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 O_2. 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 CO_2 formation, two functions essential for the high turnover rates and methyl formate selectivities reported here.

Introduction

Methanol (CH_3OH) reactions with O_2 lead to formaldehyde (HCHO), methyl formate (MF) and dimethoxymethane (DMM) products, useful as chemical intermediates,[1] on MoO_3,[2] V_2O_5[3,4] and Mo–Sn oxides.[5,6] Ru oxides[7] catalyze CH_3OH 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 liquid[8–13] and supercritical[14] media, but they have seldom been used to oxidize smaller and less reactive alcohols ($<C_4$). The oxidation of C_1–C_4 alcohols was reported to occur on "giant palladium clusters" with $Pd_{561}Phen_{60}(Oac)_{180}$ and $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ composition[15–18] (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-based[20,21] catalysts at low temperatures (<400 K).

Here we report the highest turnover rates reported for CH_3OH oxidation (up to 2.6 mol CH_3OH s^{-1} (surface Pd atom)$^{-1}$) with very high MF selectivities ($\sim$90%) at near-ambient temperatures (313 K). These materials also catalyzed ethanol oxidation with high turnover rates (0.21 s^{-1}) and acetaldehyde selectivities ($\sim$85%) at low temperatures

(353 K). CH_3OH 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 ($HCOOCH_3$ + HCHO═$HOCH_2COOCH_3$) *via* HCHO-coupling and to acetic acid *via* intramolecular isomerization ($HCOOCH_3$═CH_3COOH) 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–O_2 reactants either immediately after treatment in 20% O_2–He flow at 373 K (denoted as "PdO" sample) or after subsequent treatment of these samples in H_2 at 373 K (denoted as "Pd" sample). These two treatments led to markedly different CH_3OH oxidation rates, indicating that the Pd oxidation state strongly influences kinetically-relevant steps.

Turnover rates on PdO/Al_2O_3 (treated in 20% O_2–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 CH_3OH–O_2 reactant mixtures for 12 h, due to a very slow reaction rate. The gradual increase in CH_3OH oxidation rates on PdO samples at 333 K may indicate that PdO clusters reduce slowly during CH_3OH–O_2 reactions and that Pd metal surfaces catalyze kinetically-relevant CH_3OH oxidation steps much more efficiently than PdO surfaces, a conclusion confirmed by the marked increase in reactivity observed when these catalysts were treated in H_2 to form Pd metal clusters, as described below.

Pd metal centers were proposed to act as active sites in liquid-phase oxidation of cinnamyl[8] and benzyl[24] alcohols on Pd/Al_2O_3. Cordi and Falconer[25] reported that PdO/Al_2O_3 was less reactive than Pd/Al_2O_3 samples for the decomposition (in He) and oxidation (in O_2) of methoxide species formed *via* methanol dissociation. These reactivity differences were attributed to the

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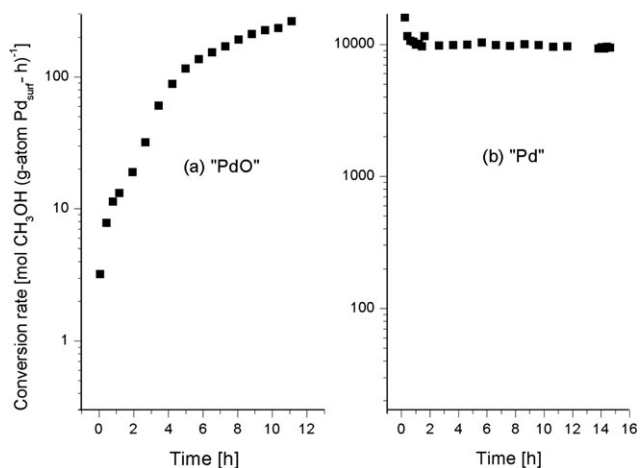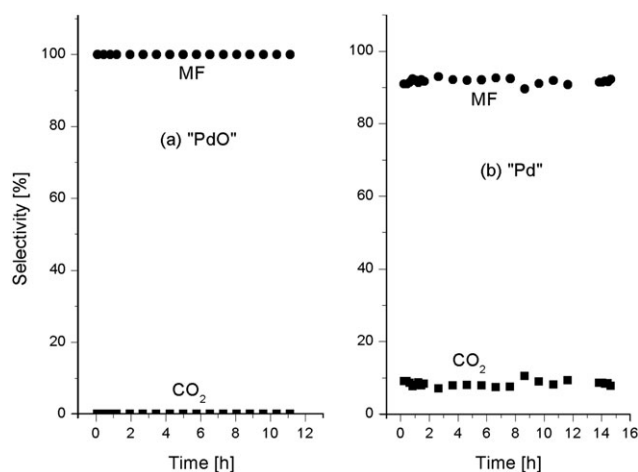
Fig. 1 (a) Methanol conversion rates with time on stream over a 4 wt% PdO/Al_2O_3 catalyst (dispersion 0.24) treated in 20% O_2–He at 675 K prior to reaction (conditions: 4 kPa CH_3OH, 9 kPa O_2, 1 kPa N_2, balance He, 1 cm^3 s^{-1} total flow, 333 K, 3.7 mg PdO/Al_2O_3, conversion: 0.02 to 1.9%, (the catalyst bed was diluted with 1 g of quartz)). (b) Methanol conversion rates with time on stream over a 1 wt% Pd/Al_2O_3 (dispersion 0.43) treated in 20% O_2–He at 675 K followed by treatment in H_2 at 373 K prior to reaction (conditions: 4 kPa CH_3OH, 9 kPa O_2, 1 kPa N_2, balance He, 1 cm^3 s^{-1} total flow, 313 K, conversion: 6.6%, (catalyst dilution: 150 mg of a 1 : 150 Pd/Al_2O_3 : Al_2O_3 internally-diluted sample and 350 mg additional Al_2O_3)).

