂O₃ : Al₂O₃ internally-diluted sample and 350 mg additional Al₂O₃)).

Slow extraction of lattice oxygen in the case of PdO. Thin PdO films (3–5 monolayers) deposited on Au substrates²⁷ did not activate CH₂OH up to 623 K, because of their low reactivity in CH₂OH dissociation and their resistance to reduction. In contrast, Pd metal films catalyzed methanol oxidation at 525 K, a temperature ~200 K higher, however, than we report here on impregnated Pd/Al₂O₃ catalysts.

The evolution of methanol oxidation reactivity with time on stream, reported here for PdO clusters at much lower temperatures, is consistent with the effectiveness of reduced Pd surfaces in the oxidative dehydrogenation of alcohols. MF was the only product detected during methanol–O₂ reactions on PdO/Al₂O₃ throughout these experiments (14 h; Fig. 2).

Pd/Al₂O₃ samples (prepared from PdO/Al₂O₃ by treatment in H₂ at 373 K for 1 h) gave much higher reaction rates at 313 K than unreduced samples (Fig. 1). Turnover rates were ~40 times higher than on PdO samples; rates remained constant throughout these experiments (15 h). These trends are markedly different from the gradual increase in rate observed on PdO clusters placed in contact with CH₂OH–O₂ reactants (Fig. 1). We conclude from these data that the Pd metal clusters remained active and that they did not oxidize during the reaction at these temperatures. We also conclude that exposed Pd atoms present within chemisorbed oxygen layers are involved in rate-determining steps, as also inferred in the liquid-phase oxidation of higher alcohols on Pd catalysts⁸⁻²⁴ and the catalytic combustion of CH₄ on PdO surfaces.²⁷

The measured negative effect in O₂ on methanol oxidation rates is consistent with the involvement of vacancies in kinetically-relevant steps. A positive reaction order was measured with respect to methanol.²⁸ These inhibition effects prevail even though O₂ is a stoichiometric reactant, specifically required for the oxidative removal of H-atoms, abstracted during methoxide decomposition, as H₂O (and of any CO, formed in side decomposition reactions, as CO₂) and for the suppression of unselective sequential dehydrogenation of methoxide intermediates to H₂ and CO. This latter role of chemisorbed oxygen is consistent with that proposed earlier based on methoxide decomposition studies on single crystal surfaces.²⁹

Supported Pd metal clusters gave very high MF selectivities (~90%) and only small amounts of CO₂ (Fig. 2). MF, CO₂, and H₂O were the only products detected; CO and HCHO products were not detected (detection limits: 0.5 and 3%, at ~10% conversion). The absence of HCHO indicates that its reaction with chemisorbed methoxide or its oxidation to CO₂ is fast. The absence of CO and H₂ among products is not surprising, because, if formed in surface reactions, they would desorb from Pd surfaces only at temperatures well above those required for methanol oxidation (>330 K for H₂; >480 K for CO₂).²⁹

Table 1 summarizes methanol oxidation turnover rates (normalized by surface metal atoms) and selectivities on supported Pd, Pt and Ru clusters. Selectivities are compared at different conversions because of the wide range reported in previous studies, as well as the high reactivity of our materials, which lead to severe catalyst temperature gradients at conversions above 10%. Pd/Al₂O₃ catalysts give rates similar to those on previously reported catalysts, but at 20–80 K lower temperatures and with higher methyl formate selectivities. Methanol oxidation gave low MF yields (<13%) at 340 K on 0.01 wt% Pd/γ-Al₂O₃ (42% dispersion).¹⁹ HCHO yields increased with temperature (maximum yield, 11% at 480 K); CO₂ was the predominant product (~67% yield; 340 K) at all conditions in these studies. The same authors observed MF (maximum yield...
CH$_3$OH oxidation turnover rates (per surface atom) and product selectivities on alumina-supported PdO, Pd, Pt and RuO$_2$ samples

