Zeolite-Confined Nano-RuO₂: A Green, Selective, and Efficient Catalyst for Aerobic Alcohol Oxidation

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Abstract: The development of green, selective, and efficient catalysts, which can aerobically oxidize a variety of alcohols to their corresponding aldehydes and ketones, is of both economic and environmental significance. We report here the synthesis of a novel aerobic oxidation catalyst, a zeolite-confined nanometer-sized RuO_2 (RuO_2–FAU), by a one-step hydrothermal method. Using the spatial constraints of the rigid zeolitic framework, we sucessfully incorporated RuO_2 nanoparticles (1.3 ± 0.2 nm) into the supercages of faujasite zeolite. Ru K-edge X-ray absorption fine structure results indicate that the RuO_2 nanoclusters anchored in the zeolite are structurally similar to highly hydrous RuO_2; that is, there is a two-dimensional structure of independent chains, in which RuO_6 octahedra are connected together by two shared oxygen atoms. In our preliminary catalytic studies, we find that the RuO_2 nanoclusters exhibit extraordinarily high activity and selectivity in the aerobic oxidation of alcohols under mild conditions, for example, air and ambient pressure. The physically trapped RuO_2 nanoclusters cannot diffuse out of the relatively narrow channels/ pores of the zeolite during the catalytic process, making the catalyst both stable and reusable.

Introduction

The aerobic oxidation of alcohols to their corresponding aldehydes and ketones is of interest for both economic and environmental reasons (Scheme 1). Many catalytic systems, for example, M^{II}-radical catalysts,[1] CuCl·Phen,[2] polyoxometalates,[3] PdL_n,[4] M-TEMPO,[5] Ru-biomimetic-coupled systems,[6] bimetallic Mo−Cu[7] and Os−Cu[8] systems, perruthenate,[9] Pt and Pt/ Bi catalysts,[10] manganese oxide octahedral molecular sieves,[11] and Ru-hydroxyapatite,[12] have been designed and developed for the aerobic oxidation of alcohols. Heterogeneous catalytic systems[3e,9a,10−12] display advantages − for example, no cocatalyst

Scheme 1. Aerobic Alcohol Oxidation
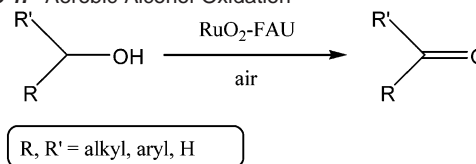
requirement and convenient separations − but their applications are limited, either to activated alcohols or by the need for pure oxygen. The search for suitable green aerobic catalysts, especially without sacrificial reducing agents, is still a significant challenge.

Recently, RuO_2 has been receiving considerable attention for its extraordinarily high catalytic activity.[13−15] For example, it can efficiently catalyze the oxidation of CO with O_2 below room temperature.[15] The outstanding catalytic ability of RuO_2(110)

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is attributed to the existence of coordinatively unsaturated ruthenium atoms.[13] Interestingly, a structure similar to that of $RuO_2(110)$ was found in amorphous hydrous RuO_2.[16] In addition, $RuO_2 \cdot xH_2O$ is a mixed electron−proton conductor. It can activate O_2 molecules without the assistance of any additional reducing agents.

Nanometer-sized materials can exhibit very different electronic, magnetic, catalytic, optical, and other properties from those of the corresponding bulk materials,[17] and nanomaterials can be novel catalysts because of the large surface area and the high density of active sites. Thus, it is expected that nanometer-sized hydrous RuO_2 clusters with a structure similar to that of the $RuO_2(110)$ surface could exhibit favorable aerobic oxidation chemistry. Here, we report a novel approach to directly synthesize RuO_2 nanoclusters in the supercages of FAU zeolite. Catalytic results indicate that zeolite-confined nano-RuO_2 is a green, selective, and efficient aerobic catalyst for alcohol oxidation. It can selectively oxidize alcohols to their corresponding carbonyls under mild aerobic conditions without using sacrificial reducing agents, pure O_2, or even solvent.

