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Facile preparation of Pd/organoclay catalysts with high performance in solvent-free aerobic selective oxidation of benzyl alcohol†

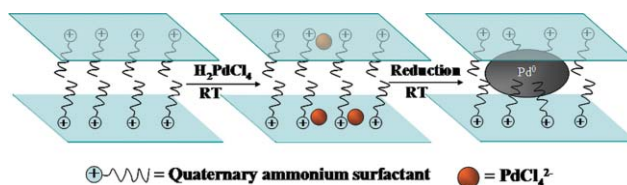**Hu Wang, Shao-Xin Deng, Zhu-Rui Shen, Jin-Gui Wang, Da-Tong Ding and Tie-Hong Chen***

A facile method to prepare Pd/organoclay catalysts was reported. At room temperature, in H_2PdCl_4 solution the quaternary ammonium surfactant modifiers intercalated in the organoclay adsorbed $PdCl_4^{2-}$ specifically and quickly. After reduction at room temperature, Pd nanoparticles were formed and well-dispersed in the organoclay matrix. The Pd/organoclay catalysts were used in aerobic oxidation of benzyl alcohol to benzaldehyde and exhibited high and stable activity. Particularly, the 0.2 wt% Pd/organoclay gave a remarkably high turnover frequency (up to 6813 h^{-1}) under base- and solvent-free conditions. Our method can be generally applied for the preparation of Ru, Au and Pt/organoclay catalysts.

Palladium is capable of catalyzing many reactions, such as hydrogenation, Heck and Suzuki couplings and aerobic oxidation of alcohols.[1,2] The preparation methods of supported Pd catalysts have been extensively investigated and different materials such as polymers,[3] carbon materials,[4] mesoporous silica,[5] zeolites,[6,7] and metal oxides[8,9] have been employed as the supports. Though the impregnation method has been widely used because of its easy manipulation,[10,11] the nucleation and dispersion of the metal particles are difficult to control and the size of the metal particles was relatively large. Alternatively, Pd/Al_2O_3[12] and Pd/SiO_2[13] have been prepared by electrostatic adsorption of metal precursors onto the inversely charged support surface. Sunagawa *et al.* prepared a series of metal oxide supported metal nanoparticles using a liquid-phase reductive deposition approach.[14] Hutchings and co-workers reported a sol-immobilization technique to prepare Au-Pd nanocrystalline catalysts supported on carbon.[15] Diamine surface-functionalized mesoporous polymers were fabricated to support highly dispersed Pd nanoparticles.[16] Metal and bimetal nanoparticles were hosted by polyaminoamine dendrimers grafted on mesoporous silica.[17]

Clay minerals have been regarded as excellent catalytic supports. The smectite-type clays, such as montmorillonite (MMT), contain negatively charged silicate layers and intercalated cations. Clay has been widely studied as the host of catalytic noble metals in its interlamellar space, and generally the ion-exchange property was utilized. For instance, Kiraly *et al.* prepared ultrafine Pd particles on cationic and anionic clays by an ion-exchange method, in which oppositely charged surfactant stabilized palladium hydrosol was added to an aqueous suspension of clay and stirred vigorously overnight to accomplish the ion exchange.[18–20] Because complete cation exchange of Pd^{2+} and Rh^{3+} ions with the interlayer cations in MMT was difficult, $[Pd(NH_3)_4]^{2+}$ and $[Rh(NH_3)_6]^{3+}$ cations were used to exchange with the cations in MMT. After reduction, Pd and Rh metal particles were formed and intercalated in the MMT.[21] The cation exchange process between the cationic metal precursors and cations in the clay could be slow and the exchange equilibrium would hinder complete loading of the metal precursors inside the clay. Sivakumar *et al.* also prepared palladium nanoparticles in the organo-modified bentonite based on an adsorption excess technique,[22] in which the Pd particles reduced by ethanol were dispersed in toluene to intercalate the clay. The catalyst preparation may be environment-unfriendly due to the employment of toxic and volatile organic solvents. Immobilization of Ru nanoparticles in ionic liquid (IL) exchanged MMT was performed by coordination of the functional groups of the ionic liquid with Ru^{3+}, followed by reduction with H_2,[23] however extra processes were needed to synthesize the specific IL.

