Benzene Hydroxylation

DOI: 10.1002/anie.201203275

A Vanadyl Complex Grafted to Periodic Mesoporous Organosilica: A Green Catalyst for Selective Hydroxylation of Benzene to Phenol[**]

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Dedicated to Professor Sir Fraser Stoddart on the occasion of his 70th birthday

Design of catalytically active periodic mesoporous organosilica (PMO) is a novel strategy for transforming a catalytically important transition-metal complex into a heterogeneous catalyst.[1] Vanadyl(IV) acetylacetonate, [VO(acac)$_2$], is an important homogeneous catalyst widely used for various organic transformations.[2] The immobilization of the [VO(acac)$_2$] complex onto silica gels, mesoporous silicas, and alumina has been achieved through a wet impregnation process followed by the calcination.[3] [VO(acac)$_2$] has also been anchored onto activated carbon materials, silica materials, and clay materials by the reaction between the carbonyl group of the acetylacetonate ligand and the amino group pre-grafted onto the material surfaces.[4] Herein, we report the synthesis of a new type of PMO grafted with catalytically active vanadyl(IV) centers and the application of the PMO as a sustainable catalyst for selective hydroxylation of benzene to phenol. Unlike those post-functionalized porous materials, where the transition-metal complexes locate at the surfaces and the pore channels,[5] our current work provides a unique way of immobilizing [VO(acac)$_2$] into PMO where the [VO(acac)$_2$] centers are homogeneously distributed at a molecular level as an integral part of the silica framework.

Selective hydroxylation of benzene to phenol is a fundamental catalytic organic reaction with great academic and commercial importance.[6] So far, many potential attempts have been made for direct hydroxylation of benzene to phenol[7] using different environmentally friendly oxidants, such as O_2,[8] H_2O_2,[9] and N_2O,[10] through a single-step process instead of a three-step cumene process reported by Hock and Lang in 1944, which has still been employed widely as a commercial process for the production of phenol.[11] Although the direct hydroxylation of benzene in the gas phase has been explored extensively, the process is associated with a major limitation, namely, the rapid deactivation of catalysts on account of the coke formation.[12] Among the reported processes, the direct hydroxylation of benzene to phenol with H_2O_2 in liquid phase has been investigated[13–18] as an environmentally friendly process. Such a process, however, is often affected by a poor selectivity, that is, a substantial overoxidation of phenol occurs, forming various by-products, such as catechol, hydroquinone, and benzoquinone.[6a] Titanium silicalite (TS-1) is a well-known catalyst for the hydroxylation of benzene to phenol in the presence of H_2O_2, offering a conversion X of 31% and a selectivity S of 95%.[13] Modified titanium silicalite catalyst, TS-1B, affords a low efficiency ($X = 4.6\%$, $S = 43\%$) for the hydroxylation.[14] Other catalysts, such as iron-impregnated carbon ($X = 50\%$, $S = 40\%$),[15] copper-containing ternary hydrotalcite ($X = 1.6\%$, $S = <100\%$),[16] and [Fe(dds)$_3$]-based microemulsions ($X = 56.1\%$, $S = 50.5\%$; dds = dodecanesulfonate)[17] have also been reported. To increase the selectivity from benzene to phenol, Bianchi et al. have developed a water/acetonitrile biphasic reaction method in which phenol is extracted into acetonitrile and the catalyst ($FeSO_4$) is soluble in the aqueous medium along with H_2O_2.[7a] By employing this method, a significant selectivity enhancement from benzene to phenol ($X = 97\%$) was observed, although the benzene conversion was found to be only 8.6%. In another report by Zhang et al., Keggin-type molybdovanadophosphoric heteropoly acids were found to be effective homogeneous catalysts for the same reaction.[18] They have achieved the maximum benzene conversion of 34.5% with a selectivity of 100% towards the phenol formation by using H_2O_2 as an oxidant in a solvent mixture of glacial acetic acid and acetonitrile. The recyclability of the catalysts and the product separation are two major issues in such system. Vanadyl complexes are another important class of catalysts because of their intrinsic ability towards the hydrocarbon oxidation, including direct hydroxylation of benzene.[19] Different vanadyl complexes have been developed to date for the catalysis in two ways: 1) homogeneous VO-catalysts,[20] and 2) VO-catalysts immobilized on different solid supports.[21] As compared with previous reports wherein either the hydroxylation selectivity from benzene to phenol or the recyclability of catalysts has always been a challenge, our [VO(acac)$_2$]-grafted PMO catalyst consistently showed a selectivity of 100% towards the phenol formation with a benzene conversion of over 27%. The catalyst shows a high