Experimental Section

Chemical reagents included fumed silica (11 nm, Sigma), tetraethyl orthosilicate (Aldrich), NaOH (Aldrich), NaAlO₂ (Allied Chemical), Al(OH)₃ (McArthur Chemical), $RuCl_3 \cdot 3H_2O$ (Aldrich), $Ru(NH_3)_6Cl_3$ (Aldrich), and RuO_2 (A. D. Macky). All other organic and inorganic chemicals were reagent grade and were used without further purification.

Synthesis of RuO_2−FAU. RuO_2 nanoclusters confined in the supercages of FAU zeolite, hereafter called RuO_2−FAU composite, were synthesized on the basis of the organic-additive-free hydrothermal crystallization method reported recently.[18] A measured amount of either $RuCl_3 \cdot 3H_2O$ or $Ru(NH_3)_6Cl_3$ was added to an aluminosilicate gel containing 5.34 g of NaOH, 2.42 g of NaAlO₂, 3.43 g of SiO_2, and 50.0 g of H_2O. The gel was aged for 2 days and then crystallized at 90 °C for 15 h with stirring. The resultant black powder was separated from solution by centrifugation and then washed completely with deionized (DI) water to remove any physically absorbed species on the zeolite surface. The synthesized samples were dried at room temperature for further characterization and catalytic investigations. ICP-MS analysis indicates that the concentration of RuO_2 incorporated in the zeolite is 0.78 mmol/g. This corresponds to about one RuO_2 nanocluster in every 2.2 supercages of FAU (on average, every 1.3 nm RuO_2 nanocluster contains 5 Ru atoms, as deduced from the bond lengths).

Aerobic Oxidation. Unless otherwise indicated, the oxidation reactions were carried out in a flask (with a condenser) containing 1
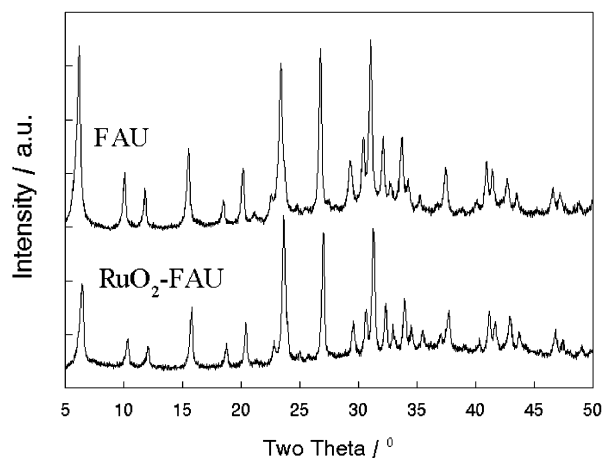

Figure 1. XRD patterns of unmodified FAU zeolite and RuO_2−FAU composite.

mmol of alcohol, 3 mL of toluene, 0.1 g of Ru−FAU catalyst, and a stir bar. The aerobic oxidation reactions were conducted in an 80 °C oil bath, in air (except as indicated) under ambient pressure. The oxidation products were analyzed and quantified by gas chromatography and identified by either GC-MS or GC with standard samples. All of the GC analyses were performed on a Supelco MDN-55 column (30 m × 0.25 mm × 0.50 μm) with a Perkin-Elmer Auto System GC equipped with an FID-detector. GC-MS for the product identification was conducted in a Perkin-Elmer Auto System XL GC with a Perkin-Elmer TurboMass mass spectrometer.

Characterization. X-ray powder diffraction patterns were recorded on a Rigaku Miniflex System using Cu Kα radiation, 30 kV, 15 mA with a scanning speed of 1° (2θ) min⁻¹, $T = 20$ °C. Ru K-edge XAFS measurements were made at the Bending Magnet Beamline of the PNC (Pacific Northwest Consortium)-CAT (Collaborative Access Team) at the Advanced Photon Source (APS) at Argonne National Laboratory. APS is a 7 GeV, third generation electron storage ring, operating typically at 100 mA injection current. All of the measurements were conducted in fluorescence mode using a Xe-filled ion chamber with filter and solar slit arrangements. High-resolution TEM images were recorded with a FEI Tecnai-12 operated at 80 kV. The EPR experiment was conducted with a Bruker ESP 300 Xband spectrometer.

