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WO_3 Nanoparticles on MCM-48 as a Highly Selective and Versatile Heterogeneous Catalyst for the Oxidation of Olefins, Sulfides, and Cyclic Ketones

Dong Hyun Koo, Min Kim, and Sukbok Chang*

Center for Molecular Design and Synthesis (CMDS), Department of Chemistry and School of Molecular Science (BK 21), Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

sbchang@kaist.ac.kr

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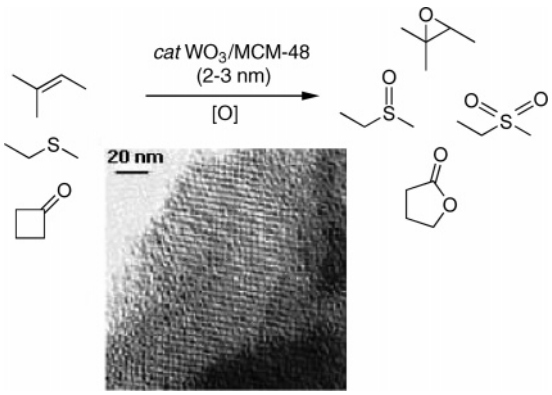
ABSTRACT



It is shown that nanosized WO_3 particles supported on MCM-48 work as a highly efficient and selective heterogeneous catalyst for the oxidation of olefins, sulfides, and cyclic ketones using hydrogen peroxide or peracetic acid. The catalytic activity of the supported tungstate was dependent on the nature of the supporting materials and particle size. The catalyst system employs environmentally benign oxidants in halide-free solvents, and it does not require phase-transfer agents and pH control.

The oxygen transfer reaction is one of the most fundamental and useful transformations in organic chemistry, and, inspired from nature, numerous metal-catalyzed oxidation procedures have been investigated.[1] Although a number of efficient homogeneous catalyst systems have been developed for that purpose, there is a strong demand for the user-friendly heterogeneous version that can utilize benign oxidants.[2] In this context, the utility of heterogeneous tungstate systems has been actively examined due to the fact that a variety of tungsten-based homogeneous catalysts are known to display high activities in useful oxidation procedures including epoxidation of alkenes,[3] alcohol oxidation,[4] oxidative cleavage or halogenation of olefins,[5] or oxidative desulfurization.[6] As a result, some promising heterogeneous systems such as

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(2) (a) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485. (b) Corma, A.; Garcia, H. *Chem. Rev.* **2003**, *103*, 4307.

(3) (a) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. (b) Herrmann, W. A.; Fridgen, J.; Lobmaier, G. M.; Spiegler, M. *New. J. Chem.* **1999**, *23*, 5.

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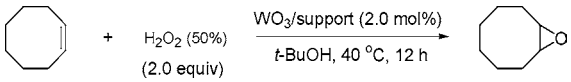
insoluble polyoxotungstates,[7] immobilized peroxotungstates,[8] triphasic phosphotungstate,[9] or pseudo-heterogeneous systems[10] have been recently reported.

Recent advances in the preparation of size-controlled nanoparticles have led us to search for applications in catalysis with a prediction that large surface areas of such particles may offer novel catalytic activities.[11] Much attention has been also paid to the use of supported nanocatalyst systems.[12] Along this line, preparative methods for the W-containing mesoporous sieves were disclosed,[13] and their catalytic activities were also preliminarily presented. Among the reactions examined, representative examples are hydroxylation of cyclohexene,[14] oxidative cleavage of cyclopentene to glutaraldehyde,[15] and dehydrogenation of 2-propanol.[16] Herein, we describe our studies on the preparation of supported WO_3 nanoparticles and their catalytic activities in the oxidations of olefins, sulfides, and cyclic ketones.[17]

We prepared tungsten(VI) oxide nanoparticles supported on a range of templates.[18] With the use of ordered mesoporous supports, the resulting WO_3 nanoparticles are uniformly dispersed on the surface of the channels. Inductively coupled plasma (ICP) analysis showed that tungstate was quantitatively supported on the supporting materials, and the weight percentage of the immobilization could be controlled at the desired weight percentage. X-ray photoelectron spectroscopy (XPS, see the Supporting Information) indicates that the binding energy of the supported tungstens's $4f_{2/7}$ is 35.8 eV, which is in a range of typical values of WO_3.[19]

While bulk powder WO_3 exhibited a low activity in the epoxidation of *cis*-cyclooctene using 50% aqueous H_2O_2 (Table 1, entry 1), downsizing the particles (30−100 nm)

