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# Oxide surface-promoted Pd-complex catalysis for intramolecular O-activated alkene hydroamination: catalyst preparation, characterization, and performance†

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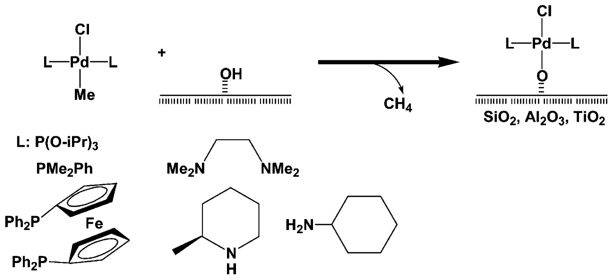
**Supported Pd–P and Pd–N complexes prepared by a selective reaction of Pd-monomer precursors with $SiO_2$, $Al_2O_3$ and $TiO_2$ surfaces and characterized by EXAFS, XPS, XRF and gas analysis exhibited oxide surface-promoted catalysis for the catalytic intrahydroamination of 3-amino propanol vinyl ether to produce a cyclic amine.**

Amine derivatives, which are valuable and important chemicals,[1] have been produced *via* several synthetic processes. Among them the direct synthesis of a new C–N bond by the addition of an amine to an unsaturated C–C bond, *i.e.* hydroamination, is of great significance. However, this reaction is generally slightly exothermic and entropically negative,[2] and the hydroamination of alkenes is highly difficult compared to that of alkynes because of the lower electron density of C=C bonds than C≡C bonds.[3] A limited number of homogeneous lanthanide[4] and late transition metal[5–7] complexes are known to be active for the reactions of activated alkenes in solutions. On the other hand, there are few reports on heterogeneous catalysts active for the hydroamination of alkynes, such as ion exchanged zeolites,[8,9] ionic-liquid supported metal complexes,[10] and $SiO_2$-tethered Pd complexes.[11,12] There are no examples of heterogeneous catalysts for alkene hydroamination. Design of active metal sites with definite structure and composition on oxide surfaces in a controllable manner is still a difficult challenge because of the lack of an established method for the design and few techniques for characterization of the surface species.[13] Here we report supported Pd-complex catalysts on $SiO_2$, $Al_2O_3$ and $TiO_2$, which are active and durable for the catalytic intrahydroamination of 3-amino propanol vinyl ether to produce the corresponding cyclic amine.

Palladium is one of the active metals for hydroamination, but its lower stability to aggregation to an almost inactive species under the reaction conditions is one of the major problems of its use as a catalyst. Furthermore, it is known that the hydroamination activity of Pd complexes greatly depends on the nature of their anionic ligands, and hence good catalytic performance of Pd complexes is expected by chemical bonding to oxide surfaces to regulate their coordination sphere. We have prepared novel Pd–P and Pd–N complexes attached on oxide surfaces *via* a Pd–O bond formed by the chemical reaction between a methyl ligand of Pd complexes and hydroxyl groups of the surfaces.[14]

Some new Pd monomers with Pd–P (P: $P(O–iPr)_3$, $PMe_2Ph$ and dppf) and Pd–N (N: tmeda, methylpiperidine and cyclohexylamine) bonds were prepared in two or three steps (see supporting information 1†).[15,16] These $PdMeClL_2$ precursors were supported on $SiO_2$, $Al_2O_3$ and $TiO_2$ surfaces (Scheme 1), where the methyl groups selectively reacted with surface hydroxyl groups to evolve $CH_4$ in the gas phase. Pd loadings in the catalysts were determined by XRF. The amounts of produced $CH_4$ per Pd were measured to be unity by GC (Table 1). The nitrogen and phosphorus ligands of the precursors did not dissociate into the solution during the attaching reaction. The chlorine ligands remained on Pd as estimated by the intensity ratios of XPS Cl 2p and Pd 3d peaks for both the supported Pd–P and Pd–N complexes (Table 1). The XPS binding energy of Pd $3d_{5/2}$ was 336.4 eV, indicating that the Pd precursors were attached on the surfaces maintaining the oxidation state of Pd(II). The curve-fitting analysis for the EXAFS Fourier-transformed spectra at Pd K edge for the Pd–P complexes on $SiO_2$ revealed the existence of a Pd–O bond at 0.212 nm (CN (coordination number) = 0.8) and Pd–P (Cl) bonds at 0.235 nm (CN = 3.1) (see supporting information 2†). The bond distances in the Pd–N complexes supported on $SiO_2$ (Pd–N (O): 0.213 nm and Pd–Cl: 0.235 nm) were similar to those in the supported Pd–P complexes (see supporting infomation 3†). The results demonstrate a similar bonding feature in the coordination sphere around Pd in the catalysts derived from both precursors.