Fig. 2 (a) Selectivities with time on stream over 4 wt% PdO/Al_2O_3 treated in 20% O_2–He at 675 K prior to reaction (conditions: 4 kPa CH_3OH, 9 kPa O_2, 1 kPa N_2, balance He, 1 cm^3 s^{-1} total flow, 333 K, 3.7 mg PdO/Al_2O_3, 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% Pd/Al_2O_3 treated in 20% O_2–He at 675 K followed by treatment in H_2 at 373 K prior to reaction (conditions: 4 kPa CH_3OH, 9 kPa O_2, 1 kPa N_2, balance He, 1 cm^3 s^{-1} total flow, 313 K, conversion: 6.6%, (catalyst dilution: 150 mg of a 1 : 150 Pd/Al_2O_3 : Al_2O_3 internally diluted sample and 350 mg additional Al_2O_3)).

slow extraction of lattice oxygen in the case of PdO. Thin PdO films (3–5 monolayers) deposited on Au substrates[26] did not activate CH_3OH up to 623 K, because of their low reactivity in CH_3OH dissociation and their resistance to reduction. In contrast, Pd metal films catalyzed methanol oxidation at 525 K, a temperature $\sim$200 K higher, however, than we report here on impregnated Pd/Al_2O_3 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–O_2 reactions on PdO/Al_2O_3 throughout these experiments (14 h; Fig. 2).

Pd/Al_2O_3 samples (prepared from PdO/Al_2O_3 by treatment in H_2 at 373 K for 1 h) gave much higher reaction rates at 313 K than unreduced samples (Fig. 1). Turnover rates were $\sim$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 CH_3OH–O_2 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 catalysts[8,24] and the catalytic combustion of CH_4 on PdO surfaces.[27]

The measured negative effect in O_2 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 O_2 is a stoichiometric reactant, specifically required for the oxidative removal of H-atoms, abstracted during methoxide decomposition, as H_2O (and of any CO, formed in side decomposition reactions, as CO_2) and for the suppression of unselective sequential dehydrogenation of methoxide intermediates to H_2 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 ($\sim$90%) and only small amounts of CO_2 (Fig. 2). MF, CO_2, and H_2O were the only products detected; CO and HCHO products were not detected (detection limits: 0.5 and 3%, at $\sim$10% conversion). The absence of HCHO indicates that its reaction with chemisorbed methoxide or its oxidation to CO_2 is fast. The absence of CO and H_2 among products is not surprising, because, if formed in surface reactions, they would desorb from Pd surfaces only at temperatures well above those required for methanol oxidation ($>$330 K for H_2; $>$480 K for CO[30]).

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/Al_2O_3 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 ($<$13%) at 340 K on 0.01 wt% Pd/γ-Al_2O_3 (42% dispersion).[19] HCHO yields increased with temperature (maximum yield, 11% at 480 K); CO_2 was the predominant product ($\sim$67% yield; 340 K) at all conditions in these studies. The same authors observed MF (maximum yield

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Table 1 CH_3OH oxidation turnover rates (per surface atom) and product selectivities on alumina-supported PdO, Pd, Pt and RuO_2 samples

Catalysts	Metal (wt%)	Temperature/K	CH_3OH conversion turnover rate to MF, HCHO and DMM/mol (g-atom M_{surf}-h)$^{-1}$ / conversion (%)	Selectivity			
				HCHO	MF	DMM	CO_2
Pd/Al_2O_3[a]	1.0	313	8460 / 6.6	—	90	—	10
PdO_x/Al_2O_3	4.0	333	234[b] / 1.6	—	100	—	—
Pd/Al_2O_3 [a,19]	0.01	340	4158 / 80	6	16	—	78
$Pt–Al_2O_3$ [21]	0.054	330	4575 / 93	1	60	—	39
RuO_2/Al_2O_3 [7]	4.4	393	70 / 20	11.6	30.1	57.4	1.0

[a] 4 kPa CH_3OH, 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_x" refers to samples treated in 20% O_2–He at 673 K for 2 h. [b] Rates on supported PdO_x clusters represent values measured after *ca.* 10 h of exposure to the CH_3OH–O_2 reactants.