Table 1. Effects of Supporting Materials on the Epoxidation[a]



entry	supporting materials	conv[b] (%)	selec[c] (%)
1[d]		30	33
2	*nano*-WO_3[e]	91	91
3	alumina	45	71
4	TiO_2	57	>98
5	activated carbon	79	94
6	CeO_2	62	>98
7	MgO	10	<5
8	Montmorillonite K 10	28	<5
9	MCM-48[f]	>99	>98
10	MCM-48[g]	78	>98

[a] Average ca. 5 wt % of WO_3 except entry 10. [b] Conversion was determined by GC using an internal standard (dodecane). [c] Selectivity for the formation of cyclooctene oxide. [d] Bulk powder WO_3 was used. [e] Nanoparticles with an average size of 30−100 nm. [f] Average size of 2−3 nm for WO_3 (5.0 wt %). [g] Average size of 3−10 nm for WO_3 (20 wt %).

resulted in a dramatic increase in the activity and selectivity (entry 2). When we examined the effects of supporting materials, it was observed that *catalytic activity of the supported tungstate was closely related to the nature of the supporting materials and size of the nanoparticles*. Whereas the use of certain supporting materials such as alumina, TiO_2, active carbon, or CeO_2 gave moderate activities, employment of MgO and Montmorillonite K 10 resulted in a sharp decrease in the epoxidation efficiency (entries 7−8). It is of special interest to see that when MCM-48, ordered silica-based 3D mesoporous materials,[20] was applied as a support, the catalytic activity of the resulting WO_3/MCM-48 was dramatically increased (entry 9). More interestingly, a diol that normally forms by an acid-catalyzed hydrolysis of epoxide was not observed. Additionally, it was seen that the catalytic activity was changed inversely to the metal content and size of the nanoparticles (entry 10).[21]

The scope of the prepared WO_3/MCM-48 catalyst system was in turn tested in the epoxidation of various olefins (Table 2).[22] It displays an excellent activity and selectivity especially

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(18) **Preparation of WO_3/MCM-48.** WCl_6 (120 mg, 0.3 mmol), MCM-48 (1.0 g), and benzene (20 mL) were placed in a 50 mL two-neck flask with a magnetic stirring bar. The color of the reaction mixture became blue from gray after being stirring for 12 h at room temperature under an argon atmosphere. The solution was filtered and washed with benzene, and the obtained solid was dried in vacuo. The light blue solid was calcined for 2 h at 300 °C flowing with H_2 gas. After being cooled to room temperature, the solid was treated with O_2 flow for 1 h at the same temperature to give a gray powder (1.0 g).

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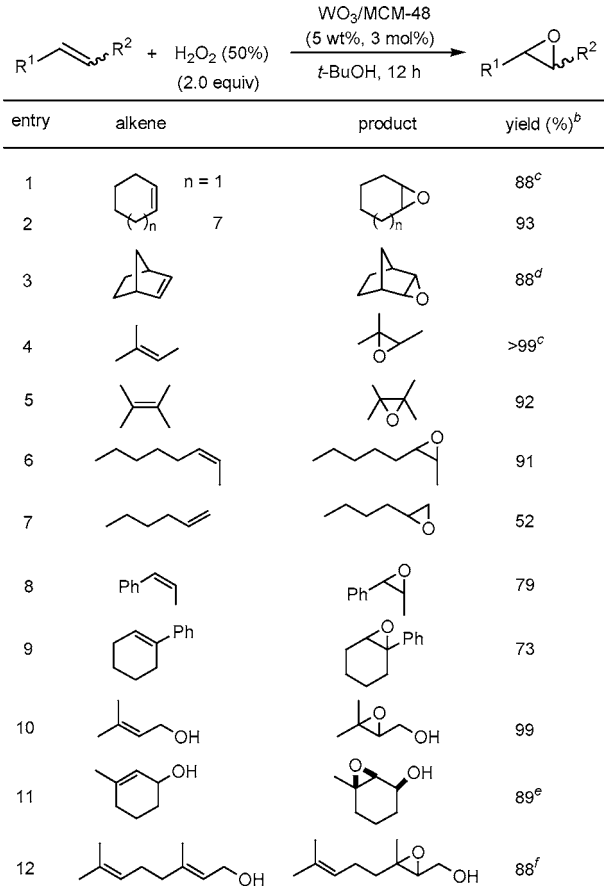
Table 2. Epoxidation of Olefins with WO_3/MCM-48[a]



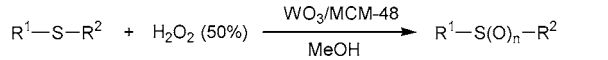
entry	alkene	product	yield (%)[b]
1	n = 1		88[c]
2	7		93
3			88[d]
4			>99[c]
5			92
6			91
7			52
8	Ph	Ph	79
9	Ph	Ph	73
10	OH	OH	99
11	OH	OH	89[e]
12	OH	OH	88[f]