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Metal (wt%)</th>
<th>Temperature/K</th>
<th>CH$<em>3$OH conversion turnover rate to MF, HCHO and DMM/mol (g-atom M$</em>{surf}$-h)$^{-1}$</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al$_2$O$_3$$^a$</td>
<td>1.0</td>
<td>313</td>
<td>8460 / 6.6</td>
<td>HCHO: 90</td>
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<tr>
<td>Pd$_{0.02}$/Al$_2$O$_3$</td>
<td>4.0</td>
<td>333</td>
<td>2340 / 1.6</td>
<td>MF: 100</td>
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<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>0.01</td>
<td>340</td>
<td>4158 / 80</td>
<td>DMM: 6</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>0.054</td>
<td>330</td>
<td>4575 / 93</td>
<td>CO$_2$: 10</td>
</tr>
<tr>
<td>RuO$_2$/Al$_2$O$_3$</td>
<td>7</td>
<td>393</td>
<td>70 / 20</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 4 kPa CH$_3$OH, 9 kPa O$_2$, 1 kPa N$_2$, balance He, 1 cm$^3$ s$^{-1}$; “Pd” refers to samples treated in H$_2$ at 373 K for 1 h; “PdO,” refers to samples treated in 20% O$_2$–He at 673 K for 2 h. $^b$ Rates on supported PdO$_2$ clusters represent values measured after ca. 10 h of exposure to the CH$_3$OH–O$_2$ reactants.

CH$_3$OH oxidation turnover rates (per surface Pd atom) (313 K, 4 kPa CH$_3$OH, 45 kPa O$_2$) and selectivities on 1 wt% Pd/Al$_2$O$_3$ catalyst (43% dispersion) as a function of methanol conversion.

Selectivities to MF, DMM (dimethoxymethane), and HCHO at low temperatures and were recently reported as the most active among metal oxide catalysts. Methanol oxidation turnover rates on these RuO$_2$ catalysts are approximately two orders of magnitude lower at 80 K higher temperatures as compared to the Pd/Al$_2$O$_3$ catalyst used in this study.

Fig. 3 shows turnover rates (per surface Pd atom) (313 K, 4 kPa CH$_3$OH, 45 kPa O$_2$) and selectivities on 1 wt% Pd/Al$_2$O$_3$ catalyst (43% dispersion) as a function of methanol conversion (varied by changing the reactant space velocity). CH$_3$OH oxidation turnover rates decreased with increasing CH$_3$OH conversion as a result of reactant depletion combined with a strong inhibition by water co-products. Such inhibition effects were also reported for methanol oxidation on Fe–Mo oxides. Selectivities were not influenced by space velocity, indicating that MF and CO$_2$ are primary products and that MF does not oxidize to CO$_2$ in secondary reactions at the conditions required for CH$_3$OH oxidation. MF can form via: (1) condensation of adsorbed methoxides with HCHO to form methoxymethanol intermediates (CH$_3$OCH$_2$OH) that then dehydrogenate to MF; (2) esterification of formic acid (HCOOH) intermediates formed by HCHO oxidation; or (3) HCHO dimerization via Tischenko-type reactions (Scheme 1). Adsorbed HCHO can also decompose to chemisorbed CO* and H* before desorption, as observed on Pd(111) surfaces, or react with chemisorbed O* to form surface formate species (HCOO*). CO* oxidation and HCOO* decomposition then lead to CO$_2$ and remove otherwise stranded strongly-adsorbed intermediates (Scheme 1). The high MF selectivities reported here indicate that fast reactions effectively scavenge HCHO to form MF, which is much less reactive than HCHO in subsequent oxidation reactions that form CO$_2$.