Results and Discussion

X-ray powder diffraction indicates that unmodified FAU zeolite and the RuO_2−FAU composite have the same structure (Figure 1). In comparison with the unmodified FAU zeolite, RuO_2−FAU displays slightly higher 2θ values in all of its diffraction peaks. Both diffraction patterns match very well with that simulated for faujasite zeolites.[19] X-ray fluorescence analysis shows that the Si/Al ratio is 1.25 for FAU and 1.34 for RuO_2−FAU, within the range of 1.0−1.5 for faujasite-X zeolite. There is no evidence for any crystal phases attributable to RuO_2 compounds, indicating that zeolite-confined RuO_2 is not highly crystalline.

Ru K-edge X-ray absorption fine structure (XAFS) was employed to study the structural configuration of the Ru species incorporated in the FAU zeolite. Figure 2 shows the X-ray absorption near-edge structure (XANES) spectra of various Ru species. The XANES spectra of synthetic RuO_2−FAU composite materials are very different from those of $RuCl_3$ and $Ru(NH_3)_6Cl_3$ but resemble that of hydrous RuO_2. There is no

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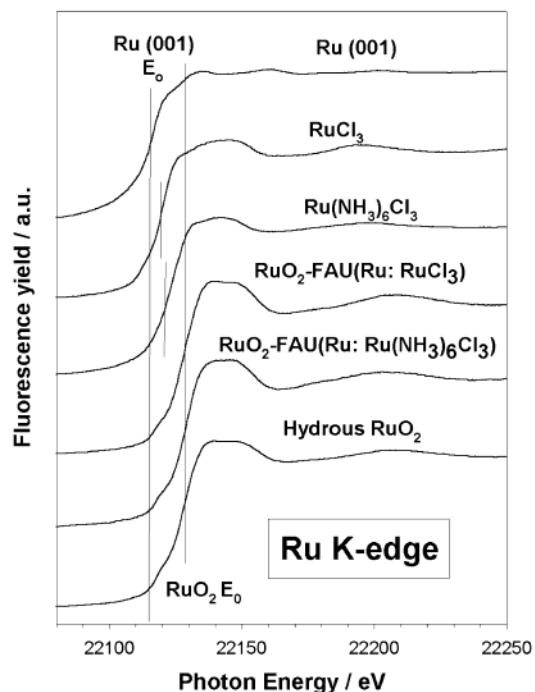
Figure 2. X-ray absorption near-edge structure (XANES) spectra for different types of Ru species, as indicated.
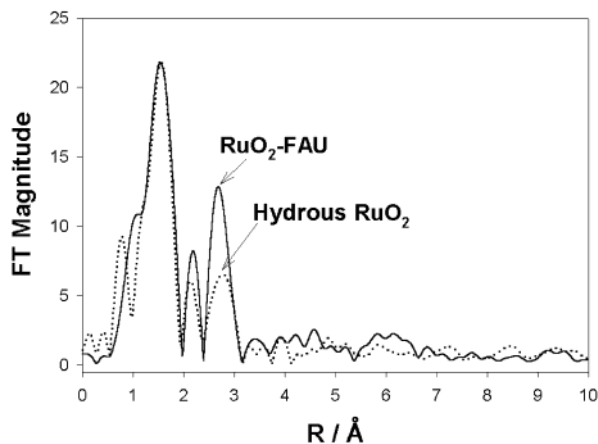

Figure 3. The radial distribution function from the Fourier transform of the k^2-weighted extended X-ray absorption fine structure (EXAFS) for RuO$_2$−FAU and hydrous RuO$_2$.

spectral difference between the two RuO$_2$−FAU samples, synthesized with either RuCl$_3$ or Ru(NH$_3$)$_6$Cl$_3$, indicating that all ruthenium species are oxidized to Ru(IV) under the hydrothermal crystallization conditions. The absence of Ru(III) species in the RuO$_2$−FAU composites was also evidenced by the EPR experiment: all of the synthesized composites are EPR silent at both room temperature and 120 K. The similarity of the XANES spectra of the RuO$_2$−FAU composites and hydrous RuO$_2$ clearly demonstrates that hydrous RuO$_2$ and zeolite-confined Ru species have similar nearest-neighbor octahedral environments, that is, distorted "RuO$_6$".[16]