[a] Ran at 40 °C except entry 8 (70 °C). [b] Avergae isolated yields of two runs. [c] GC yields based on an internal standard (dodecane). [d] >99% *endo*-selectivity determined by ^{1}H NMR. [e] Mixture of *syn/anti* epoxide (4.4:1) determined by ^{1}H NMR. [f] H_2O_2 (1.3 equiv) was used and a mixture of 2,3-epoxide/6,7-epoxide (6.8:1) determined by ^{1}H NMR.

for aliphatic internal double bonds at 40 °C in *tert*-butyl alcohol using 50% aqueous H_2O_2.[23] Norbornene was epoxidized stereoselectively to give *endo* product (*endo*/*exo*, >99:1, entry 3). While di-, tri-, and tetrasubstituted aliphatic olefins were all excellent substrates, terminal olefins turned out to be rather slow in reacting (entry 7). Reaction of electron-deficient double bonds was sluggish under the conditions, and acceptable yields were obtained only at higher temperatures (entry 8). It is especially interesting to note that the reaction takes place in a functional group-directed manner. For example, an allylic alcohol was epoxidized stereoselectively to give *syn*-epoxy alcohol as a major product (*syn/anti*-epoxide = 4.4:1, entry 11). In addition, reaction on an allylic double bond was much faster than a remote isolated one (entry 12). When the solid catalyst was filtered out at the same reaction temperature after reaching 50% conversion, tungsten was not detected from the filtrate by an ICP analysis. In addition, no further conversion was observed from the filtrate, thus strongly suggesting that the oxidation proceeds under the heterogeneous conditions.

We next examined the catalytic efficiency of WO_3/MCM-48 in the oxidation of sulfides.[24] When the catalyst (1.0 mol %) was employed, a selective oxidation was readily achieved upon the control of equivalents of hydrogen peroxide oxidant (Table 3).[25] When sulfides were treated with 1.1 equiv of aqueous H_2O_2 (50%) for 4 h at 25 °C in methanol (condition A), the corresponding sulfoxides were produced in high yields with excellent selectivity. On the other hand, the use of excessive H_2O_2 (3.0 equiv) at higher temperatures (60 °C, condition B) resulted in a complete conversion to sulfones within 12 h. Scope of the oxidation turned out to be broad

Table 3. Selective Oxidation of Sulfides Using WO_3/MCM-48[a]



entry	sulfide	condition[b]	yield (%)[c] sulfoxide	yield (%)[c] sulfone
1	S	A	94(91)	6
2		B	5	95(93)
3	Ph S Ph	A	>99(98)	—
4		B	—	>99(97)
5	Ph S	A	97(93)	<3
6		B	—	>99(96)
7	Ph S Cl	A	95(92)	5
8		B	—	>99(95)
9	Ph S Ph	A	98(96)	<2
10		B	—	>99(96)

[a] Sulfide (0.5 mmol), 50% H_2O_2, and WO_3/MCM-48 (5.0 wt %, 2−3 nm, 1.0 mol %) in MeOH (2.0 mL). [b] Condition A: 1.1 equiv of H_2O_2, 25 °C, 4 h. Condition B: 3.0 equiv of H_2O_2, 60 °C, 12 h. [c] Average NMR yields of two runs based on an internal standard (anisole), and the numbers in parentheses are isolated yields.

(22) **General Procedure of Epoxidation.** To a suspension of an olefin (0.5 mmol), WO_3/MCM-48 (3.0 mol %), and dodecane (0.5 mmol) in *t*-BuOH (1.0 mL) was added H_2O_2 (50 wt % solution in water, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 12 h at either 40 or 70 °C depending on substrates employed. The epoxide products were isolated by using a silica gel column chromatography.

(23) When 30% H_2O_2 was used, the reaction rate was slowed and more than 36 h (vs 12 h with 50% H_2O_2) was required for a complete conversion of *cis*-cyclooctene, although the selectivity was still high.

(24) (a) Choudary, B. M.; Bharathi, B.; Reddy, C. V.; Kantam, M. L. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2069. (b) Ayala, V.; Corma, A.; Iglesias, M.; Sanchez, F. *J. Mol. Catal. A: Chem.* **2004**, *221*, 201.