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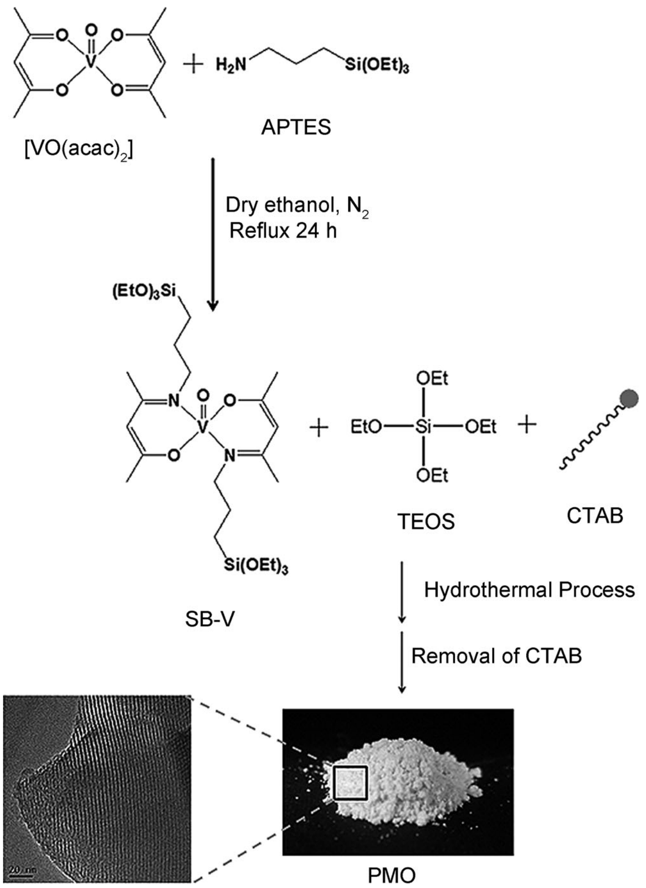
[**] We thank the Singapore National Research Foundation Fellowship (NRF2009NRF-RF001-015), Singapore National Research Foundation CREATE program—Singapore Peking University Research Centre for a Sustainable Low-Carbon Future, and Nanyang Technological University for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203275.

recyclability and can be used for many cycles. Furthermore, the benzene hydroxylation by the [$VO(acac)_2$]-grafted PMO catalyst is an environmentally friendly catalytic process in terms of the selectivity and recyclability.

To prepare a PMO for catalytic applications, it is desirable to have a high degree of functionality within PMO by choosing an organic precursor with suitable complexity and molecular size. Another crucial requirement associated with the preparation of a PMO is to synthesize an organic precursor with at least two terminal alkoxysilanes.[22] In the current work, an essential organic precursor (denoted as SB-V) was synthesized (Scheme 1) through the Schiff base condensation between the amino group of 3-aminopropyltriethoxysilane (APTES) and the carbonyl unit of [$VO(acac)_2$] (see the Supporting Information for the synthetic procedure). The formulation of SB-V was confirmed by mass spectrometry, elemental analysis, X-ray photoelectron spectroscopy (XPS), and FTIR spectroscopy. Compared with the FTIR spectrum of [$VO(acac)_2$] (Supporting Information, Figure S1), the FTIR spectrum of SB-V shows the appearances of new bands centered at 1608 and 1579 cm^{-1} that are due to the combinational vibration of newly formed C=N bonds, and a complete disappearance of the band at 1556 cm^{-1}, which is assigned to the initial C=O bonds in [$VO(acac)_2$].[23] The observations provide solid evidence for the formation of SB-V by the Schiff base condensation between [$VO(acac)_2$] and APTES.