Although much progress to improve the preparation method for supported noble metal catalysts has been made, industrial applications of those methods were still limited by the disadvantages of preparations, such as tedious synthesis and post-treatment procedures of the supports, employment of toxic and volatile organic solvents, energy-wasting in calcination and high costs of some specific reactants. A facile, mild, cheap and environmentally benign method is still demanded for the preparation of supported metal catalysts. Herein, we present a facile and cost-effective approach to prepare organoclay supported Pd catalysts. As shown in Scheme 1, at room temperature the quaternary ammonium surfactants in the interlamellar space of the organo-MMT adsorbed $PdCl_4^{2-}$ ions specifically from an aqueous solution of H_2PdCl_4. After reduction by $NaBH_4$

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**Scheme 1** Illustration of the preparation of Pd/organoclay catalyst.

solution at room temperature, well dispersed Pd nanoparticles were hosted in the organoclay matrix. Aerobic oxidation of alcohols has received much attention in recent years due to its economic and environmental advantages,[24] and different noble metal supported catalysts have been widely studied on this respect.[2] Here we studied the catalytic performance of the Pd/organoclay catalysts in liquid-phase oxidation of benzyl alcohol to benzaldehyde with oxygen (formula 1), and to our knowledge this is the first time that Pd/organo-MMT catalysts were used in the aerobic alcohol oxidation process.

$$C_6H_5CH_2OH + \tfrac{1}{2}O_2 \xrightarrow[Pd/organoclay]{} C_6H_5CHO + H_2O \quad (1)$$
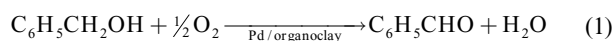
Organo-MMT (commercial name DK1, MMT > 95%) with a cation-exchange capacity (CEC) of 110 mmol per 100g was supplied by FengHong Company (Zhejiang, China). The organic modifiers in the organoclay were a mixture of octadecyltrimethyl ammonium cations (70%) and cetyltrimethyl ammonium cations (30%). Typically, 1 g DK1 was suspended in 25 mL of aqueous H_2PdCl_4 solution of desired concentration and stirred at room temperature for 10 minutes. The resulted precipitate was filtered, washed with distilled water for several times, and then dried at 60 °C. The obtained light orange power (denoted as Pd/DK1) was reduced with a freshly prepared solution of $NaBH_4$ (2 wt%) at room temperature, filtered, washed extensively with distilled water, and dried at 60 °C to obtain the black powder of catalyst (denoted as Pd/DK1-RE). We also prepared Au/DK1-RE catalyst by the same method with $HAuCl_4$ solution.

During the preparation process, when the organo-MMT (DK1) was added to the H_2PdCl_4 (or $HAuCl_4$) solution under stirring, within several minutes the color of DK1 changed from white to light orange (Fig. S1, ESI).† After filtration, the filtrate became transparent and colorless. ICP analysis indicated that the concentration of Pd in the starting solution and the filtrate after adsorption were 380 ppm and 2.3 ppm (for the case of 1.0 wt% Pd loading), respectively, indicating that over 99% of the total $PdCl_4^{2-}$ ions were adsorbed by DK1, and thus the loading of Pd on the organoclay could be easily controlled by the concentration of the H_2PdCl_4 solution. The interaction between the quaternary ammonium cations and $PdCl_4^{2-}$ could not simply be ascribed to electrostatic interaction of opposite charges, because when Na^+-MMT was used in the preparation, the color of Na^+-MMT and the solution did not change, even after 12 h (Fig, S1, ESI).† This implies that the coordination between the intercalated quaternary ammonium cations and $PdCl_4^{2-}$ anions could be responsible for the rapid adsorption of $PdCl_4^{2-}$. The d-spacing of DK1 was 2.1 nm, and after adsorption of $PdCl_4^{2-}$ the d-spacings of Pd/DK1 were slightly increased to 2.2 nm (Fig. 1a, b and c), indicating the intercalation of $PdCl_4^{2-}$ in the organo-MMT layers. The XPS spectrum of Pd 3d (Fig. 2a) displayed two peaks at 342.6 eV ($3d_{3/2}$) and 337.2 eV ($3d_{5/2}$), which were ascribed to Pd^{2+}, and the presence of chlorine was also confirmed by XPS analysis of Pd/DK1 (Fig. S2, ESI).†

When $PdCl_4^{2-}$ ions were reduced with $NaBH_4$ solution at room temperature, Pd nanoparticles were produced and dispersed inside the interlamellar space of the clay. Meanwhile, the quaternary ammonium surfactant would play a role to stabilize the Pd nanoparticles. Based on XRD patterns the d-spacings of Pd/DK1-RE remained unchanged or increased slightly after
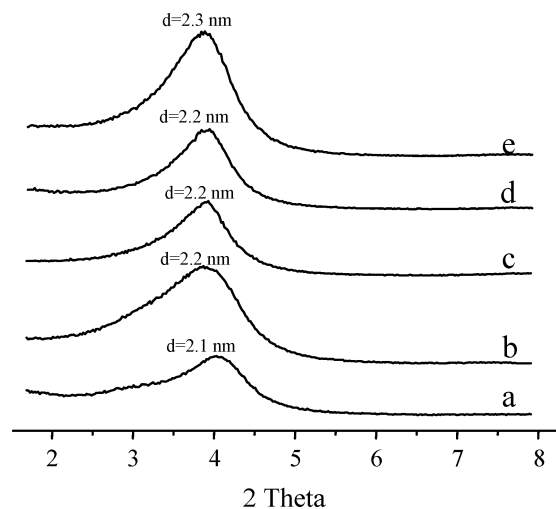