MF and CO$_2$ selectivities were not influenced by Pd dispersion (Fig. 4). MF synthesis turnover rates (extrapolated to zero residence time and conversion), however, increased markedly as Pd dispersion decreased, indicating that surfaces on large Pd clusters are much more reactive than on smaller ones. Similar trends were reported previously for CH$_4$-oxidation on PdO clusters at low temperatures. The latter reaction is limited by C–H activation on vacancy-oxygen (*–O*) site pairs and Pd dispersion effects were attributed to a smaller number of vacancies as the binding energy of chemisorbed oxygen increased with decreasing ensemble size as previously shown for Pd$^{32}$ and Pt$^{33,34}$ clusters. This trend reflects, in turn, the higher coordinative unsaturation of Pd surface atoms exposed on smaller clusters. The similar trends observed for CH$_3$OH oxidation in the present study are also consistent with the requirement for reduced Pd surfaces, possibly vacancies on clusters densely covered by chemisorbed oxygen. The availability of such vacancies would decrease with increasing Pd metal dispersion as a result of the stronger binding of oxygen on coordinatively unsaturated metal atoms prevalent on small clusters. The absence of dispersion effects on selectivity suggests that MF and CO$_2$ form via the same surface intermediates, the number, but not the reactive properties, of which depends on cluster size.

Fig. 3 Methanol conversion turnover rates and product selectivities as a function of methanol conversion changed by varying residence time, 1 wt% Pd/Al$_2$O$_3$, 4 kPa CH$_3$OH, 45 kPa O$_2$, balance He, 313 K, catalyst dilution: 300 mg of a 1 : 150 Pd/Al$_2$O$_3$ : Al$_2$O$_3$ internally diluted sample and 200 mg additional Al$_2$O$_3$. This journal is © the Owner Societies 2007.
Supported Pd clusters also catalyze the selective oxidation of ethanol to acetaldehyde with extraordinary rates and very high selectivity to acetaldehyde and ethyl acetate at low temperatures (353 K) (Table 2). No CO was detected among the reaction products. Ethyl acetate can form via: (1) acetic acid esterification with ethanol, (2) oxidative condensation of acetaldehyde with ethanol, or (3) condensation of acetaldehyde. Acetic acid was not detected, but both acetaldehyde and acetic acid have been reported as products of ethanol oxidation on Pd/MgAl2O4 and Pt/MgAl2O4 at 453 K and also on Pt/Al2O3. At the lower temperatures of our experiments, any acetic acid formed may not desorb, except perhaps via condensation reactions that form ethyl acetate. Acetic acid desorption/decomposition on Pd(111) surfaces in the presence of chemisorbed oxygen led to acetic acid desorption only above 420 K, because adsorbed acetate precursors were stabilized against decomposition by chemisorbed oxygen.

Table 2 compares ethanol oxidation rates on the Pd/Al2O3 catalysts used here with those reported previously on RuO2/SnO2 and V2O5/TiO2–SiO2. Supported RuO2 clusters were recently reported as the most active catalysts for ethanol and methanol oxidation. Reaction rates are ~10 times higher on RuO2 clusters than on supported V2O5 catalysts. The Pd/Al2O3 catalysts reported here give turnover rates ~10 times greater than on RuO2 clusters at ~40 K lower reaction temperature, with >90% selectivity to desired acetaldehyde and ethyl acetate products.

**Experimental**

Supported Pd catalysts were prepared by incipient wetness impregnation of γ-Al2O3 (Alcoa, HiQ31, BET surface area: 280 m² g⁻¹, pore volume: 0.497 cm³ g⁻¹) with aqueous Pd(NO3)2·2H2O solutions (Aldrich, 99.9%) at ambient temperature. Impregnated powders were treated in ambient air at 398 K overnight and then in flowing dry air (Praxair, zero-grade, 0.7 cm³ g⁻¹ s⁻¹) by heating to 673 K at 0.17 K s⁻¹ and holding for 2 h. Al2O3 was treated in flowing dry air at 873 K for 5 h before impregnation with aqueous Pd solutions.

Pd dispersion was measured using O2 chemisorption at 308 K in a volumetric unit (Quantachrome, Autosorb-1) after treating samples in H2 (Praxair) after treating samples in H2 (Praxair, UHP) at 373 K for 1 h and evacuating at 373 K for 1 h to remove chemisorbed hydrogen. Saturation uptakes were measured by extrapolating isotherms to zero pressure and used to estimate the number of exposed Pd metal atoms by assuming one chemisorbed oxygen atom per exposed Pd atom. Metal dispersions were 0.10–0.43, corresponding to clusters ~2–10 nm in diameter for the Pd/Al2O3 samples used here.