Scheme 1. The synthesis of SB-V and periodic mesoporous organosilica materials (PMOs). TEOS = tetraethyl orthosilicate, CTAB = cetyltrimethylammonium bromide.

A reported procedure[1c] was modified to synthesize the novel PMO through the co-condensation of tetraethyl orthosilicate (TEOS) and SB-V using cetyltrimethylammoniumbromide (CTAB) as the structure-directing template. As the phase separation and the self-condensation of organosilica precursors are two major disadvantages for the preparation of PMOs, an optimum reaction condition is needed to obtain a periodic mesoporous structure grafted covalently with organic functionality. For the optimization of synthetic condition, a series of PMOs were prepared by using TEOS and SB-V with different molar ratios ranging from 80:20 to 95:5. Although we were able to synthesize mesoporous materials with all the molar ratios, inductively coupled plasma (ICP) analysis results show very low vanadium contents for most of the prepared PMO samples, except for two PMO samples prepared with molar ratios of 80:20 and 85:15 (denoted as PMO-1 and PMO-2, respectively). Therefore, we limit our scope of discussions within PMO-1 and PMO-2.

The FTIR spectra (Figure 1) of PMO-1 and PMO-2 show the characteristic peaks of MCM-41 type materials (Supporting Information, Figure S2),[24] indicating the formation of mesoporous organosilicas. Peaks in the range of 1550 to 1400 cm^{-1} assigned to the SB-V unit can be observed in both the FTIR spectra, providing clear evidence of grafting the SB-V unit onto the organosilica framework. The predominant band of physisorbed water centered at 1630 cm^{-1} overlaps completely with the peak of the C=N bonds. A broad band around 3426 cm^{-1} is attributed to the O–H stretching vibration of hydrogen bonded silanols on PMOs.[25]

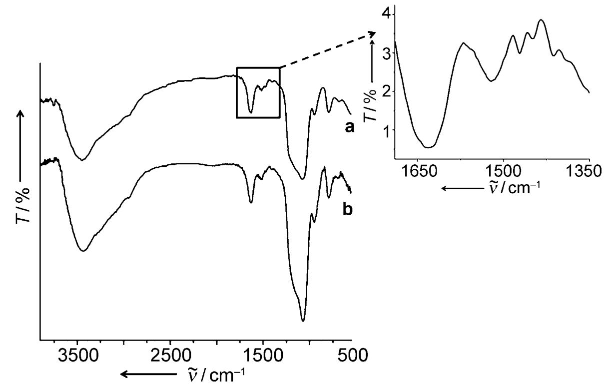


Figure 1. FTIR spectra of a) PMO-1 and b) PMO-2.

The solid-state ^{13}C cross-polarization magic angle spinning (CP MAS) NMR spectra of PMO-1 and PMO-2 (Figure 2) exhibit strong signals at 9.1, 22.0, 30.0, 42.6, and 63.4 ppm, which are attributed to different aliphatic primary and secondary carbon atoms (Figure 2, inset). Along with these signals, two minor peaks at 162 and 185 ppm are assigned to the carbon atoms from the imine and enol groups of the incorporated SB-V. These observations further dem-