Fig. 1 XRD patterns of (a) DK1, (b) 0.2 wt% Pd/DK1, (c) 1.0 wt% Pd/DK1, (d) 0.2 wt% Pd/DK1-RE and (e) 1.0 wt% Pd/DK1-RE.
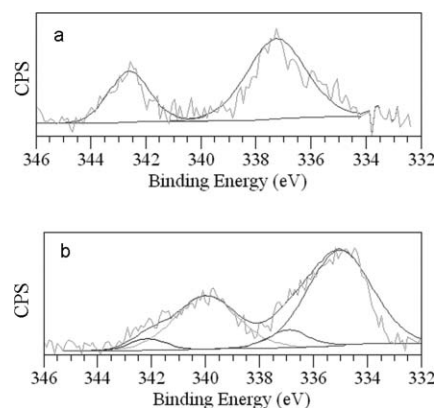
Fig. 2 Pd 3d XPS spectra of 1.0 wt% Pd/DK1-RE: (a) before $NaBH_4$ reduction and (b) after reduction.

reduction (Fig. 1d and e), probably due to the small size of the Pd nanoparticles. This point was also supported by the wide-angle XRD pattern (Fig. S3, ESI),† which did not display diffraction peaks of Pd, implying that the size of Pd nanoparticles was too small to be detected by XRD. Fig. 2b shows the Pd 3d XPS spectra of 1.0 wt% Pd/DK1-RE and the peaks at 339.9 eV (Pd $3d_{3/2}$) and 335.0 eV (Pd $3d_{5/2}$) were ascribed to Pd^0 in the catalyst. The shoulder at 342.1 eV (Pd $3d_{3/2}$) and 336.9 eV (Pd $3d_{5/2}$) were due to surface oxidation of the palladium nanoparticles upon exposure in air. In the XPS analysis of Pd/DK1-RE no Cl could be detected (Fig. S2, ESI),† indicating that after reduction the Cl^- anions were washed out of the organoclay. TEM images (Fig. 3) of Pd/DK1-RE show that Pd nanoparticles were well-dispersed within the organoclay.

The commercially available organoclay was low cost compared with other supports prepared by complex and tedious processes. The specific interaction between the quaternary ammonium surfactant and $PdCl_4^{2-}$ at room temperature offered an easy control of Pd loadings. Meanwhile, without using organic solvents and calcination, the method reported here is environmentally benign. This method could be used as a versatile way to preparing other organoclay-supported nanosized noble metal catalysts by altering the metal precursors.
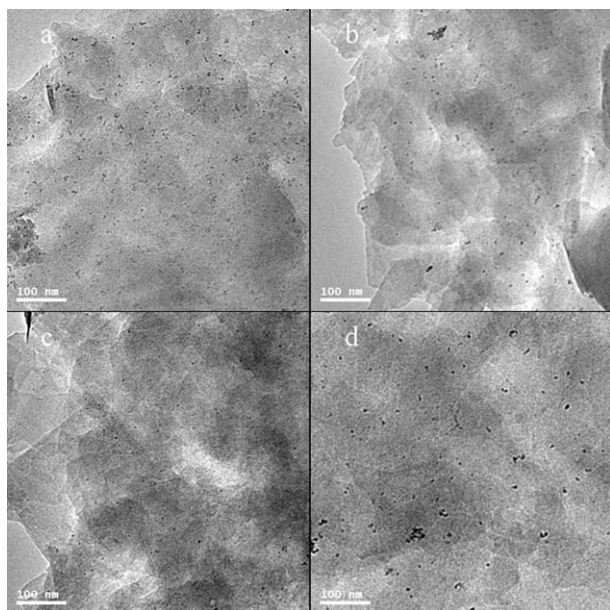
Fig. 3 TEM images of Pd/DK1-RE, with Pd loading of 1 wt% (a), 0.5 wt% (b), 0.2 wt% (c) and 1 wt%Pd/DK1-RE after reuse for three cycles (d).

