Heterogeneous Catalysis

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Efficient Heterogeneous Epoxidation of Alkenes by a Supported Tungsten Oxide Catalyst**

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Epoxides are important chemical intermediates in the laboratory as well as the chemical industry.[1] Catalytic epoxidation of alkenes with H_2O_2 has attracted much attention because of the sustainable nature of the reaction, for example the use of catalysts, the high content of active oxygen species in H_2O_2, and the formation of water as the sole by-product. A number of efficient methods for the epoxidation of alkenes with transition-metal catalysts, such as Ti, V, Mn, Fe, W, Re, Pt, have been reported.[1] However, most of these catalysts are homogeneous, and require the separation and recycling of the expensive catalyst.[2] Therefore, immobilization of homogeneous catalysts has been attempted through ion exchange, adsorption, covalent linkage, encapsulation, and substitution, depending on the nature of the metals and supports.[3] Some of these immobilized systems have disadvantages, such as significant decreases in activity after immobilization, leaching of the catalytically active species, poor thermal stability, and low recycling rates. Although titanium-containing zeolites are highly efficient heterogeneous catalysts, their application to the epoxidation of bulky substrates is limited, owing to the steric constraints imposed by the micropores.[3] In this context, developing an easily recycled, highly active, and widely applicable heterogeneous catalyst for epoxidation is desirable.

Heterogeneous epoxidation of alkenes with H_2O_2 and a supported catalyst is one of the simplest and most reliable solutions to the problems described above. A combination of ethylbenzene hydroperoxide and a heterogeneous Ti/SiO_2 catalyst has been used for the industrial production of 1,2-epoxypropane. However, the Ti/SiO_2 catalyst is not effective for the epoxidation of propene with aqueous H_2O_2 because the presence of water inhibits the reaction. Therefore, $> 95\,\%$ H_2O_2 is required to attain a high selectivity for 1,2-epoxypropane, and to minimize the formation of by-products.[3] Tungsten-based catalysts, including polyoxometalates, utilize H_2O_2 in a highly efficient manner and are highly selective for epoxides.[4] Such catalysts have been immobilized by ion exchange or covalent methods on surface-modified supports, or by simple adsorption on silica or alumina. However, the catalysts produced by using these methods are not so effective.[3–5] Supported tungsten oxide catalysts have been used for various chemical processes, including the isomerization of alkanes,[6] alkene metathesis,[7] and the selective reduction of NO_x.[8] These catalysts often contain additives, such as promoters and passivating agents,[6–9] but have not yet been applied to liquid-phase oxidation with H_2O_2. Herein, we report the efficient, heterogeneous, and selective oxidation of various alkenes, amines, silanes, and sulfides with H_2O_2, catalyzed by tungsten and zinc oxides supported on SnO_2 (W–Zn/SnO_2). To our knowledge, the epoxidation of a wide range of alkenes, including propene, with aqueous H_2O_2 and a reusable, supported catalyst is unprecedented.

Supported tungsten oxide catalysts with various additives (W–X/SnO_2, X = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Y, La, Ce, Pr, Sm, Eu, Dy, Yb, Ni, Cu, Ag, Zn, Cd, Ga, and In) were prepared in two steps (see the Supporting Information for details). Firstly, the metal X was loaded onto the SnO_2 support (X/SnO_2), then the X/SnO_2 was impregnated with an aqueous

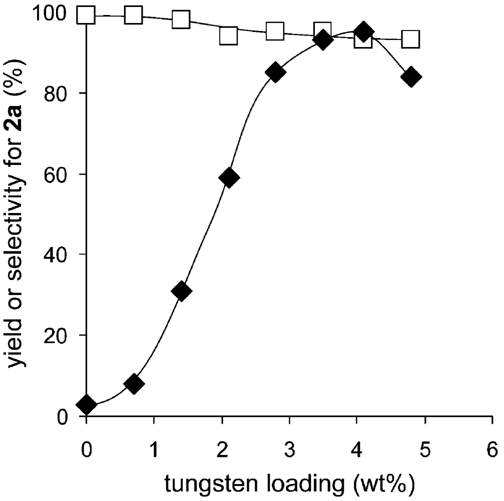

Figure 1. Plots of the yield of **2a** ◆ and selectivity for **2a** □ against the tungsten loading of W–Zn/SnO_2 (W: 0–4.8 wt%; Zn: 0.8 wt%). Reaction conditions: W–Zn/SnO_2 (W: 3.3 mol% with respect to H_2O_2), **1a** (5 mmol), 60% aqueous H_2O_2 (1 mmol), DMC (3 mL), 333 K, 4 h.