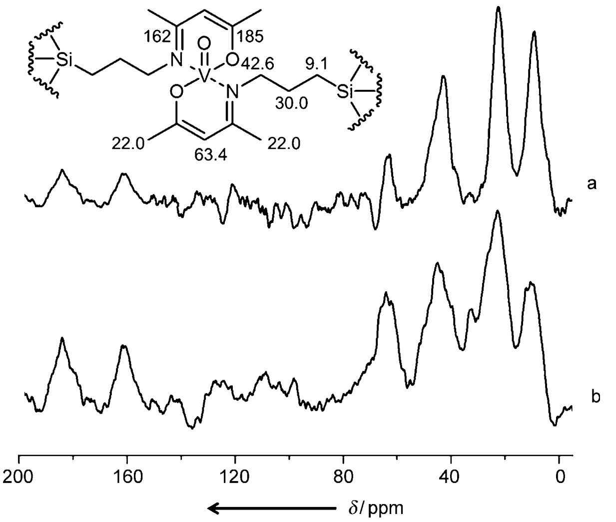


Figure 2. ^{13}C CP MAS NMR spectra of a) PMO-1 and b) PMO-2.

onstrate that the structure of grafted SB-V is intact within the silica framework.

Isothermal N_2 adsorption/desorption measurement indicates that the sizes of mesopores in both PMO-1 and PMO-2 are 4.5 and 4.1 nm in diameter, respectively. From the adsorption isotherm under the lowest pressure, the BET surface areas of PMO-1 and PMO-2 were measured to be 455 and 591 $m^2 g^{-1}$, respectively (Supporting Information, Figures S3, S4). The increase in the surface area of PMO-2 over PMO-1 is due to larger total pore volume of PMO-2 (Table 1). Results from the ICP analysis in Table 1 also confirm the vanadium contents in PMO-1 and PMO-2 quantitatively, which are 0.066 and 0.058 $mmol g^{-1}$, respectively. The high-resolution transmission electron microscopy (HR-TEM) analysis (Figure 3) shows good mesostructural morphologies for both PMO-1 and PMO-2. It can be clearly seen that both PMO-1 and PMO-2 present periodic mesopore channels. The mesopore diameters measured from the TEM images are well consistent with those obtained from the N_2 adsorption/desorption analysis.

Table 1: Analytical, textural, and porosity data of different catalysts.

No.	Catalyst	V content from ICP [$mmol g^{-1}$]	Atomic content from XPS [%]		BET surface area [$m^2 g^{-1}$]	Mesopore diameter [nm]	Total pore volume [$cm^3 g^{-1}$]
			N	V			
1	PMO-1	0.066	2.7	1.3	455	4.5	0.5
2[a]	PMO-1	0.064	2.4	1.3	–	–	–
3	PMO-2	0.058	2.5	1.1	591	4.1	0.6

[a] PMO-1 recovered after three catalytic cycles.

X-ray photoelectron spectroscopy (XPS) spectra of PMO-1 and PMO-2 (Supporting Information, Figures S5, S6) demonstrate the presences of carbon, nitrogen, and vanadium atoms in the PMO materials, along with the silica and oxygen atoms that are obviously present in all silica-based materials.

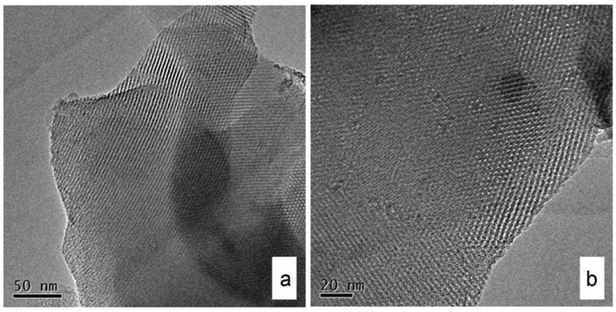


Figure 3. HR-TEM images of a) PMO-1 and b) PMO-2.