60% at 330 K), HCHO, and CO_2 during methanol oxidation on 0.054 wt% Pt–Al_2O_3 (71% dispersion)[21] at modest temperatures (320–400 K) (Table 1). Similar MF selectivities ($\sim 50\%$ at 333 K and 60% conversion) were reported on 1 wt% Pt–Al_2O_3 [20] with low MF synthesis rates of 0.017 mol g^{-1} (atom Pd_{total})$^{-1}$ s^{-1}. Liquid phase methanol oxidation on "giant Pd clusters" ($Pd_{561}Phen_{60}(Oac)_{180}$; phen = 1,10-phenanthroline) gave methyl formate formation rates (0.005 mol g^{-1} (atom Pd_{total})$^{-1}$ s^{-1} at 293 K)[15] much lower than reported here (0.564 mol g^{-1} (atom Pd_{total})$^{-1}$ s^{-1} at 313 K). These large organometallic Pd clusters gave MF and CO_2 selectivities of 78 and 22%, respectively, at low methanol conversions (1.25% after 1 h in batch reactor). Table 1 also shows rates and selectivities on supported RuO_x catalysts, which also gave high combined selectivities to MF, DMM (dimethoxymethane), and HCHO at low temperatures and were recently reported as the most active among metal oxide catalysts.[7] Methanol oxidation turnover rates on these RuO_x catalysts are approximately two orders of magnitude lower at 80 K higher temperatures as compared to the Pd/Al_2O_3 catalyst used in this study.

Fig. 3 shows turnover rates (per surface Pd atom) (313 K, 4 kPa CH_3OH, 45 kPa O_2) and selectivities on 1 wt% Pd/Al_2O_3 catalyst (43% dispersion) as a function of methanol conversion (varied by changing the reactant space velocity). CH_3OH oxidation turnover rates decreased with increasing CH_3OH 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.[31] Selectivities were not influenced by space velocity, indicating that MF and CO_x are primary products and that MF does not oxidize to CO_x in secondary reactions at the conditions required for CH_3OH oxidation. MF can form *via*: (1) condensation of adsorbed methoxides with HCHO to form methoxymethanol intermediates (CH_3OCH_2OH) that then dehydrogenate to MF; (2) esterification of formic acid (HCOOH) intermediates formed by HCHO oxidation; or (3) HCHO dimerization *via* Tischenko-type reactions[2] (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*).[29] 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.[27] This 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_3OH 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.
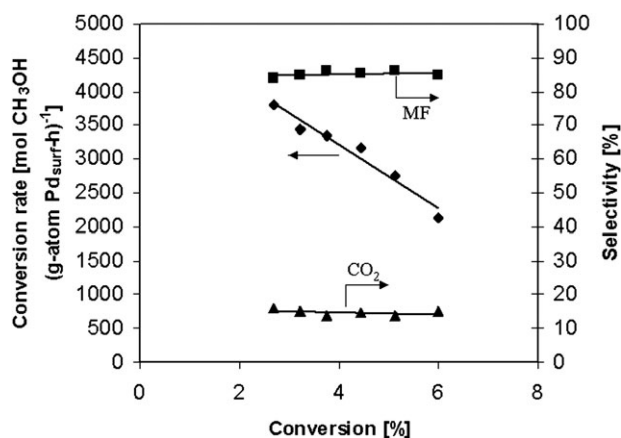
Fig. 3 Methanol conversion turnover rates and product selectivities as a function of methanol conversion changed by varying residence time, 1 wt% Pd/Al_2O_3, 4 kPa CH_3OH, 45 kPa O_2, balance He, 313 K, catalyst dilution: 300 mg of a 1 : 150 Pd/Al_2O_3 : Al_2O_3 internally diluted sample and 200 mg additional Al_2O_3.
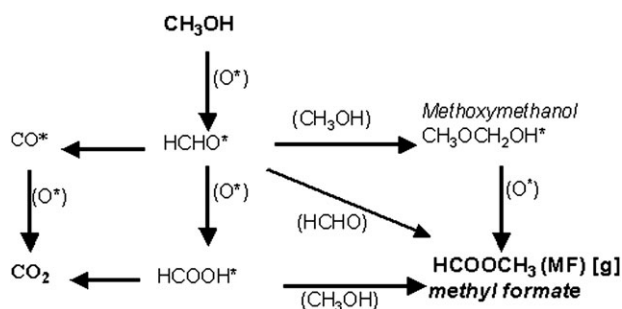
Scheme 1 Proposed reaction pathways (* represents adsorbed species).
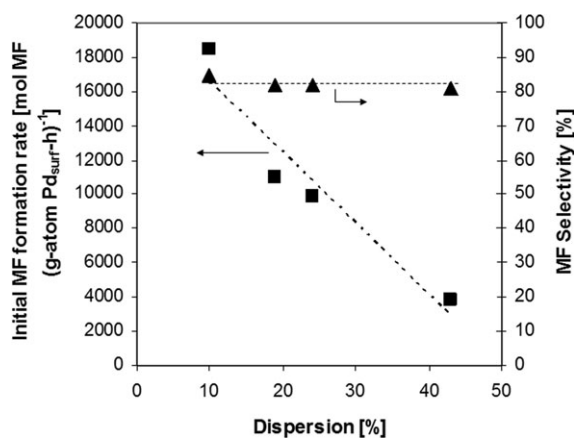
Fig. 4 Primary MF synthesis turnover rates and selectivities as a function of Pd dispersion measured by O_2 chemisorption, 4 kPa CH_3OH, 45 kPa O_2, balance He, 313 K, 0.005% wt Pd irrespective of the Pd content in the starting material.