Extended X-ray absorption fine structure (EXAFS) was further used to define the fine structure of RuO$_2$ anchored in the zeolite. Figure 3 shows the radial distribution function (RDF) from the Fourier transform of the k^2-weighted EXAFS for RuO$_2$−FAU, along with the hydrous RuO$_2$ standard. The EXAFS of the latter is virtually the same as that for amorphous

Scheme 2. Ru, Larger Six-Coordinate Spheres; O, Smaller Spheres; Si, Two Spheres Indicated for RuO$_2$−FAU
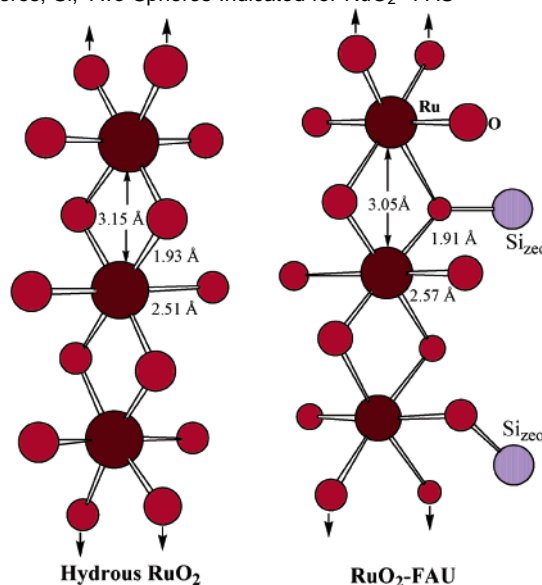
RuO$_2$·2.32H$_2$O, which has been systematically studied by McKeown et al.[16] It has a two-dimensional structure of independent chains, in which RuO$_6$ octahedra are connected together by two shared oxygen atoms (Scheme 2). The EXAFS results indicate that the Ru(IV) species anchored in the zeolite likely form amorphous RuO$_2$ with a 2D-chain structure, consistent with the XRD findings. The main peak in the FT corresponds to a Ru−O interatomic distance of 1.91 ± 0.01 Å. Analysis using phase shift from the standard shows that the Ru−O bond in RuO$_2$−FAU is slightly shorter on average (by 0.02 Å) than that of hydrous RuO$_2$. The shorter Ru−O bond of RuO$_2$−FAU therefore leads to a shorter Ru−Ru distance of 3.05 $\pm$ 0.01 Å, as compared with 3.15 Å for hydrous RuO$_2$. The 2.2 Å peak, only present in highly hydrated RuO$_2$, was assigned to the Ru−OH$_2$ or the Ru−OH bond.[16] The corresponding bond length is 2.57 Å in the RuO$_2$−FAU composite, longer than 2.51 Å in the hydrous RuO$_2$ reference. Reasonable explanations for the longer Ru−OH$_2$ or Ru−OH bond and shorter Ru−O and Ru−Ru bonds in RuO$_2$−FAU are the very polarized zeolitic framework[20] and the strong interaction between RuO$_2$ chains and the zeolitic framework in the form "Ru−O−Si$_{zeo}$", where Si$_{zeo}$ is a zeolitic framework atom.[21] The interactions could occur either on the terminal oxygen atoms or on the bridge oxygen atoms as shown in Scheme 2. This interaction may be the driving force for the successful inclusion of RuO$_2$ nanoclusters into the zeolitic supercages during the hydrothermal synthesis.