The XPS atomic percentages (Table 1) show that atomic ratio of nitrogen to vanadium is about 2 in PMOs, proving that one vanadium atom coordinates with two nitrogen atoms in all the phases. The XPS spectrum of SB-V in the V 2p region (Figure 4) shows the characteristic V $2p_{3/2}$ peak with a binding energy (BE) of 516 eV, which is essentially similar to the V 2p band profile of [VO(acac)$_2$]. The observations indicate that the integrity of the vanadyl(IV) unit in SB-V is remained after the modification reaction. The V 2p band was also observed in the cases of PMO-1 and PMO-2 (Figure 4), confirming the presence of the vanadyl(IV) unit in PMOs. As compared with the V 2p band of SB-V, slight band shift to low binding energy in PMO-1 and PMO-2 is attributed to a new chemical environment around the vanadyl complex in PMOs. A similar V 2p band profile can be observed after PMO-1 is used for three catalytic cycles (denoted as PMO-1_Used), which confirms the strong stability of the vanadyl complex within the silica framework during the catalytic process.

The catalytic activity of PMOs for selective hydroxylation of benzene to phenol was evaluated at 50 °C using acetonitrile as a solvent and H_2O_2 as an oxidant. The results (Figure 5) show that both PMO-1 and PMO-2 afford a selectivity of 100 % towards the phenol formation with a benzene conversion of about 27 % under a catalyst/benzene molar ratio of 1:200 and a benzene/H_2O_2 molar ratio of 1:3. It can be clearly seen from the turnover number (TON_V) and H_2O_2 efficiency data that the immobilized vanadyl groups in PMOs are more catalytically active compared with that of the [VO(acac)$_2$] complex. The [VO(acac)$_2$] complex, a homogeneous catalyst, presents a poor selectivity of only 76.9 % under the same experimental conditions. Much better selectivity towards the phenol formation offered by the PMO-based catalysts can be attributed to the presence of the silanol groups on PMOs. According to the information obtained by the FTIR analysis, the framework of PMOs is weakly acidic on account of the hydrogen bonded silanol groups acting as Brönsted acidic sites.[26] Based upon this fact, we can rationally assume that the weakly basic benzene can be easily adsorbed onto the acidic framework of the PMO catalysts through electrostatic

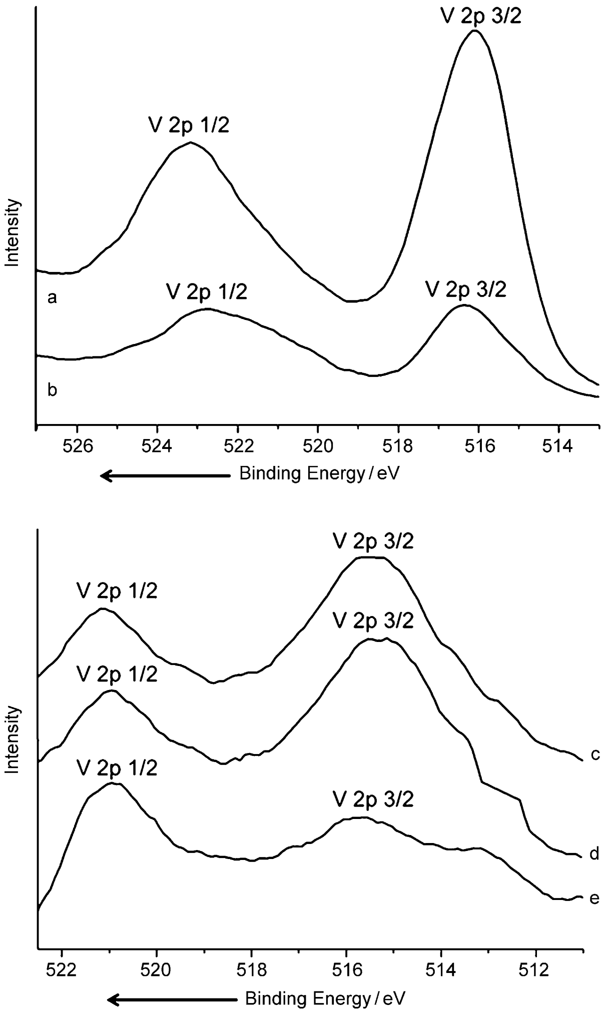


Figure 4. High-resolution XPS spectra at the V2p region for a) [VO-(acac)$_2$], b) SB-V, c) PMO-1, d) PMO-2, and e) PMO-1_Used.