(25) **General Procedure for Sulfide Oxidation.** To a solution of a sulfide (0.50 mmol) in methanol (2.0 mL) was added WO_3/MCM-48 (1.0 mol %) followed by hydrogen peroxide (0.56 mmol, 50 wt % in aqueous solution) dropwise over 5 min at 0 °C. The reaction mixture was stirred for 4 h at room temperature (condition A). For the formation of sulfone, the reaction was carried out at 60 °C for 12 h using 3.0 equiv of 50% hydrogen peroxide (condition B). WO_3/MCM-48 was removed by filtration and washed with ethyl acetate. The crude product was extracted with ethyl acetate and washed with brine. The extracted organic layers were separated, dried over anhydrous $MgSO_4$, and then filtered. The products were isolated by a silica gel column chromatography.

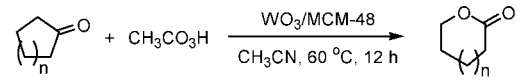
such that sulfides substituted with alkyl, benzyl, and aryl groups were all converted to the corresponding sulfones in excellent yields. As expected, when a sulfoxide was subjected to the condition B, a sulfone was quantitatively generated, suggesting that oxygenation of sulfides to sulfones takes place stepwise via sulfoxide.

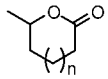
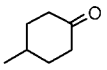
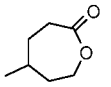
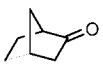
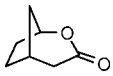
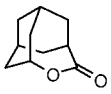
Catalytic activity of WO_3/MCM-48 was also examined in the Baeyer−Villiger oxidation, which is of considerable synthetic interest.[26] When the catalyst (5.0 mol %) was used in combination with peracetic acid in CH_3CN, ketones were smoothly converted to lactones at 60 °C within 12 h (Table 4).[27] No lactone was obtained in the absence of catalyst under these conditions, and hydrogen peroxide turned out to be much less effective in this case. Although the efficiency of the conversion was dependent on the ring size of cyclic ketones, selectivity for the formation of lactones was excellent in all cases examined. Whereas reaction of cyclobutanone occurs readily to afford γ-butyrolactone in high yield (entry 3), the use of 5- or 6-ring ketones resulted in lower product formation (entries 1−2). As expected, preferential migration of more substituted carbon was observed (entries 4, 5, and 7). Reaction of adamantanone takes place readily, leading to the corresponding lactone in excellent yield (entry 8).

The supported nanocatalyst of WO_3 was quantitatively recovered by a simple filtration or centrifugation after the reactions and was readily reused in the next runs without losing its catalytic activity. For example, the epoxidation of cylooctene could be carried out more than five cycles with almost consistent activity using the recovered catalyst.[28] Additionally, the reaction was easily processed up to gram scale without giving any practical difficulties.

In summary, we have shown that WO_3 nanoparticles supported on MCM-48 work as a highly efficient and selective heterogeneous catalyst for the oxidation of olefins, sulfides, and cyclic ketones with a broad substrate scope. The catalytic activity turned out to be dependent on the nature of the supporting materials and particle size of the metal oxide. In addition, the catalyst system uses only environmentally benign oxidants in halide-free solvents, and it does not require phase-transfer agents and pH control, thus making its further applications highly promising.

Table 4. WO_3/MCM-48-Catalyzed Baeyer−Villiger Oxidation[a]



entry	ketone	product	conv (%)[b]	selec (%)[c]
1	 n = 2		85	93
2	1		67	95
3	0		>99	97
4	 n = 2		95	84
5	1		60	96
6			88	83
7			80	>98
8			>99	>98

[a] Cyclic ketone (0.5 mmol), WO_3/MCM-48 (5.0 wt %, 2−3 nm, 5.0 mol %), and peracetic acid (32%, 1.5 mmol) in CH_3CN (1.0 mL). [b] Average conversion of two runs based on ^1H NMR using an internal standard (anisole). [c] Selectivity for the desired lactone formation.

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Supporting Information Available: Detailed methods for the preparation of the supported WO_3 catalysts and typical oxidations procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) For recent selected examples of heterogeneous Bayer−Villiger reactions, see: (a) Corma, A.; Nemeth, L. T.; Renz, M.; Valencia, S. *Nature* **2001**, *412*, 423. (b) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Rev.* **2004**, *104*, 4105.

(27) **General Procedure of the Baeyer−Villiger Oxidation.** To a solution of a cyclic ketone (0.5 mmol) in CH_3CN (1.0 mL) was added WO_3/MCM-48 (5.0 mol %) followed by peracetic acid (1.5 mmol, 32 wt %). The reaction mixture was stirred for 12 h at 60 °C. WO_3/MCM-48 was removed by filtration, and the crude product was extracted with ethyl acetate washing with brine. The lactone products were isolated by a silica gel column chromatography.

(28) On the other hand, the recovered WO_3 nanaoparticles without supporting materials revealed that the catalytic activity was lost down to ca. 70% of the original activity.