Porous Materials

# Nanoporous Metal-Containing Nickel Phosphates: A Class of Shape-Selective Catalyst**

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The discovery of a large family of nanoporous aluminum phosphates in the early 1980s has generated widespread interest in non-aluminosilicate-based microporous materials,[1] and there has been an enormous growth in the chemical diversity of open-framework inorganic materials in new compositional domains during the last decade.[2] Commercial applications of open-framework materials continue to be dominated by the aluminosilicate zeolites,[3] but attempts are

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being made to exploit some of the exciting properties of the newly discovered systems.[4] Recent synthetic efforts have led to the discovery of many new phases,[2,5] for example, V-P-O, Fe-P-O, Co-P-O and Zn-P-O. However, as is the case with most nonsilicate open frameworks, the poor thermal stability of these systems leads to the collapse of the pore structures on activation, thus rendering them unsuitable for applications that require porosity. The challenge, therefore, is to design a nanoporous system that is thermally stable with respect to chemical or structural degradation and can be applied in catalytic reactions that are carried out at relatively high temperatures. In this respect, the need for new classes of catalysts has led a quest for creating novel nanoporous materials that might also exhibit catalytic activity.

We recently showed that the open-framework nickel(II) phosphate, VSB-1 (Versailles/Santa Barbara-1), is sufficiently stable to be rendered nanoporous and exhibits typical zeolitic properties, making it the first example of a nanoporous nickel(II) phosphate material.[6] The VSB-1 structure is based on a 3D network of $NiO_6$ and $PO_4$ tetrahedra defining a large, unidimensional channel, with an estimated free diameter of 8.8 Å.[6] Structural analysis indicates that $HPO_4$ and extra-framework cations ($NH_4^+$ or $K^+$) line the channel in VSB-1. Its surface area and chemical composition are 183 $m^2g^{-1}$ (after dehydration) and $Ni_{18}(HPO_4)_{14}(OH)_3F_9(H_3O/NH_4)_4\cdot 12H_2O$, respectively. We also discovered a second nickel phosphate molecular sieve (VSB-5); this has several applications such as hydrogen storage[7] and selective hydrogenation and base catalysis.[8] Catalytically active centers in porous oxides can give rise to highly selective new catalysts that are of great importance in the development of clean technology.[9] Here, we describe a new class of shape-selective catalyst based on nanoporous nickel phosphates.

We first tested the acid–base properties of VSB-1 by examining its reactivity with 2-methyl-3-butyn-2-ol (MBOH) as a model reaction for acid–base catalysis, showing that VSB-1 possesses only weak acidity and basicity (see Supporting Information).

To examine the possible accessibility of Pd species in the pores during catalytic reactions, we have explored catalytic activities of $Pd^{II}$-exchanged VSB-1 (Pd-VSB-1) for the direct formation of $H_2O_2$ from $H_2$ and air in aqueous media. Such a process is an attractive alternative[10] to the current technology that involves the hydrogenation of an alkylanthraquinone to the corresponding hydroquinone, followed by the reaction of the hydroquinone with oxygen to yield $H_2O_2$. We previously demonstrated that $Pd^{II}$-exchanged zeolite catalysts (Pd-BEA) exhibit more effective performance relative to those prepared from other types of zeolites.[11] In this work, Pd-VSB-1 containing 0.72 wt% Pd is fairly active for the reaction, yielding more $H_2O_2$ than Pd-BEA, as illustrated in Table 1. It is evident that the nanoporous structure of VSB-1 is suitable as a catalyst support of palladium to produce $H_2O_2$.