**Scheme 1** Preparation of the supported Pd–P and Pd–N monomers on $SiO_2$, $Al_2O_3$ and $TiO_2$.

**Table 1** Pd loadings, amounts of $CH_4$ evolved during the attachment of Pd precursors, amounts of Cl remaining in the catalysts, and Pd $3d_{5/2}$ binding energies

| Ligand | Support | Pd loading[a]/wt% | $CH_4$/Pd[b] | Cl/Pd[c] | Pd $3d_{5/2}$/eV[d] |
|---|---|---|---|---|---|
| $P(O–iPr)_3$ | $SiO_2$ | 0.23 | 0.9 | — | — |
| $PMe_2Ph$ | $SiO_2$ | 0.34 | 1.0 | 1.0 | 336.4 |
| dppf | $SiO_2$ | 0.11 | 0.9 | 1.1 | — |
| tmeda | $SiO_2$ | 0.44 | 1.1 | — | — |
| Cyclohexylamine | $SiO_2$ | 0.25 | 1.1 | — | — |
| Methylpiperidine | $SiO_2$ | 0.16 | 1.0 | 1.1 | 336.4 |
| Methylpiperidine | $Al_2O_3$ | 0.25 | 1.0 | 1.0 | 336.4 |
| Methylpiperidine | $TiO_2$ | 0.28 | 1.0 | 1.1 | 336.3 |

[a] Measured by XRF. [b] All gaseous products in a closed system were analyzed by GC. [c] Estimated by the ratios of Cl 2p and Pd 3d XPS signals. [d] Binding energies were referred to those of Si 2p of $SiO_2$ (103.8 eV), Al 2p of $Al_2O_3$ (74.2 eV), and Ti $2p_{3/2}$ of $TiO_2$ (458.5 eV).

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† Electronic supplementary information (ESI) available: experimental details of Pd precursors and EXAFS spectra of supported Pd complexes. See http://www.rsc.org/suppdata/cc/b4/b408419e/

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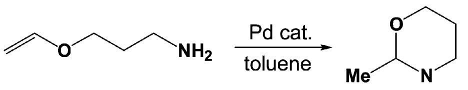
The reactivity of some of the Pd precursors to the oxide surfaces was low at ambient temperature. We found that evacuation of the supported precursors at 298–343 K promoted the chemical attachment of the Pd precursors on the surfaces without any decomposition though homogeneous Pd complexes are easy to decompose to Pd black under such conditions. Indeed, there are no peaks attributed to Pd–Pd bonding in the EXAFS spectra independent of Pd loading. Thus we have concluded that the structures of supported Pd complexes are Pd monomers with a Pd–O (surface) bond, a Pd–Cl bond, and two Pd–L (L: P or N) bonds (Scheme 1). The attachment temperatures were carefully regulated between the temperature for the Pd complexes to react with the surface hydroxyl groups and that for the supported Pd complexes to decompose on the surface. However, the Pd–P complexes on $Al_2O_3$ and $TiO_2$ decomposed to metal aggregates before complete attachment to the surface.

Table 2 shows the catalytic activities of the hydroamination of 3-amino propanol vinyl ether in toluene at 343 K. The homogeneous Pd precursors in toluene solutions were completely inactive for the reaction; instead the Pd precursors decomposed. Both Pd–P and Pd–N complexes exhibited significant catalytic activities after attaching on the oxide surfaces, and there is no leaching of the Pd complexes during the catalysis as proved by XRF on all three surfaces (Table 2). The catalytic reactions on all the supported catalysts proceeded linearly with reaction time and the catalysts were reusable after filtration (Table 2). The filtrate did not have any activity for the reaction. Furthermore, no change in the coordination numbers and bond distances around the Pd center after the catalytic reaction was observed in the EXAFS analysis, suggesting that the supported Pd complexes are not only active but also durable for the catalytic hydroamination. Decomposed metal aggregates formed by heating these precursors at high temperatures; these precursors did not exhibit any catalytic activity for the reaction. There are significant differences in the catalytic performances between the P and N ligands. The $SiO_2$-supported phosphorus-ligand complexes are more active for the reaction compared to the nitrogen-ligand complexes (Table 2). The coordination of the C=C bond of alkenes is an important step for the hydroamination, which is affected by the electron density of the Pd center. In the Pd–P complexes it may positively be regulated by a Pd–P orbital hybridization.