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_x 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.[35] Acetic acid was not detected, but both acetaldehyde and acetic acid have been reported as products of ethanol oxidation on $Pd/MgAl_2O_4$ and $Pt/MgAl_2O_4$ at 453 K[36] and also on Pt/Al_2O_3.[37] 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.[38]

Table 2 compares ethanol oxidation rates on the Pd/Al_2O_3 catalysts used here with those reported previously on RuO_2/SnO_2[7] and V_2O_5/TiO_2–SiO_2.[39] Supported RuO_x clusters were recently reported as the most active catalysts for ethanol and methanol oxidation.[7] Reaction rates are ~ 10 times higher on RuO_x clusters than on supported V_2O_5 catalysts. The Pd/Al_2O_3 catalysts reported here give turnover rates ~ 10 times greater than on RuO_x 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-Al_2O_3 (Alcoa, HiQ31, BET surface area: 280 m^2 g^{-1}, pore volume: 0.497 cm^3 g^{-1}) with aqueous $Pd(NO_3)_2 \cdot 2H_2O$ 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 cm^3 g^{-1} s^{-1}) by heating to 673 K at 0.17 K s^{-1} and holding for 2 h. Al_2O_3 was treated in flowing dry air at 873 K for 5 h before impregnation with aqueous Pd solutions.

Pd dispersion was measured using O_2 chemisorption at 308 K in a volumetric unit (Quantachrome, Autosorb-1) after treating samples in H_2 (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.[40] Metal dispersions were 0.10–0.43, corresponding to clusters ~ 2–10 nm in diameter for the Pd/Al_2O_3 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 μm 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% O_2 (Praxair, 99.999%)/He (Praxair, UHP) flow (1.67 cm^3 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 H_2 (Praxair)

Table 2 CH_3CH_2OH oxidation rates and product selectivities on supported Pd, RuO_2 and V_2O_5 clusters

Catalysts	Metal (wt%)	Temperature/K	CH_3CH_2OH conversion turnover rate/mol (g-atom M_{surf}-h)$^{-1}$	CH_3CH_2OH conversion rate/mol (g-atom M_{total}-h)$^{-1}$ / conversion (%)	Selectivity			
					Acetaldehyde	Ethyl ether	Ethyl acetate	Acetal
Pd/Al_2O_3 [a]	4.0	353	747	179 / 2.3	84.5	—	13	2.5
RuO_2/SnO_2 [a,7]	4.1	393	76.3	16.4 / 10–15	93.4	—	2.0	4.6
V_2O_5/TiO_2–SiO_2 [b,39]	3.56	373	—	0.12 / —	92.4	2.7	—	4.9

[a] 4 kPa CH_3CH_2OH, 9 kPa O_2, 1 kPa N_2, balance He, 1 cm^3 s^{-1}. [b] 0.73 cm^3 h^{-1} CH_3CH_2OH (liquid), 0.086 cm^3 s^{-1} O_2 (gas), 0.37 cm^3 s^{-1} He (gas).[39]

(0.5 cm³ 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_3OH (99.9%, EMD 2–8 kPa) or C_2H_5OH (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 on-line 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_3OH and C_2H_5OH 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_3OH or C_2H_5OH converted appearing as each product.

Pd dispersion effects were examined by dilution of Pd/Al_2O_3 catalysts (1, 4 and 6% wt Pd) prepared by mixing these catalysts with additional Al_2O_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_2O_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.

Acknowledgements

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