Supporting Information

WO₃ 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*

General Methods. Solvents were dried over standard drying agents and freshly distilled prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 and 100 MHz, respectively). Column chromatography was carried out using silica gel 60 (230-400 mesh, ASTM, Merck). Tungstate precursors and supporting materials including alumina, TiO₂, activated carbon, CeO₂, MgO, and Montmorillonite K 10 were purchased from Aldrich or TCI, and used as such without further purification. Alkenes, sulfides, and cyclic ketones were also purchased from Aldrich or TCI, and used as obtained. X-ray photoelectron spectra were recorded on a VG Sci ESCA Lab200R with a dual anode (Mg and Al) apparatus. The pressure in the spectrometer was about 10⁻¹⁰ torr. For energy calibration, the alumina 1s photoelectron line was used and the alumina 1s binding energy was taken to be 74.0 eV. High resolution transmission electron microscopy (TEM) images were obtained with a Hitachi H9000-NAR operated at 300 kV. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RC (12 kW) system using graphite-monochromatic Cu-K radiation at 40 KV and 45 mA.

Preparation of WO₃ nanoparticles.¹ WCl₆ (400 mg) was slowly added to 20 mL of benzyl alcohol with vigorous stirring at room temperature. The reaction vessel was covered and the solution was heated to 100 °C, and then aged for 48 h at the same temperature. After cooling the reaction mixture to room temperature, the resulting suspension was centrifuged, and then thoroughly washed with 99% ethanol. The WO₃ nanoparticles (100 mg) were obtained after drying the obtained solid in *vacuo* overnight. The average size of the particles was determined to be 30-100 nm by TEM images.

Figure S1. TEM image of WO₃ nanoparticles

Preparation of MCM-48. It was prepared according to a reported procedure.² Silica source used in the present synthesis was an aqueous solution of sodium tetrasilicate (11.3 wt% of Na₂Si₄O₉ and 88.6 wt% of H₂O), which was in turn prepared with colloidal silica Ludox HS40 (39.5 wt% of SiO₂, 0.4 wt% of Na₂O, and 60.1 wt% of H₂O, Aldrich), distilled water, and NaOH. The surfactant mixture was prepared by dissolving a cationic surfactant and a neutral surfactant simultaneously with heating in distilled water. The surfactant solution was cooled to room temperature. The silica source and the surfactant solution were quickly poured into a large polypropylene bottle at room temperature. The bottle was capped and shaken rapidly and vigorously. The gel mixture thus obtained was heated for the formation of the surfactant-silica mesophases under static conditions at 100 °C. The mesophases formed afloat at an early stage of heating. When this happened, a bottle containing the reaction mixture was sometimes agitated in order to induce precipitation on the bottom. Precipitated products from the reaction mixture were filtered, washed with distilled water, and then dried in an oven at 120 °C. After removal of surfactants by washing with HCl-ethanol solution (0.5 and 20 mL per gram of MCM-48, respectively), the solid was calcined at 550 °C in air.

Figure S2. XRD of MCM-48

Preparation of WO₃/MCM-48.³ All operations for the preparation of WO₃/MCM-48 were conducted under an atmosphere of argon gas, and standard Schlenk-type glassware were used. The WO₃/MCM-48 catalyst was prepared by a slight modification of a reported impregnation method.³

WCl₆ (120 mg, 0.3 mmol), MCM-48 (1.0 g), and benzene (20 mL) were placed in a 50 mL two-neck flask with magnetic stirring bar under argon gas. Color of the reaction mixture became blue from gray after stirring it for 12 h at room temperature. The solution was filtered washing with benzene, and the obtained solid was dried in *vacuo*. The light blue solid was calcined for 2 h at 300 °C flowing with H₂ gas. After cooling to room temperature, the solid was treated with O₂ flowing for 1 h at the same temperature to give a grey powder (1.0 g). ICP analysis showed that tungsten was contained in 5.0 wt%. Higher loadings of WO₃/MCM-48 (e.g. 20 wt%) were readily achieved by using the same procedure as above except that 480 mg (1.2 mmol) of WCl₆ was employed.