Methanol and ethanol oxidation rates and selectivities were measured using a packed-bed quartz microreactor (1 cm inner diameter). Catalyst samples (0.5–4 mg) were diluted either with quartz or with alumina to prevent temperature gradients and used as 75–125 mm particles (pressed into wafers at 41 MPa, crushed and sieved). The catalyst bed height of the diluted samples was at least 1 cm in all runs. Samples were treated in 20% O2 (Praxair, 99.999%)/He (Praxair, UHP) flow (1.67 cm³ s⁻¹) by heating to 673 K at 0.083 K s⁻¹ and holding for 2 h. After this treatment, the samples were either used directly in methanol oxidation (“PdO sample”) or treated in H2 (Praxair)
(0.5 cm$^3$ s$^{-1}$) at 373 K for 1 h by heating from ambient temperature at 0.03 K s$^{-1}$ before methanol oxidation catalysis (“Pd sample”). Catalytic oxidation reactions were carried out using a mixture of CH$_3$OH (99.9%, EMD 2–8 kPa) or C$_2$H$_5$OH (99.5%, Aldrich, 4 kPa) and premixed 90% O$_2$–N$_2$ (Praxair, UHP, 9 kPa O$_2$) with He as balance (Praxair, UHP). Methanol and ethanol were introduced into the system using a syringe pump (Cole Parmer 74900). All lines were heated to > 353 K to prevent condensation of reactants or products.

Reactant and product concentrations were measured by online gas chromatography (Hewlett-Packard 6890GC) using a methylsilicone capillary column (HP-1, 50 m × 0.25 mm, 0.25 μm film thickness) and Porapak Q packed (80–100 mesh, 1.82 m × 3.18 mm) columns connected to flame ionization and thermal conductivity detectors, respectively. CH$_3$OH and C$_2$H$_5$OH oxidation turnover rates are reported on the basis of the Pd dispersion measured from O$_2$ chemisorption uptakes in reduced samples. Product selectivities are reported on a carbon basis as the percentage of the carbon in the CH$_3$OH or C$_2$H$_5$OH converted appearing as each product.

Pd dispersion effects were examined by dilution of Pd/Al$_2$O$_3$ catalysts (1, 4 and 6% wt Pd) prepared by mixing these catalysts with additional Al$_2$O$_3$ to give 0.005% wt Pd irrespective of the Pd content in the starting material (by mixing, pressing into pellets, crushing and sieving as described above). These samples were then treated in 20% O$_2$–He by heating at 0.083 K s$^{-1}$ to 675 K and holding for 2 h and then cooled to ambient temperature and treated in H$_2$ by heating at 0.03 K s$^{-1}$ to 373 K and holding for 1 h. This procedure was used to prepare samples with 43, 24 and 19% dispersions (for 1, 4 and 6% wt Pd). A sample with 10% dispersion was prepared by treating the 6% wt Pd/Al$_2$O$_3$ at 573 K instead of 373 K in H$_2$.

Concluding remarks

Supported Pd clusters catalyze methanol oxidation to methyl formate with significant turnover rates and > 90% selectivity at near-ambient temperatures. Pd metal clusters give higher turnover rates than PdO particles. Taken together with the observed inhibition of reaction rates by the reactant O$_2$, these data suggest that uncovered Pd ensembles on surfaces nearly covered by chemisorbed oxygen catalyze kinetically-relevant steps. Chemisorbed oxygen removes H-atoms formed in C–H bond activation steps and inhibits oxidation of methoxide intermediates to CO$_2$. Turnover rates are lower on smaller ensembles because their coordinatively unsaturated surfaces bind chemisorbed oxygen more strongly and decrease the concentration of Pd ensembles.

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References

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