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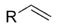
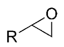
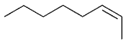
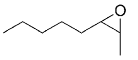
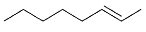
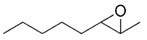
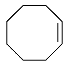
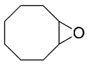
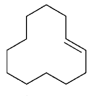
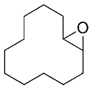
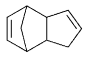
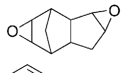
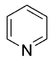
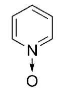
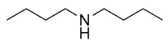
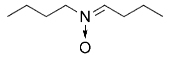
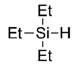
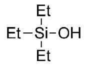
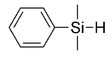
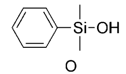
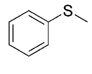
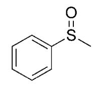
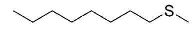
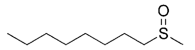
solution of H_2WO_4 (the pH value was adjusted to 7.0 by using 28 % aqueous NH_3). The epoxidation of 1-hexene (**1a**) with 60 % aqueous H_2O_2 was carried out in the presence of W–X/SnO_2 (see Table S1 in the Supporting Information). The catalytic activity of W–X/SnO_2 was strongly dependent on the additives. W–Zn/SnO_2 gave the highest yield (93 %), with a 95 % selectivity for 1,2-epoxyhexane (**2a**).[10] Catalysts containing Group 10–14 elements, such as Ni, Cd, In, and Ga were moderately active, and catalysts with Group 1–3 elements or lanthanides were not active. The yield of **2a** reached a maximum at a tungsten loading of 4.1 wt %, whereas the selectivity for **2a** did not depend significantly on the tungsten loading (Figure 1).

The effect of different solvents on the epoxidation of **1a** with H_2O_2 and W–Zn/SnO_2 was investigated (see Table S2 in the Supporting Information). Dimethyl carbonate (DMC) was the best solvent for the reaction. Propylene carbonate was also effective; however, the yield of isolated **2a** was lower than that obtained from the reaction with DMC. The epoxidation reaction in DMC proceeded efficiently even at 305 K or with 30 % aqueous H_2O_2, without significantly affecting the yield of the product or the selectivity of the reaction. Although ethyl acetate (EtOAc) was also a good solvent, EtOAc hydrolyzed under the reaction conditions used. On the other hand, the yield of methanol in the reaction with DMC remained constant (2 %), regardless of the presence of the catalyst. This finding suggests that DMC was intrinsically stable during the reaction. Other polar aprotic solvents, such as methyl ethyl ketone, acetonitrile, and tetrahydrofuran, as well as polar protic solvents, such as *tert*-butanol, 1-butanol, and ethanol, gave **2a** in moderate yields. Nonpolar toluene and *n*-hexane were poor solvents for this reaction. The epoxidation reaction did not proceed in *N*,*N*-dimethylformamide (DMF), probably because of a strong coordination between the DMF and the tungsten center. The catalytic activity of W–Zn/SnO_2 was compared with other tungsten and zinc catalysts (see Table S3 in the Supporting Information). The precursor of W–Zn/SnO_2, H_2WO_4, had a low catalytic activity and low selectivity for **2a** as a result of the hydrolysis of **2a** to the corresponding diol. The epoxidation reaction barely proceeded in the absence of W–Zn/SnO_2, or in the presence of $Zn(NO_3)_2{\cdot}6H_2O$, SnO_2, WO_3, $ZnWO_4$, ZnO, or Zn/SnO_2. Other supports, such as Al_2O_3, SiO_2, TiO_2, ZrO_2, and ZnO, were not effective (see Table S4 in the Supporting Information).