Figure S3. TEM image (left) and XPS spectrum (right) of WO₃/MCM-48

Preparation of WO₃/Al₂O₃.⁴ To a solution of ammonium paratungstate (35 mg) in water (2.0 mL) was added Al₂O₃ (500 mg). After stirring the reaction mixture for 2 h at room temperature under an argon atmosphere, the solvent was removed by evaporation in an oven at 100 °C for 3 h. The obtained solid was calcined in air for 3 h at 550 °C leading to a white powder (500 mg). ICP analysis indicated that tungsten is contained in 5.0 wt%.

Figure S4. XRD and TEM image of WO₃/Al₂O₃

Preparation of WO₃/TiO₂.⁵ To a solution of ammonium paratungstate (35 mg) in water (2.0 mL) was added TiO₂ (500 mg). After stirring the reaction mixture for 2 h at room temperature under argon atmosphere, the solvent was removed by evaporation in an oven at 100 °C for 3 h, and then the remaining solid was calcined in air for 3 h at 550 °C leading to a white powder (500 mg). ICP analysis of the solid indicated that tungsten is contained in 4.9 wt%.

Figure S5. XRD and TEM image of WO₃/TiO₂

Preparation of WO₃/MgO.⁶ To a solution of ammonium paratungstate (35 mg) in distilled water (2.0 mL) was added MgO (500 mg) with vigorous stirring. After stirring the reaction mixture for 2 h at room temperature, solvent was removed by slow evaporation in an oven at 100 °C over 12 h. The remaining solid was then calcined at 550 °C for 3 h in air. After cooling to room temperature, white powder (500 mg) was obtained and an ICP analysis indicated that tungsten was contained in 5.0 wt%.

Figure S6. XRD and TEM image of WO₃/MgO

Preparation of WO₃/Activated Carbon.⁷ To a solution of ammonium paratungstate (35 mg) in distilled water (2.0 mL) was added activated carbon (500 mg) with vigorous stirring. After stirring the reaction mixture for 6 h at room temperature, the solvent was removed slowly by evaporation in an oven at 100 °C over 12 h. The remaining solid was then calcined at 550 °C for 3 h in air. After cooling to room temperature, a black powder (500 mg) was obtained and an ICP analysis indicated that tungsten was contained in 5.0 wt%.

Figure S7. XRD and TEM image of WO₃/activated carbon

Preparation of WO₃/Montmorillonite K 10. To a solution of ammonium paratungstate (35 mg) in distilled water (2.0 mL) was added Montmorillonite K 10 (500 mg) with vigorous stirring. After stirring the reaction mixture at room temperature for 12 h under argon atmosphere, the solvent was slowly removed by placing the mixture in an oven at 100 °C for 3 h. The remaining solid was calcined at 550 °C for 3 h in air. After cooling to room temperature, a beige powder (500 mg) was obtained and an ICP analysis indicated that tungsten was contained in 4.6 wt%.

Figure S8. XRD and TEM image of WO₃/Montmorillonite K 10

Preparation of WO₃/CeO₂.⁸ To a solution of ammonium paratungstate (35 mg) in distilled water (2.0 mL) was added CeO₂ (500 mg) with vigorous stirring. After stirring the reaction mixture for 4 h at room temperature, solvent was removed by placing the mixture in an oven at 100 °C for 5 h. The remaining solid was calcined in air at 50 °C for 5 h, at 105 °C for 12 h, and then at 400 °C for 4 h. After cooling to room temperature, a white powder (500 mg) was obtained and an ICP analysis indicated that tungsten was contained in 5.1 wt%.

Figure S9. XRD and TEM image of WO₃/CeO₂

Figure S10. XPS of nanosized WO₃ particles supported on various materials

General Procedure of Epoxidation. To a suspension of an olefin (0.5 mmol), WO₃/MCM-48 (3.0 mol %), and dodecane (0.5 mmol) in *t*-BuOH (1.0 mL) was added H₂O₂ (50 wt% solution in water, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 12 h at either 40 °C or 70 °C depending on substrate employed. The yields were determined by GC analysis based on the integration of an internal standard (dodecane). In case of nonvolatile epoxides, the products were isolated by using a silica gel column chromatography.