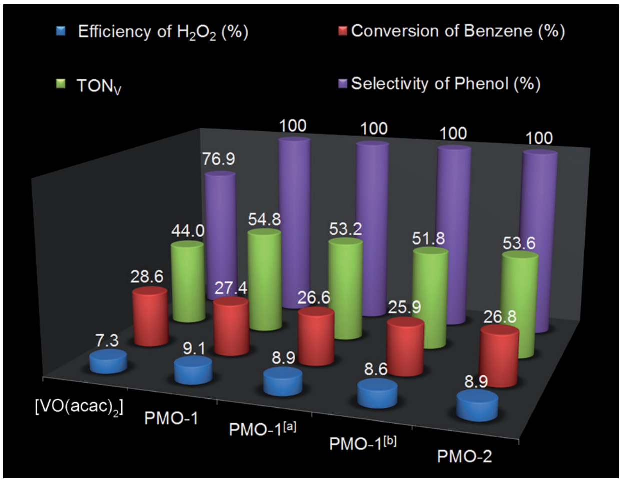


Figure 5. Conversion and selectivity of benzene to phenol with different catalysts. Reaction conditions: $C_6H_6/H_2O_2 = 1:3$, C_6H_6/catalyst = 200:1, acetonitrile solvent, 50 °C. [a] PMO-1 catalyst recovered from the first catalytic cycle and then reused. [b] PMO-1 catalyst recovered from the second catalytic cycle and then reused.

interactions. Once benzene is converted into phenol, an acidic molecule, within the framework, acidic phenol is desorbed immediately from the acidic framework, thus preventing further formation of overoxidized products. Moreover, higher benzene conversion of PMO-1 than that of PMO-2 is obvious, as the latter contains less amount of the vanadyl complexes.

A series of catalytic experiments using PMOs were carried out to understand the variation of the benzene-to-phenol conversion as a function of reaction time (Table 2).

Table 2: Catalytic activity of PMO-1 as functions of reaction time and benzene/H_2O_2 (B:H) molar ratio.[a]

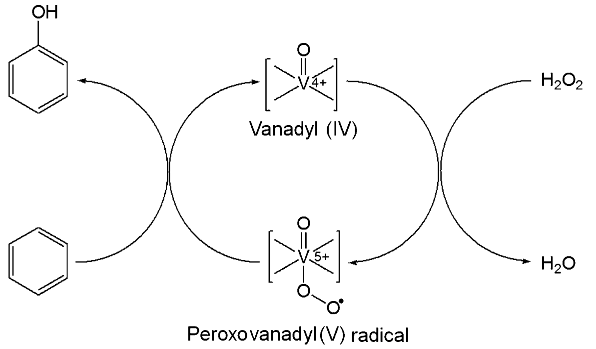
No.	Catalyst	B:H	Reaction time [h]	X_B [%]	S_P [%]	TON_V	E_O
1	PMO-1	1:3	8	27.4	100	54.8	9.13
2	PMO-1	1:3	16	32.6	76.9	50.15	8.36
3	PMO-1	1:3	24	38.2	64	49.0	8.17
4	PMO-1	1:2	8	12.6	100	25.2	6.30
5	PMO-1	1:5	8	32.6	79.3	51.7	5.17

[a] Reaction conditions: C_6H_6/catalyst = 200:1, acetonitrile solvent, 50 °C. X_B: Conversion of benzene based upon the FID-GC (GC equipped with a flame-ionization detector) results. S_P = selectivity of phenol calculated by total moles of phenol formed/total moles of benzene converted. TON_V = turnover number calculated by moles of phenol formed/one mole of V in the catalyst. $E_O = H_2O_2$ efficiency calculated by 100 × moles of phenol formed/total moles of H_2O_2 added.