The scope of the W–Zn/SnO_2 system for the oxidation of various alkenes, amines, silanes, and sulfides with H_2O_2 was also investigated (Table 1). Non-activated C_3–C_{12} terminal alkenes **1a**–**1d** were selectively transformed into the corresponding epoxides **2a**–**2d** in high yields (Table 1, entries 1–5). The configurations around the C=C moiety of *cis*- and *trans*-2-octenes (**1e** and **1f**) were retained in the corresponding epoxides **2e** and **2f** (Table 1, entries 6 and 7). These results suggest that free-radical intermediates are not involved in the mechanism of the W–Zn/SnO_2-mediated epoxidation. Under stoichiometric conditions (substrate:H_2O_2 = 1:1), the bulky cyclic alkenes cyclooctene (**1g**) and cyclododecene (**1h**) were also epoxidized in high yields, (Table 1, entries 8 and 9). The epoxidation of dicyclopentadiene (**1i**) with two equivalents of H_2O_2 gave the corresponding di-epoxide **2i** as the main product, with an 87 % selectivity (Table 1, entry 10). Pyridine (**1j**) and di-*n*-butyl amine (**1k**) were oxidized to the corresponding N-oxide **2j** and nitrone **2k** in 92 % and 93 % yields,

Table 1: Oxidation of various substrates with H_2O_2 catalyzed by W-Zn/SnO_2.[a]

Entry	Substrate		t [h]	Yield [%]	Product (Selectivity [%])	
1[b]		R = CH_3 **1b**	5	84		R = CH_3 **2b** (89)
2[c]		R = CH_3 **1b**	6	75		R = CH_3 **2b** (93)
3		R = n-C_4H_9 **1a**	4	91		R = n-C_4H_9 **2a** (95)
4		R = n-C_6H_{13} **1c**	4	81		R = n-C_6H_{13} **2c** (93)
5		R = n-$C_{10}H_{21}$ **1d**	4	80		R = n-$C_{10}H_{21}$ **2d** (93)
6		**1e**	2	85		**2e** (96)
7		**1f**	4	89		**2f** (99)
8		**1g**	4	99		**2g** (> 99)
9		**1h**	4	96		**2h** (> 99)
10		**1i**	6	76		**2i** (87)
11		**1j**	7	92		**2j** (99)
12		**1k**	0.5	99		**2k** (93)
13[d]		**1l**	6.5	92		**2l** (99)
14[d]		**1m**	3.3	94		**2m** (84)
15[e]		**1n**	1.5	99		**2n** (81)
16[e]		**1o**	1	> 99		**2o** (84)

[a] Reaction conditions: W(3.5 wt %)-Zn(0.8 wt %)/SnO_2 (W: 3.3 mol % with respect to H_2O_2), substrate (entries 3–5, 5 mmol; entries 6 and 7, 2 mmol; entries 8, 9, 11, and 13–16, 1 mmol; entries 10 and 12, 0.5 mmol), DMC (3 mL), 60 % aqueous H_2O_2 (1 mmol), 333 K. The catalyst was placed under vacuum for 2 h at ambient temperature before the reaction. The yields of product and selectivity were determined by GC. Yield [%] = (moles of products/initial moles of H_2O_2)x100. [b] **1b** (6 atm). [c] **1b** (6 atm), DMC (6 mL), 30 % aqueous H_2O_2 (1 mmol). [d] 315 K. [e] W(3.5 wt %)-Zn(0.8 wt %)/SnO_2 (W: 0.5 mol % with respect to H_2O_2), DMC (1 mL), 293 K.

respectively (Table 1, entries 11 and 12). Triethylsilane (**1l**) was efficiently oxidized to the corresponding silanol **2l**, without the formation of a disiloxane by self-condensation of **2l** (Table 1, entry 13). In addition, the more sterically exposed dimethylphenylsilane (**1m**) was obtained with a high selectivity for dimethylphenylsilanol (**2m**), which readily self-condenses to form a disiloxane (Table 1, entry 14). Thioanisole (**1n**) and methyl-*n*-octyl sulfide (**1o**) were converted into the corresponding sulfoxides **2n** and **2o** in high yields, under stoichiometric conditions (substrate/$H_2O_2 = 1{:}1$; Table 1, entries 15 and 16).

