

Catalytic performance of Keplerate polyoxomolybdates in green epoxidation of alkenes with hydrogen peroxide

Fariba Jalilian^a, Bahram Yadollahi^{a*}, Mostafa Riahi Farsani^b, Shahram Tangestaninejad^a, Hadi Amiri Rudbari^a, Rouhollah Habibi^c

^a*Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran*

^b*Department of Chemistry, Shahrekord Branch, Islamic Azad University, Shahrekord, Iran*

^c*Kimiatrava Tech. Co., Science & Technology Town (STT), Isfahan University of Technology, Iran*

Supporting Information

1. General Methods and Materials: Mo₁₃₂, Mo₇₂V₃₀, Mo₇₂Fe₃₀ and Mo₇₂Cr₃₀ prepared according to the literature methods [1–3]. All common laboratory chemicals were reagent grade, commercially prepared and used without further purification. Elemental analyses for C, S, Cr, Fe, V, Mo and K were carried out on a Perkin-Elmer 7300 DV and Leco CHNS-932 elemental analyzer. Infrared spectra (KBr pellets) were recorded on a JASCO FT/IR-6300 instrument. ¹H NMR spectra were recorded on a Bruker 400 (296 K) using CDCl₃ as solvent and TMS as an internal reference. The oxidation products were quantitatively analyzed by gas chromatography (GC) on a Chrompack CP 9001 instrument using a SIL-5CB column (50 m, 32 mm, 5 μm) and

* Corresponding Author. Tel: +98-311-7932742; fax: +98-311-6689732; e-mail: yadollahi@chem.ui.ac.ir, yadollahi.b@gmail.com

FID detector. Powder X-ray diffraction (XRD) data were obtained on a D8 Advanced Bruker using Cu K α radiation ($2\theta = 5\text{--}80^\circ$).

2. Synthesis of Mo₇₂Cr₃₀: CrCl₃·6H₂O (8.6 g, 32.27 mmol) was added to a solution of Na₂MoO₄·2H₂O (9.0 g, 37.2 mmol) in a H₂O (80 mL)/CH₃COOH (100%; 35 mL) mixture. After stirring for 5 min it was acidified with 1M HCl (17 mL; resulting pH ~2), and the solution was heated under reflux for 45 min. The cooling of resulting green solution to room temperature gave the pale green precipitate. Elemental analysis: Found: C, 2.53; Cr, 8.86; Mo, 38.80. Calc. for Mo₇₂Cr₃₀: C, 2.58; Cr, 8.81; Mo, 38.99%. IR (KBr pellet, cm⁻¹): 1622 (m, H₂O), 1547 (m, COO), 1423 (w, COO), 953 (m, (Mo=O)), 796 (s), 635 (w), 580 (s), 455 (w).

3. Synthesis of Mo₇₂Fe₃₀: To a stirred orange-red solution of FeCl₃·6H₂O (1.1 g, 4.1 mmol) and CH₃COONa·H₂O (1.1 g, 8.1 mmol) in H₂O (75 mL), the NH₄⁺ salt of Mo₁₃₂ (1.4 g, 0.05 mmol) was added. The resulting mixture was vigorously stirred in an open 100-mL Erlenmeyer flask (wide-necked) for 24 h. After acidification with HCl (1M, 1 mL) and addition of NaCl (2.0 g), the stirred reaction mixture was heated to 90°C and then filtered while still hot. The golden yellow filtrate was cooled to 20 °C, and yellow, rhombic crystals of Mo₇₂Fe₃₀ formed over a period of 2-3 day. The crystals were collected by filtration through a glass frit, washed twice with a little iced water (to remove the adhering NaCl), and dried in air. Elemental analysis: Found: C, 1.50; Fe, 8.83; Mo, 38.67. Calc. for Mo₇₂Fe₃₀: C, 1.54; Fe, 8.95; Mo, 39.96%. Characteristic IR bands (KBr pellet, cm⁻¹): 1622 (m, (H₂O)), 1535 (m, COO), 1404 (s-m, COO), 965 (m, Mo=O), 851 (m), 776 (s), 621 (m), 571 (s), 435.

4. Synthesis of Mo₇₂V₃₀: A solution of VOSO₄·5H₂O (2.53 g, 10 mmol) in H₂O (35 mL) was added to a stirred solution of Na₂MoO₄·2H₂O (2.42 g, 10 mmol) in H₂SO₄ (0.5 M; 8 mL) in a conical flask. The resulting dark purple mixture was stirred at room temperature for 30 min (flask

closed with a rubber stopper) and then treated with KCl (0.65 g, 8.72 mmol). After additional stirring for 30 min the solution was stored in the flask which was closed with a rubber stopper. After 5 days, the purple-black rhombic crystals were collected by filtration, washed with cold water, and finally dried in air. Elemental analysis: Found: K, 4.87; Mo, 35.1; S, 2.05; V, 8.38. Calc. for $\text{Mo}_{72}\text{V}_{32}$: K, 4.92; Mo, 36.23; S, 2.02; V, 8.55. IR (KBr pellet, cm^{-1}): 1622 (m, H_2O), 1198 (w), 1130 (w), 1055 (w, SO_4), 964 (s, $\text{V}=\text{O}/(\text{Mo}=\text{O})$), 791 (vs), 631 (w), 575 (s), 449 (w). The structure of prepared $\text{Mo}_{72}\text{Fe}_{30}$, $\text{Mo}_{72}\text{V}_{30}$ and $\text{Mo}_{72}\text{Cr}_{30}$ was confirmed very well by FT-IR, elemental analysis and XRD patterns (Figure S1).