The results show an increasing trend in the benzene-to-phenol conversion and remarkable decreases in the selectivity as well as in TON_V upon increasing the reaction time. A similar variation of the benzene-to-phenol conversion as a function of the benzene/H_2O_2 molar ratio was also examined. A selectivity of 100 % for the phenol formation was observed when the benzene/H_2O_2 molar ratio is 1:2 or 1:3, while the conversion rate (27.4 %) of using the 1:3 molar ratio is much higher. A significant increase of the benzene conversion (32.6 %) was obtained when the benzene-to-H_2O_2 molar ratio increases from 1:3 to 1:5, but the selectivity decreases greatly, from 100 % to 79.3 %. A decreasing trend for the H_2O_2 efficiency upon increasing the reaction time was also observed, which may be mainly due to the self-decomposition of H_2O_2.

Thus, it can be concluded that the best experimental condition for the phenol formation is to use a benzene/H_2O_2 molar ratio of 1:3 under a reaction time of 8 h, providing a benzene conversion rate of 27.4 % and a selectivity of 100 % towards the phenol production. Actually, during the catalytic evaluation process, we also observed relatively low selectivity of the phenol production under a few reaction conditions (Table 2, No. 2, 3, and 5). The qualitative analysis of the product mixture carried out by gas chromatography–mass spectrometry (GC-MS) reveals that the low selectivity is due to the formation of overoxidized products, namely hydroquinone and benzoquinone. Furthermore, the polymerization of phenol was also observed when the catalytic oxidation time was extended to 16 h and 24 h.

It has been well demonstrated that the peroxo vanadyl complex can catalyze heterolytic oxygen transfer.[27] For example, Mimoun et al. have reported a mechanism study regarding catalytic properties of V^{5+} peroxo complexes where they have concluded that the peroxo group is responsible for the benzene hydroxylation.[9d] Based upon this knowledge, we propose a reversible V^{4+}/V^{5+} redox mechanism (Scheme 2) for the catalytic cycle of the vanadyl(IV) complex grafted PMOs in the hydroxylation of benzene to phenol. In the catalytic process, H_2O_2 oxidizes V^{4+} to a peroxo vanadyl radical ($V^{5+}{-}O{-}O^{\bullet}$) followed by the insertion of oxygen atom in one of the C–H bonds of benzene and the regeneration of V^{4+} species. Thus, an efficient regeneration of V^{4+} is essential for recycling use of the catalyst.



Scheme 2. Representation of the catalytic cycle of V^{4+} during selective oxidation of benzene to phenol using H_2O_2 as an oxidant.

The efficacy of a heterogeneous catalyst is also evaluated from its recyclability and stability (for example, no metal leaching). PMO-1 presents a tremendous recyclability towards the phenol formation with a consistent 100% selectivity over three catalytic cycles. The excellent recyclability of PMO-1 can be ascribed to the absence of the metal leaching, which was confirmed by the ICP analysis of the reused catalysts. The ICP results indicate that the vanadium content in PMO-1 remains around 0.066 $mmol\,g^{-1}$ over three catalytic cycles. As the PMO catalyst possesses such a nice recyclability, the benzene conversion rate can be even enhanced after several catalytic cycles. No metal leaching and the consistent integrity of catalytic metal centers make the present PMO a remarkable catalyst for selective hydroxylation of benzene to phenol.

In conclusion, a novel type of PMO embedded with $[VO(acac)_2]$ has been successfully synthesized for the selective hydroxylation of benzene to phenol. The benzene hydroxylation by the $[VO(acac)_2]$-grafted PMO catalyst is an environmentally friendly catalytic process, as the incorporation of the homogeneous $[VO(acac)_2]$ catalyst onto PMO improves not only the selectivity towards the phenol production, but also affords a robust recyclability, making the catalytic process more benign from environmental and commercial point of view. The promising results encourage us to extend our research further to tailor different catalytically active PMOs cable of industrially feasible applications.

Received: April 28, 2012

Keywords: benzene oxidation · heterogeneous catalysis · hydroxylation · mesoporous organosilica · vanadium

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