To verify that the active catalyst was the solid W–Zn/SnO_2 and not tungsten or zinc species which had been leached into the reaction mixture, the epoxidation of **1b** was carried out under the conditions described in Figure 2. The W–Zn/SnO_2 catalyst was then removed from the reaction mixture by filtration, in approximately 40% yield. After the removal of the W–Zn/SnO_2 catalyst, **1b** (6 atm) was introduced into the filtrate, and the solution was heated again to 333 K for 4 hours. In this case, no reaction occurred. Negligible leaching of tungsten and zinc species into the reaction mixture was confirmed by inductively coupled plasma atomic emission spectroscopy ($W < 0.01\%$ and $Zn < 0.02\%$ with respect to fresh W-Zn/SnO_2). These results ruled out leached tungsten or zinc species from contributing to the catalysis, and confirmed that the nature of the catalysis was truly heterogeneous.[11]

The epoxidation of **1b** with W–Zn/SnO_2 and H_2O_2 proceeded efficiently to give **2b** in 84% yield (Figure 2). This reaction had an 89% selectivity for **2b**, which increased to 93% in the presence of 30% aqueous H_2O_2 (Table 1, entry 3). The catalyst recovered from this reaction was reused four times, without significant loss of activity or selectivity. The yield of **2b** after reusing the catalyst for the first time was 85%, followed by 94% for the second reuse, 91% for the third reuse, and 85% for the fourth reuse (Figure 2). In addition, the catalyst used for the epoxidation of bulky **1g** was also reused successfully (Figure 2). Although titanium-based materials with large porosities, such as Ti-β zeolites, Ti–MCM-41 molecular sieves, and titania–silica aerogels, can catalyze the epoxidation of bulky alkenes,[3,12a–c] these systems often require organic hydroperoxides, such as *tert*-butyl hydroperoxide or cumene hydroperoxide. The delaminated Ti–MCM-22 zeolite has high turnover numbers (TONs) for the epoxidation of bulky cycloalkenes, including cyclododecene, with H_2O_2; however, the conversions are still low.[12d] To our knowledge, a high-yielding epoxidation of both small and bulky alkenes with aqueous H_2O_2 and a reusable, supported catalyst has not been reported.

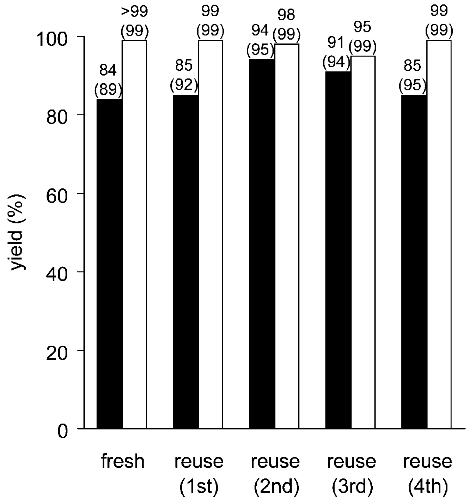
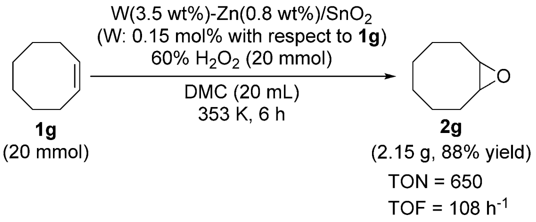


Figure 2. Recycling of W–Zn/SnO_2 for the epoxidation of **1b** (black bar) and **1g** (white bar) with H_2O_2. Reaction conditions: W–Zn/SnO_2 (W: 3.5 wt%, 3.3 mol% with respect to H_2O_2; Zn: 0.8 wt%), substrate (**1b** (6 atm) or **1g** (1 mmol)), 60% aqueous H_2O_2 (1 mmol), DMC (3 mL), 333 K, reaction time 5 h (**1b**) or 4 h (**1g**). The values in parentheses are the selectivity for **2b** or **2g**. The yields of **2b** and **2g** are the average values of three reactions with **1b** and five reactions with **1g**, and the errors are ±5% and ±1%, respectively.

The treatment of W–Zn/SnO_2 with H_2O_2 resulted in new absorption bands at 860 and 550 cm^{-1} in the Raman spectrum. These bands were assigned as ν(O-O) and $\nu(W(O_2))_{asym}$, respectively. In contrast, the intensity of the ν(W=O) band changed very little (see Figure S1(b) in the Supporting Information). These results demonstrated that peroxo species were formed without significant changes in the W–Zn/SnO_2 structure. The Raman spectra of the catalyst before use and after recovery from a reaction were not significantly different (see Figure S1(c) in the Supporting Information). In addition, the rate of the epoxidation of **1g** with recovered W–Zn/SnO_2 ((4.55 ± 0.17) mM min^{-1}) was approximately the same as the rate of reaction recorded with a fresh sample of catalyst ((4.60 ± 0.40) mM min^{-1}; see Figure S2 in the Supporting Information). All these results suggest that the W–Zn/SnO_2 catalyst is intrinsically stable.