The morphology and particle sizes of RuO$_2$ clusters in FAU zeolite were characterized using high-resolution TEM, as shown in Figure 4. The additional dark spots in RuO$_2$−FAU crystals, not seen in pure FAU but homogeneously distributed through the RuO$_2$−FAU sample, are reasonably attributed to the RuO$_2$ particles. Figure 4 clearly indicates that these particles are very uniform, in the size range 1.3 $\pm$ 0.2 nm. This is the same size as the supercages in FAU zeolite. The RuO$_2$ clusters are likely incorporated into the supercages of FAU zeolite during the hydrothermal crystallization process, and the growth of RuO$_2$

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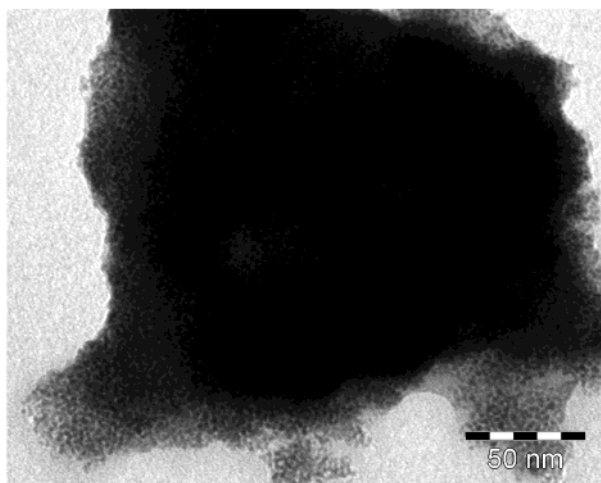(21) Dutta, P. K.; Das, S. K. *J. Am. Chem. Soc.* **1997**, *119*, 4311.

Figure 4. High-resolution TEM image of RuO$_2$−FAU composite.

clusters is constrained by the rigid zeolitic framework. Furthermore, due to the structure of FAU zeolite, with larger supercages tetrahedrally connected by smaller 12-membered rings, once incorporated, the nanoclusters of RuO$_2$ are physically confined in the supercages and cannot diffuse out through the relatively narrow channels. This physical occlusion, supported by the catalytic results (vide infra), is of significance in the prevention of leaching of the active sites, a common problem for supported transition-metal catalysts.[22]

Various activated (benzylic and allylic) and unactivated (saturated) alcohols were used to investigate the aerobic oxidation over RuO$_2$−FAU. Table 1 presents the aerobic catalytic results. In a control experiment, unmodified faujasite zeolite was used as a "catalyst" for aerobic oxidation of benzyl alcohol. No oxidation product was detected from GC analysis after 4 h of refluxing, indicating that the unmodified zeolite itself is inert for alcohol oxidation under the experimental conditions (entry 1). Using pure hydrous RuO$_2$, that is, not encapsulated in the zeolite, as a catalyst, we found that 16% of the benzyl alcohol was oxidized to benzaldehyde within 1.5 h at 80 °C.[23] However, benzyl alcohol was completely oxidized to benzaldehyde within 1.5 h with more than 99% selectivity when RuO$_2$−FAU was used as catalyst under the same reaction conditions (entry 2). (Dried RuO$_2$−FAU gave the same results as entry 2.) These results clearly indicate that zeolite-confined nano-RuO$_2$ is much more active than the bulk RuO$_2$ and that the Ru species incorporated in the zeolitic frameworks are the catalytically active sites for the alcohol oxidation. The significantly higher activity of nano-RuO$_2$−FAU composite, as compared with that of bulk hydrous RuO$_2$, is attributed to the much higher density of active sites in nano-RuO$_2$.

We note that RuO$_2$−FAU also displays high activity in the oxidation of unactivated alcohols (Table 1, entries 3−8). For example, *n*-heptanol was selectively oxidized to *n*-heptaldehyde with 44% conversion in 4 h (entry 3). After 20 h, the reaction was essentially complete with over 99% selectivity for *n*-hepta-

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(23) The control reaction was conducted in a 25 mL flask containing 0.078 mmol of hydrous RuO$_2$, 1 mmol of benzyl alcohol, and 3 mL of toluene solvent. The mixture was heated in air at 80 °C with stirring. GC analysis indicated that 16% of benzyl alcohol was selectively oxidized to benzaldehyde within 1.5 h.