Employing the nanoporous VSB-1 material as a support for a noble metal enables the shape-selective properties of the nanoporous structure to be conferred on the hydrogenation function. For instance, the combination of noble metal/nanoporous material is expected to be beneficial for selective hydrogenation of cycloolefins.[12] As shown in Figure 1, Pd-VSB-1 containing 0.72 wt% Pd exhibits shape selectivity for competitive hydrogenation of 1-octene, cyclohexene, and cyclododecene. Negligible hydrogenation rates are found for larger substrates such as cyclododecene, clearly demonstrating the sieving properties of the catalyst. Furthermore, it proves that the active hydrogenation centers are mainly located within the micropores of Pd-VSB-1, which indicates the potential of the noble metal in the VSB-1 system to act as a new type of shape-selective catalyst.

***Table 1:*** Direct production of $H_2O_2$ from $H_2$ and air over Pd-exchanged VSB-1 and zeolite catalysts.[a]

| Catalyst | Pd loading [wt%][b] | $[H_2O_2]$ [mM] | TOF[c] |
|---|---|---|---|
| Pd-VSB-1 | 0.72 | 7.1 | 414 |
| Pd-BEA | 0.70 | 5.6 | 338 |
| Pd-L | 0.95 | 2.7 | 119 |

[a] Reaction conditions: $T=20°C$, $P=1$ atm, 0.01 M HCl (400 mL), $H_2$:air = 10:40 mL min$^{-1}$, 0.1 g catalyst, 1 h. [b] Analyzed by ICP-MS. [c] TOF (turnover frequency) = moles of $H_2O_2$ formed per mole of Pd per hour.

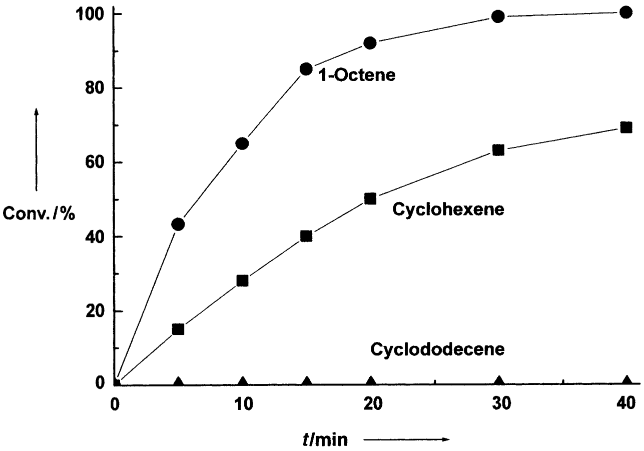

***Figure 1.*** Competitive hydrogenation of an olefin mixture over Pd-VSB-1 containing 0.72 wt% Pd. Reaction conditions: substrate = 1 mol% each of 1-octene, cyclohexene, and cyclododecene in *n*-hexane (90 mL), $T=30°C$, $H_2$ pressure = 2 atm, catalyst weight = 0.2 g.

Catalytic hydroxylation of phenol to dihydroxybenzenes such as catechol and hydroquinone is an important industrial reaction for the production of fine chemicals and has been extensively investigated.[13] Microporous titanosilicates with large surface areas have proved to be the most important catalysts for phenol hydroxylation with hydrogen peroxide, mainly in organic solvents.[14] However, in this work, $Cu^{II}$-exchanged VSB-1 (Cu-VSB-1) exhibits promising catalytic activity for phenol hydroxylation with $H_2O_2$ in an aqueous solution. Cu-VSB-1 was prepared by ion-exchange from VSB-1 and was applied to phenol hydroxylation in an aqueous solution. As shown in Table 2, it is found that Cu-VSB-1 is very active for phenol hydroxylation. Phenol conversion with Cu-VSB-1 increases up to 40.1% after 3 h when increasing the copper content to 2.9 wt% (corresponding to 70% ion exchange). It gives high catechol selectivity (67–70%) regardless of the copper content, which is higher than that