To demonstrate the W–Zn/SnO_2 system on a larger scale, the epoxidation reaction was performed on 20 mmol of **1g**, with one equivalent of H_2O_2 (with respect to **1g**). In this case, the yield of isolated **2g** was 88% [Eq. (1)]. The TON of this reaction was 650 and the turnover frequency (TOF) was 108 h^{-1}.

 (1)

Under approximately stoichiometric conditions (**1g**:$H_2O_2 = 1{:}1$–1.5),[5,13,14] the TON and TOF values were larger than the corresponding values for other heterogeneous tungsten catalysts (TON: 6–148, TOF: 1–14 h^{-1}; see Table S5 in the Supporting Information) as well as the homogeneous $H_3PW_{12}O_{40}$/cetylpyridinium chloride (TON: 20, TOF: 1 h^{-1}), and $[(n\text{-}C_4H_9)_4N]_2[SeO_4\{WO(O_2)_2\}_2]$ systems (TON: 47, TOF: 9 h^{-1}). The TON and TOF values for W–Zn/SnO_2 were also comparable with those for the homogeneous $Na_2WO_4{\cdot}2H_2O$/$NH_2CH_2PO_3H_2$/$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ system (TON: 490, TOF: 123 h^{-1}).

The molecular structure of W–Zn/SnO_2 (Zn: 0.8 wt%, W: 0.7–4.8 wt%) was investigated by using Raman and IR spectroscopy. In addition to the absorption bands for the SnO_2 support,[15] the Raman spectrum of W(0.7 wt%)–Zn/SnO_2 had a broad absorption band at 936 cm^{-1}. This band was assigned as the W=O stretching mode (ν(W=O); Figure 3a), and was close to that observed in the spectrum of the aqueous monotungstate $[WO_4]^{2-}$ (932 cm^{-1}).[9] Upon increasing the loading of tungsten, new ν(W=O) absorption bands appeared at higher wavenumbers. The intensities of the absorbance bands at 230 cm^{-1} in the Raman spectrum and at 880 cm^{-1} in the IR spectrum also gradually increased with increases in the loading of tungsten. These bands were assigned to the W-O-W bending and the W-O stretching modes of polytungstates, respectively. [4,9,16,17] At a tungsten loading of 4.8 wt%, weak absorbance bands appeared at 815, 715, and 270 cm^{-1} in the Raman spectrum, which were assigned to crystalline WO_3.[18] These results suggest that the W–Zn/SnO_2 catalyst consists of three possible molecular structures, which are dependent on the loading of tungsten: monotungstates at 0.7 wt% or less, polytungstates at 0.7–4.1 wt%, and polytungstates/crystalline WO_3 at 4.8 wt%.

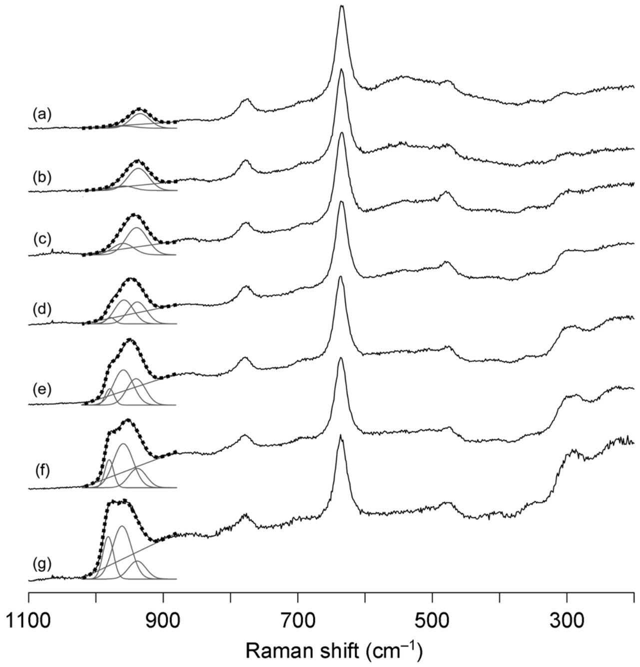
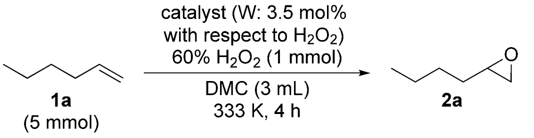