The catalytic activities of Pd/DK1-RE catalysts were tested by aerobic oxidation of benzyl alcohol and the results are listed in Table 1. The main product was benzaldehyde, however further oxidation of benzaldehyde could occur to give benzoic acid, and benzylbenzoate was produced by esterification of benzoic acid and benzyl alcohol. The Pd/DK1-RE catalysts exhibited good performance in the presence of toluene as a solvent at 100 °C (Table 1, entries 1 and 2). The 0.2 wt% Pd/DK1-RE gave a turnover frequency (TOF) as high as 6916 h^{-1} (substrate : Pd= 10 319). As reported in literature, 0.3% Pd/hydroxyapatite

catalyst gave TOFs less than 500 h^{-1} with PhCF$_3$ as solvent,[2] and the TOF was 1585 h^{-1} for the commercial 0.5 wt% Pd/Al$_2$O$_3$ working in supercritical CO$_2$.[25] The Pd/DK1-RE catalysts were also highly effective under base- and solvent-free conditions (Table 1, entry 3). The 0.2 wt% Pd/DK1-RE catalyst exhibited a remarkably high TOF of 6813 h^{-1} (substrate : Pd= 10 319). TOFs of other catalysts for the oxidation of benzyl alcohol under solvent-free conditions, such as 3300 h^{-1} for 0.32 wt% Pd/Al$_2$O$_3$[12] and 2900 h^{-1} for 5% Au/MnO$_2$[26] were reported. The performance of the Pd/DK1-RE catalyst was much higher than that of the 1.0 wt% Pd/Al$_2$O$_3$ prepared by the conventional impregnation method (Table 1, entry 4).

We also examined the recycling of the 1.0 wt% Pd/DK1-RE catalyst and, as listed in Table 1, the conversion of benzyl alcohol decreased very slightly after three repeated uses, and this small variation could also be due to the loss of some catalyst during the re-collecting process by centrifugation. This indicated that the catalysts were stable and could be readily re-used. TEM measurements for the 1.0 wt% Pd/DK1-RE after the third re-use revealed that the mean size of Pd nanoparticles was slightly larger than that of the fresh catalyst. The stabilization effect of the quaternary ammonium surfactants and the confinement in the interlamellar space of the organoclay would prevent the Pd nanoparticles from leaching. When extra benzyl alcohol (1 mL) was added into the filtrate after extraction of the catalyst, and after 1 h at the same reaction condition, no further conversion was detected by GC. This indicated that no observable leaching of the Pd nanoparticles into the solution during the reaction.

In summary, a facile and environmentally benign method was presented to prepare organoclay supported noble metal catalysts. With organoclay as support, after simple adsorption of PdCl$_4$$^{2-}$ anions and reduction at room temperature, Pd/organoclay catalysts with well-dispersed Pd nanoparticles were prepared and exhibited high and stable activity in aerobic oxidation of benzyl alcohol. Due to employment of a commercial organoclay, the facile preparation process and the high activities, the catalysts could be promising in practical applications. Further extension of these catalysts to other reactions catalyzed by supported Pd nanoparticles, as well as preparation of other noble metal catalysts (Au, Ru and Pt) supported on organoclay and their catalytic applications, are currently in progress.

Acknowledgements

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Table 1 Performance of the Pd/DK1-RE catalysts in the aerobic selective oxidation of benzyl alcohol to benzaldehyde[a]

Entry	Catalyst	Time/h	Conv. (%)	Selec.[b] (%)	TOF[c]/h^{-1}
1[d]	1.0 wt% Pd/Dk1-RE	1	89	97	1837
		2	95	96	981
		3	99	93	681
		2[e]	88	96	908
		2[f]	92	96	950
2[d]	0.2 wt% Pd/Dk1-RE	1	67	98	6916
		4	94	98	2426
3[g]	0.2 wt% Pd/Dk1-RE	1	66	91	6813
		2	83	90	4283
4[h]	1.0 wt% Pd/Al$_2$O$_3$	1	39	79	1006
		2	70	78	903

[a] Without catalysts (or with pure DK1 as catalyst) the conversion of benzyl alcohol was less than 1% after 2 h of reaction. Without oxygen gas with the Pd-catalyst the conversion was less than 4% after 2 h of reaction. [b] Entry 1–3, the by-products were benzoic acid and benzylbenzoate; entry 4, the by-product was toluene. [c] TOF (turnover frequency) was calculated by the moles of substrates converted per mole of Pd per hour. [d] O$_2$ flow, 25 mL min^{-1}; 100 °C; catalyst 0.05 g; benzyl alcohol 9.7 mmol; K$_2$CO$_3$ 0.1 g; 10 mL toluene as solvent. [e] Second use of the catalyst. [f] Third use of the catalyst. [g] Base- and solvent-free reaction; O$_2$ flow, 25 mL min^{-1}; 100 °C; catalyst 0.25 g; benzyl alcohol 48.5 mmol. [h] The Pd/Al$_2$O$_3$ catalyst was prepared by conventional impregnation method and 0.1 g catalyst was used under base- and solvent-free condition.

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