***Table 2:*** Activity of Cu-VSB-1 for phenol hydroxylation with $H_2O_2$, in terms of copper content.[a]

| Catalyst[b] | Phenol conv. [%][c] | $H_2O_2$ efficiency [%][d] | Product selectivity [%][e] | | |
|---|---|---|---|---|---|
| | | | CAT | HQ | BQ |
| Cu-VSB-1 (14) | 17.2 | 61.9 | 68.7 | 28.3 | 3.0 |
| Cu-VSB-1 (39) | 25.1 | 65.8 | 67.6 | 30.0 | 2.4 |
| Cu-VSB-1 (50) | 28.0 | 64.8 | 68.3 | 29.7 | 2.0 |
| Cu-VSB-1 (70) | 40.1 | 73.4 | 69.8 | 30.2 | – |

[a] Reaction conditions: 0.2 g catalyst, solvent: water (60 mL), phenol/$H_2O_2$ molar ratio = 1:1, amount of phenol used = 22 mmol, 3 h, $T = 60$ °C. [b] Numbers in parenthesis denote the degree of ion-exchange, as determined by ICP-MS. [c] Phenol conversion [%] = 100 × [phenol before reaction (moles) − phenol after reaction (moles)]/phenol before reaction (moles). [d] $H_2O_2$ efficiency [%] = 100 × [products (CAT+HQ+BQ) (moles)]/total $H_2O_2$ (moles) converted. [e] Product selectivity was calculated for the dihydroxybenzenes and benzoquinone. CAT = catechol, HQ = hydroquinone, BQ = benzoquinone.

of the titanosilicate TS-1 (49 %) reported in the literature,[14] revealing that the large-pore VSB-1 material exhibits reduced pore limitation in the formation of diphenols, compared to TS-1. No catalyst deactivation or leaching of copper species from the substrate was observed when catalytic measurements were twice repeated over a catalyst that had been filtered after being used for a first run. XP spectra of Cu-VSB-1 indicates that the VSB-1 structure produces copper oxide clusters in the pore together with the exchanged copper cations upon ion-exchange of copper (see Supporting Information), which suggests that not only copper cations but also copper oxide species within the pore of VSB-1 are effective for the hydroxylation of phenol with $H_2O_2$. These two species might provide a beneficial effect to improve the catalytic activity. In the $H_2O_2/Cu^{II}$ oxidation system, cupric ions ($Cu^{2+}$) added to hydrogen peroxide were found to generate hydroxyl radicals ($HO^{\cdot}$) capable of benzoate hydroxylation.[15] In the present case, copper(II) species dispersed in the pores of VSB-1 might also generate the hydroxyl radicals from $H_2O_2$ that are active for the phenol hydroxylation.

We prepared Fe-doped VSB-1 (Fe-VSB-1) and explored the framework iron species as a chromophore and a redox site for photoinduced chemistry or catalysis. We believe that the unique and fascinating properties of zeolites involving transition-metal ions within the zeolite frameworks or cavities open up new possibilities for light-induced applications, not only in photocatalysis but also for various photochemical processes.[16] This is because the micropore of a zeolite confines the organic reactant in a nanoscopic vessel and, moreover, the transition-metal ions in metal-containing porous materials are considered to be highly dispersed at the atomic level and well defined, existing in a specific structure within the zeolite framework. The UV/Vis DRS spectrum of Fe-VSB-1 shows a strong absorption in the 250–350 nm interval, which is typically assigned to an $O^{2-}$ to $Fe^{3+}$ charge-transfer transition ($[Fe^{3+} \leftarrow O^{2-}]$) of isolated $Fe^{3+}$ species.[17] It is confirmed that the framework $Fe^{III}$ species, possibly octahedral iron species, are sensitive to UV irradiation, which leads to photoreduced $Fe^{II}$ species (see Supporting Information). Thus, UV irradiation for Fe-VSB-1 containing 0.69 wt % Fe gives rise to a decrease in the intensity of the charge transfer ($[Fe^{3+} \leftarrow O^{2-}]$) band centered at 280 nm due to enhancement of charge separation, and leads to the formation of the corresponding charge-transfer excited state, $[Fe^{2+}\text{-}O^{-}]^{*}$. Moreover, UV irradiation for methanol-adsorbed Fe-VSB-1 also decreases the intensity of the $O^{2-}$ to $Fe^{3+}$ charge-transfer band due to electron transfer from MeOH to $Fe^{3+}$. These results encouraged us to utilize Fe-VSB-1 as a photocatalyst. As an example, we have investigated UV photochemical oxidation of ammonia in an aqueous solution using Fe-VSB-1, assisted by $H_2O_2$. It follows the pathway of the photo-Fenton reaction for the degradation of pollutants, in which photoreduced transition-metal species lead to the formation of $HO^{\cdot}$ radicals[18] and thereby convert ammonia to nitrate or nitrite ions. VSB-1 itself shows negligible activity for this reaction, but Fe-VSB-1 exhibits very good activity to oxidize ammonia into nitrate and nitrite ions under UV irradiation (Table 3). The activity is much better than that of anatase $TiO_2$ (P25) as a typical photocatalyst and pure $FeCl_2$ as a photo-Fenton reagent, and its superiority is evident when the activity is displayed in terms of turnover frequency (TOF). This result indicates that highly dispersed $Fe^{III}$ sites in the framework of VSB-1 can behave as active centers for intrazeolite photocatalysis.