Table 1. Aerobic Oxidation Results of Alcohols Using RuO$_2$−FAU Catalyst

Entry	Time (h)	Substrate	Product (mol%)	Conv.[a] (mol%)	TON[b]
1[c]	4	⬡—CH$_2$OH	–	–	–
2	1.5	⬡—CH$_2$OH	⬡—CHO >99	100	13
3	4	∼∼∼OH	∼∼∼=O >99	44	6
4	20	∼∼∼OH	∼∼∼=O >99	93	12
5	4	∼∼OH	∼∼=O >99	69	9
6	4	⬡—OH	⬡=O >99	17	2
7[d]	4	⬡—OH	⬡=O >99	43	6
8[d]	4	∼∼∼OH	∼∼∼=O >99	98	13
9	4	⬡—OH	⬡=O >99	68	9
10	8	⬡—OH	⬡=O >99	100	13
11	4	∼∼OH	∼∼=O >99	95	12
12[e]	20	⬡—CH$_2$OH	⬡—CHO >99	22	28
13[f]	24	⬡—CH$_2$OH	⬡—CHO >99	58	7
14[f,g]	24	⬡—CH$_2$OH	⬡—CHO >99	75	10
15[f,h]	24	⬡—CH$_2$OH	⬡—CHO >99	23	3
16[i]	1.5	⬡—CH$_2$OH	⬡—CHO >99	100	13

[a] Conversion of alcohols. [b] Turn over number based on the substrate turn over per mole of RuO$_2$. [c] Unmodified zeolite (0.1 g) was used as "catalyst". [d] O$_2$ bubbling. [e] Alcohol (30 mmol), RuO$_2$−FAU (0.3 g), 80 °C, air atmosphere. [f] Alcohol (1 mmol), RuO$_2$−FAU (0.1 g), toluene (10 mL), ambient temperature, O$_2$ bubbling. [g] Chlorobenzene (10 mL) instead of toluene solvent. [h] 4-Picoline (3 mmol) added to the reaction mixture. [i] Oxidation result for the fifth run.

ldehyde (entry 4). In comparison with unactivated primary alcohols, we found that secondary noncyclic aliphatic alcohols are more reactive to oxidation by RuO$_2$−FAU: 69% of 2-heptanol was selectively oxidized (to 2-heptanone) in 4 h (entry 5). This trend is different from that observed in the monomeric ruthenium catalysts, such as RuCl$_2$(PPh$_3$)$_3$[5d] and RuHAP.[12] However, only 17% of cyclohexanol was selectively oxidized to cyclohexanone in the same reaction period (entry 6). This is further confirmed by a competitive reaction,[24] which indicates that 1-heptanol is about 3 times more active than cyclohexanol with the RuO$_2$−FAU catalyst. This result matches very well with the individual reactions (entries 3 and 6). The oxidation reactions can be significantly promoted in a pure O$_2$ atmosphere: the conversions were 43% for cyclohexanol and 98% for *n*-heptanol in 4 h when the oxidation was conducted with an O$_2$ atmosphere (entries 7 and 8), that is, about 3 times faster than that conducted in air (entries 3 and 6).

(24) The competitive reaction was done by mixing together 0.5 mmol of *n*-heptanol and cyclohexanol with 3 mL of toluene solvent and 0.1 g of RuO$_2$−FAU catalyst. The reaction was carried out at 80 °C in air with stirring. GC analysis indicated that the conversions of *n*-heptanol and cyclohexanol in 2 h were 32 and 12%, respectively.

The corresponding allylic alcohol is oxidized much more easily: 68% of 2-cyclohexenol was selectively oxidized to 2-cyclohexenone in 4 h over RuO$_2$−FAU (Table 1, entry 9), about 4 times the reactivity of cyclohexanol. The aerobic oxidation of 2-cyclohexenol was completed in 8 h (entry 10). The selective oxidation of 2-buten-1-ol to 2-butenal occurred with 95% conversion in 4 h (entry 11). Furthermore, aerobic oxidation can be carried out without using an organic solvent. For example, neat benzyl alcohol was selectively oxidized to benzaldehyde with a conversion of 22% in 20 h. The TON now reaches 28 (entry 12).

The RuO$_2$−FAU catalyst is so active that it can catalyze the aerobic oxidation of benzyl alcohol at ambient temperature (Table 1, entries 13−15). The substrate is selectively oxidized to benzaldehyde with 58% conversion in 24 h (entry 13). This oxidation reaction is noticeably enhanced using chlorobenzene as solvent: a conversion of 75% was achieved under the same conditions (entry 14). On the other hand, addition of tertiary amines, which coordinate more strongly to Ru than alcohols, can inhibit the reaction. The oxidation reactivity is significantly dropped to 23% by adding 3 mmol of 4-picoline to the reaction mixture (entry 15).