Figure 3. Raman spectra (200–1100 cm^{-1}) of W–Zn/SnO_2 (Zn: 0.8 wt%; W: a) 0.7 wt%, b) 1.4 wt%, c) 2.1 wt%, d) 2.8 wt%, e) 3.5 wt%, f) 4.1 wt%, and g) 4.8 wt%). The SnO_2 support produced strong absorption bands at 780 (B_{2g}), 635 (A_{1g}), and 480 cm^{-1} (E_g).[15] The spectra in the region of 880–1020 cm^{-1} were closely reproduced by the sum (dotted lines) of the deconvoluted bands (solid lines).

The broad absorbance band in the Raman spectrum, which was assigned as ν(W=O), could be reproduced by combining the three deconvoluted bands at 936, 959, and 980 cm^{-1} (Figure 3). It has been reported that the ν(W=O) absorptions of supported tungsten oxides on SiO_2, Al_2O_3, and TiO_2 occur at 932–951, 950–973, and 981–984 cm^{-1}. These bands have been assigned as monotungstates, polytungstates with dioxo groups ($[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ (paratungstate)), and polytungstates with monoxo groups ($[W_{10}O_{32}]^{4-}$ and $[H_2W_{12}O_{40}]^{6-}$ (metatungstate)), respectively (see Figure S4 in the Supporting Information).[9,16] Therefore, the absorbance bands at 936, 959, and 980 cm^{-1} in the Raman spectrum of W–Zn/SnO_2 were assigned as monotungstates, polytungstates with dioxo groups, and polytungstates with monoxo groups, respectively.

When the areas of each deconvoluted absorbance band in the Raman spectrum were normalized (with respect to the tungsten content) and plotted against the loading of tungsten (see Figure S5 in the Supporting Information), the area corresponding to polytungstates with dioxo groups reached a maximum at 4.1 wt% of tungsten. Similarly, the yields of epoxide products reached a maximum at 4.1 wt% of tungsten (Figure 1). In a separate series of experiments, various tungstates ($[WO_4]^{2-}$, $[W_7O_{24}]^{6-}$, $[H_2W_{12}O_{42}]^{10-}$ (paratungstate), and $[H_2W_{12}O_{40}]^{6-}$ (metatungstate)) were loaded onto a Zn/SnO_2 support (W_n–Zn/SnO_2 ($n = 1$, 7, 12(para), and 12(meta); see the Supporting Information for details) by the ion exchange method. The W_7–Zn/SnO_2 and $W_{12(para)}$–Zn/SnO_2 catalysts had higher catalytic activities for the epoxidation of **1a** than the W_1–Zn/SnO_2 and $W_{12(meta)}$–Zn/SnO_2 catalysts [Eq. (2)]. These results support the idea that polytungstates with dioxo groups play an important role in the present epoxidation.[19]



(2)

W_7-Zn/SnO_2: 84% yield, 89% selectivity for **2a**
$W_{12(para)}$-Zn/SnO_2: 78% yield, 95% selectivity for **2a**
$W_{12(meta)}$-Zn/SnO_2: 30% yield, 96% selectivity for **2a**
W_1-Zn/SnO_2: 28% yield, 95% selectivity for **2a**

In summary, a combination of tungsten and zinc oxides on a SnO_2 support was an effective and reusable solid catalyst for selective oxidation with aqueous H_2O_2. Various organic substrates such as alkenes, amines, silanes, and sulfides could be converted into the corresponding epoxides, N-oxides, silanols, and sulfoxides, in high yields. The catalysis was heterogeneous and the catalyst could be recovered from reactions and reused several times, without an appreciable loss of its high catalytic performance. Experimental evidence suggests that polytungstates with dioxo groups in W–Zn/SnO_2 play an important role in the oxidation process.

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