**Table 2** The catalytic activities (turnover frequencies: TOF) of unsupported and supported Pd-complex catalysts for the hydroamination of 3-amino propanol vinyl ether[a]



| Ligand | Support | Pd loading/wt% | TOF/$h^{-1}$ |
|---|---|---|---|
| $P(O–Pr^i)_3$ | Unsupported | [b] | 0 |
| $PMe_2Ph$ | Unsupported | [b] | 0 |
| Methylpiperidine | Unsupported | [b] | 0 |
| Cyclohexylamine | Unsupported | [b] | 0 |
| $P(O–iPr)_3$ | $SiO_2$ | 0.23 | 15.3 |
| $PMe_2Ph$ | $SiO_2$ | 0.34 | 18.8 |
| dppf | $SiO_2$ | 0.11 | 22.6 |
| tmeda | $SiO_2$ | 0.44 | 1.1 |
| Cyclohexylamine | $SiO_2$ | 0.25 | 9.1 |
| Methylpiperidine | $SiO_2$ | 0.16 | 5.0 |
| Methylpiperidine[c] | $SiO_2$[c] | 0.16[c] | 4.8[c] |
| Methylpiperidine | $Al_2O_3$ | 0.32 | 1.6 |
| Methylpiperidine | $Al_2O_3$ | 0.25 | 1.8 |
| Methylpiperidine[c] | $Al_2O_3$[c] | 0.25[c] | 1.7[c] |
| Methylpiperidine | $TiO_2$ | 0.28 | 3.7 |
| Methylpiperidine | $TiO_2$ | 0.22 | 3.5 |
| Methylpiperidine[c] | $TiO_2$[c] | 0.20[c] | 3.4[c] |

[a] The hydroamination of 3-amino propanol vinyl ether was performed in a toluene solution at 343 K under a nitrogen atmosphere. *N*-octane was added as an internal standard. Pd/3-amino propanol vinyl ether/toluene = 1/200/17000. The reaction was monitored by FID–GC and GC–MASS. [b] 3-Amino propanol vinyl ether/Pd = 200 (molar ratio); Pd: $5.5 \times 10^{-4}$ mol $l^{-1}$; toluene: 30 ml. [c] Reuse.

To examine support effect, the Pd–methylpiperidine complex was supported on three different supports, $SiO_2$, $Al_2O_3$, and $TiO_2$. The structures of the supported Pd complexes were also characterized to have a Pd–O (surface) bond (0.213 nm), a Pd–Cl bond (0.235 nm), and two Pd–N bonds (0.213 nm) by EXAFS, XPS, XRF, and gas analysis. Significant support effect on the catalytic activity was observed as shown in Table 2. The activity of the supports alone is zero for the hydroamination. The $SiO_2$ support is most favorable for the Pd catalysis, while the catalytic activity on $Al_2O_3$ is less than one third of that on $SiO_2$. $TiO_2$ shows an intermediate support effect. The order of the activities for the support is the same as that of $pK_a$, $SiO_2 > TiO_2 > Al_2O_3$. The most ionic bond Pd–OSi is favorable for the hydroamination of alkenes, while the Pd–OAl bond with relatively more covalent character does not efficiently promote the reaction.

In conclusion, we have prepared the $SiO_2$, $Al_2O_3$, and $TiO_2$-supported Pd-monomer catalysts, and characterized the local structures of active Pd species by means of XRF, XPS, EXAFS, and $CH_4$ analysis. The supported Pd catalysts exhibit high catalytic performances with high durability for the intrahydroamination of 3-amino propanol vinyl ether to form the cyclic amine. To our knowledge, these are the first heterogeneous catalysts for alkene hydroamination. The Pd–O (surface) bond provides not only the stability of supported Pd complexes to prevent from gathering but also the catalytic activity for the hydroamination by a change in the nature of the Pd center through the Pd–surface interaction.

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14 All manipulations for catalyst preparation were performed under an $N_2$ (99.9999% purity) atmosphere. Synthesized Pd precursors (see supporting information 1) were supported at 293 K on $SiO_2$ (Aerosil 200), $Al_2O_3$ (Degussa, $Al_2O_3$ C), and $TiO_2$ (Degussa, P-25) calcined at 773 K for 2 h. Solvents used in this study were as follows: *n*-hexane ($P(O–iPr)_3$ and $PMe_2Ph$), toluene (dppf), and dichloromethane (tmeda, methylpiperidine, and cyclohexylamine). After evaporation of the solvents, further treatment under vacuum was done: $P(O–iPr)_3$ 323 K, 1 h; $PMe_2Ph$ 318 K, 1 h; dppf 343 K, 1 h; tmeda 323 K, 1 h; cyclohexylamine 343 K, 1 h. EXAFS spectra were measured at KEK-PF BL-10B at 15 K in a transmission mode. Background subtraction was conducted by the AUTOBK program, and Fourier-transformed spectra ($k$ = 3–14, $R$ = 1.2–2.4) were fitted in R space by FEFFIT program.
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