The RuO$_2$−FAU catalyst also displays substrate shape-selectivity imposed by the zeolitic framework. In a competitive reaction, equimolar (0.5 mmol) benzyl alcohol and 9-hydroxy-fluorene were mixed with the RuO$_2$−FAU catalyst (0.1 g) in toluene (10 mL) at 80 °C, air atmosphere. GC analysis indicated that the benzyl alcohol was completely and selectively oxidized to benzaldehyde in 1.5 h, and no oxidation products attributed to 9-hydroxyfluorene were detected. However, 9-hydroxyfluorene was readily oxidized to the corresponding ketone when pure hydrous RuO$_2$ was used as catalyst.[25] The 9-hydroxyfluorene molecule is rigid and bulky and can only pass through the narrow 12-member ring zeolite channel in one orientation, leaving the hydroxyl group too far away from the active site of the RuO$_2$ cluster to be oxidized. This shape-selectivity on the substrates of the RuO$_2$−FAU catalysis provides strong evidence that the RuO$_2$ nanoclusters are confined in the supercages of the FAU zeolite and that any physically adsorbed RuO$_2$ species on the zeolite surface are removed by washing with DI water.

Furthermore, the RuO$_2$−FAU catalyst is stable and can be *reused* after aerobic oxidation. After reaction with benzyl alcohol, RuO$_2$−FAU was separated from the reaction mixture by centrifugation, thoroughly washed with acetone, and then reused as catalyst for the next run under the same conditions.

The catalytic results indicate that there is no difference in either activity or selectivity between the first and fifth runs (entries 2 and 16). Ru leaching was negligible during the above recycles. The Ru concentration in the filtrate is less than 2.5 ppb as found by ICP. X-ray powder diffraction patterns indicated that the crystallinity of recycled RuO$_2$−FAU sample is the same as that of the fresh sample, showing that the zeolitic framework is retained in the oxidation process. Although the mechanism of alcohol oxidation over RuO$_2$−FAU catalyst is not very clear, we think that it is similar to that of bulk RuO$_2$ as proposed by Madhavaram.[14] Aerobic oxidation is first initiated by OH dissociation leading to the formation of a Ru-alcoholate species. Our evidence for this is inhibition of benzyl alcohol oxidation in the presence of 4-picoline and no reaction for the oxidation of 9-hydroxyfluorene due to the steric effect. The alcoholated species, then, undergoes dehydrogenation to produce the corresponding carbonyl compound and ruthenium hydride. The latter can either react with Ru−OH species to give water and then uptake oxygen to finish a catalytic cycle[14] or react with O$_2$ through a hydroperoxide route.[12]

Conclusion

Nanometer-sized hydrous RuO$_2$ was successfully incorporated into supercages of faujasite zeolite using a one-step hydrothermal synthesis. Zeolite-anchored hydrous nano-RuO$_2$ has a 2D-chain structure, in which the RuO$_6$ units are connected together by two shared oxygen atoms. The zeolite-confined nano-RuO$_2$ displays extraordinarily high activity and selectivity in the oxidation of both activated and unactivated alcohols to the corresponding aldehydes and ketones under aerobic conditions without using either a cocatalyst or a sacrificial reducing agent. Zeolite-confined nano-RuO$_2$ is much more active than bulk hydrous RuO$_2$ in the aerobic oxidation of benzyl alcohol under the same conditions. The Ru leaching was observed to be negligible, and the crystallinity of recycled RuO$_2$−FAU was retained, showing that the RuO$_2$−FAU catalyst can be reused.

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(25) The reaction was done by mixing together 0.078 mmol of hydrous RuO$_2$, 0.5 mmol of 9-hydroxyfluorene, and 10 mL of toluene solvent. The mixture was heated in air at 80 °C with stirring. GC analysis indicated that 51% of 9-hydroxyfluorene was selectively oxidized to 9-fluorenone within 1.5 h.