General Procedure for the Sulfide Oxidation to Sulfoxides. To a solution of a sulfide (0.50 mmol) in methanol (2.0 mL) was added WO₃/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. WO₃/MCM-48 was removed by a simple filtration washing with ethyl acetate. The crude product was extracted with ethyl acetate washing with brine. The extracted organic layers were separated, dried over anhydrous MgSO₄, and then filtered. NMR yield was obtained based on the integration of an internal standard (anisole), and the product was isolated by a silica gel column chromatography.

General Procedure for the Sulfide Oxidation to Sulfones. The reaction was carried out under the same condition as above except that hydrogen peroxide (50%) was used in 3.0 equiv to sulfides. In addition, the reaction was carried out at 60 °C for 12 h.

General Procedure of the Baeyer-Villiger Oxidation. To a solution of a cyclic ketone (0.5 mmol) in CH₃CN (1.0 mL) was added WO₃/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. WO₃/MCM-48 was removed by a simple filtration and the crude product was extracted from the filtrate with ethyl acetate washing with brine. Selectivity for the formation of the desired lactones was calculated by comparing the integration of lactone with that of an internal standard (anisole) using ¹H-NMR spectroscopy. Nonvolatile products were isolated by a silica gel column chromatography.

General Procedure for the Recovery and Reuse of WO₃/MCM-48 Catalyst System. After the oxidations, WO₃/MCM-48 catalyst was recovered quantitatively either by a centrifugation or by a filtration washing with the solvents employed. The isolated solid was dried in *vacuo* at 100 °C for 12 h, and the recovered catalyst could be reused in the next runs with almost identical catalytic activity. Particularly, in case of epoxidation reaction, the catalyst was reused up to five runs without losing any activity.

Gram Scale Epoxidation Reaction. There were no practical difficulties in the oxidation reactions up to a gram scale even using reduced amounts of the catalyst. For example, an epoxidation reaction of *cis*-cyclooctene (1.1 g, 10.0 mmol) could be carried out using only 0.5 mol% of WO₃/MCM-48 catalyst under otherwise identical conditions as in the small scale reaction to afford 1.2 g (95%) of the desired epoxide.

References

- (1) Niederberger, M.; Bartl, M. H.; Stucky, G. D. *J. Am. Chem. Soc.* **2002**, *124*, 13642.
- (2) (a) Ryoo, R.; Kim, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 711. (b) Ryoo, R.; Joo, S. H.; Kim, J. M. *J. Phys. Chem. B.* **1999**, *103*, 7435.
- (3) (a) Wojciechowska, M.; Gut, W.; Szymenderska, V. *Catal. Lett.* **1990**, *7*, 431. (b) Neumann, R.; Levin-Elad, M. *J. Catal.* **1997**, *166*, 206.
- (4) Martín, C.; Solana, G.; Malet, P.; Rives, V. *Catal. Today* **2003**, *78*, 365.
- (5) Kwon, Y. T.; Song, K. Y.; Lee, W. I.; Choi, G. J.; Do, Y. R. *J. Catal.* **2000**, *191*, 192.
- (6) Pérez-Cadenas, A. F.; Moreno-Castilla, C.; Maldonado-Hódar, F. J.; Fierro, J. L. G. *J. Catal.* **2003**, *217*, 30.
- (7) Alvarez-Merino, M. A.; Carrasco-Marín, F.; Fierro, J. L. G.; Moreno-Castilla, C. *J. Catal.* **2000**, *192*, 363.
- (8) (a) Baker, B. G.; Clark, N. J. *Stud. Surf. Sci. Catal.* **1987**, *30*, 483. (b) Bigey, C.; Hilaire, L.; Maire, G. *J. Catal.* **2001**, *198*, 208.