***Table 3:*** Activities of $TiO_2$, $FeCl_2$, and Fe-VSB-1 in the photo-Fenton oxidation of ammonia in water.[a]

| Catalyst | $NH_3$ conversion [%] | TOF[b] |
|---|---|---|
| $TiO_2$ (P-25) | 11 | 1.8 |
| $FeCl_2$ | 18 | 4.7 |
| Fe-VSB-1[c] | 43 | 7200 |

[a] Reaction conditions: $NH_4OH$ (758 ppm), 30 % $H_2O_2$ (20 mL), $H_2O$ (660 mL), 0.5 g catalyst, UV wavelength: 200 nm, UV power: 450 W, irradiation time: 10 min. [b] TOF (turnover frequency) is moles of $NH_3$ decomposed per mole of Ti (or Fe) per hour. [c] Fe content = 0.69 wt %.

In summary, the novel material, VSB-1, is found to have important properties such as nanoporosity, zeolitic properties, and very weak acidity and basicity. When VSB-1 is modified with metal ion-exchange or metal-incorporation into the framework, it can offer promising catalytic properties: e.g., shape selectivity, redox catalysis, and photocatalysis. Indeed, the catalytic results exemplified in this work clearly demonstrate that nanoporous metal-containing nickel phosphates can be classified as a new class of shape-selective catalyst.

## *Experimental Section*

Syntheses of VSB-1 and metal-modified VSB-1 materials: VSB-1 was initially prepared in a hydrothermal reaction at 180 °C for 6 days between nickel(II) chloride hexahydrate and phosphoric acid (85 % by weight) in the presence of tris(2-aminoethyl)amine in a pyridine/HF/water solvent system; further details are given elsewhere.[6] Iron-incorporated VSB-1 was synthesized likewise using an aqueous solution of $FeCl_2 \cdot 4H_2O$ (Aldrich, 99%). For the $Pd^{II}$ and $Cu^{II}$ ion-exchanged materials, palladium and copper were introduced by ion exchange of the proton form of VSB-1 using a 0.01 M aqueous solution of $[Pd(NH_3)_4Cl_2]$ and a 0.02 M aqueous solution of $Cu(NO_3)_2$, respectively. The resulting metal-loaded materials were dried at 120 °C overnight and calcined at 350 °C for 4 h in air. For catalytic measurements, Pd-VSB-1 was reduced for 4 h in 5% $H_2$ at 300 °C. Metal loading in the final products was determined with ICP-MS.

Catalytic measurements were conducted with a plug-flow reactor (for MBOH decomposition) or a glass reactor (for $H_2O_2$ production, olefin hydrogenation, phenol hydroxylation, and ammonia decomposition). Detailed methods for catalytic measurements and analysis are described in the Supporting Information.

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