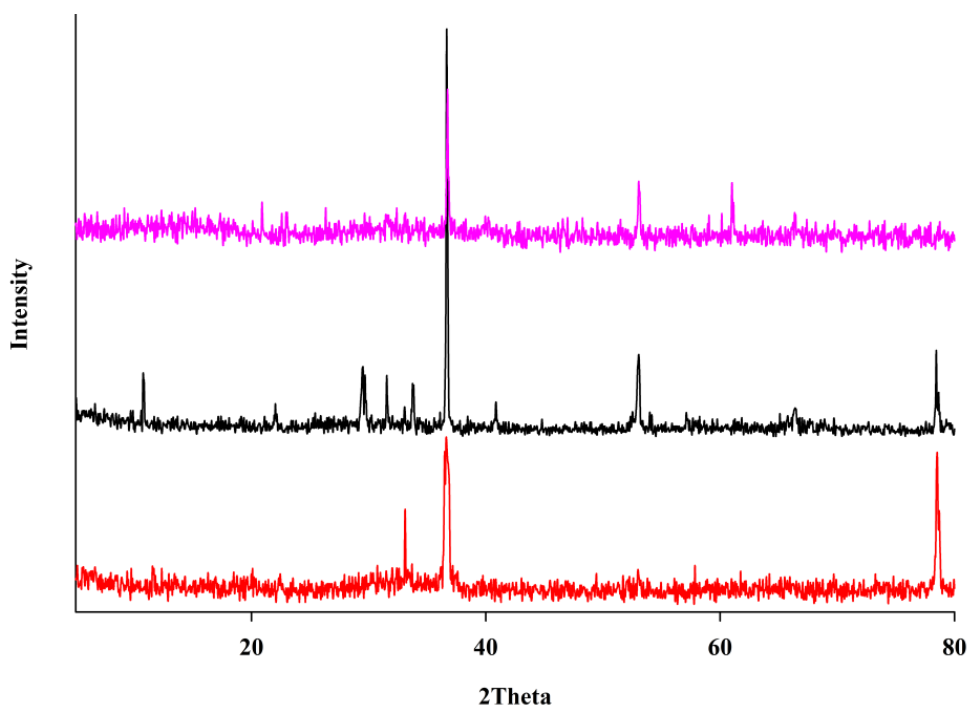


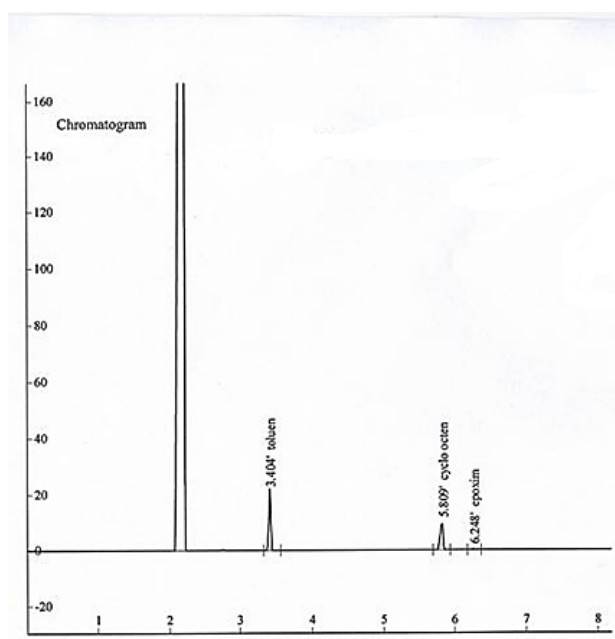
Figure S1. XRD pattern of $\text{Mo}_{72}\text{V}_{30}$ (pink), $\text{Mo}_{72}\text{Fe}_{30}$ (black) and $\text{Mo}_{72}\text{Cr}_{30}$ (red)

5. General procedure for epoxidation of alkenes: The Keplerate catalyst (10 μmol), an alkenes (1 mmol) and water (3 mL) were added to a glass tube under air. Then, hydrogen peroxide (1 mmol, 30%) was added and the reaction mixture was stirred for appropriate time in a preheated oil bath at 50 $^{\circ}\text{C}$. The reaction progress was monitored by TLC and GC, and the yield of products

was determined by GC analysis using toluene as the internal standard. After completion of the reaction ethyl acetate, 3×2 mL was added, and the extraction of organic phase was followed by evaporation of solvent. Higher purification of products was achieved by chromatography over silica gel (eluent: n-hexane/ethyl acetate 80:20). For the recyclability reactions, an aqueous solution of catalyst was used for the next runs.

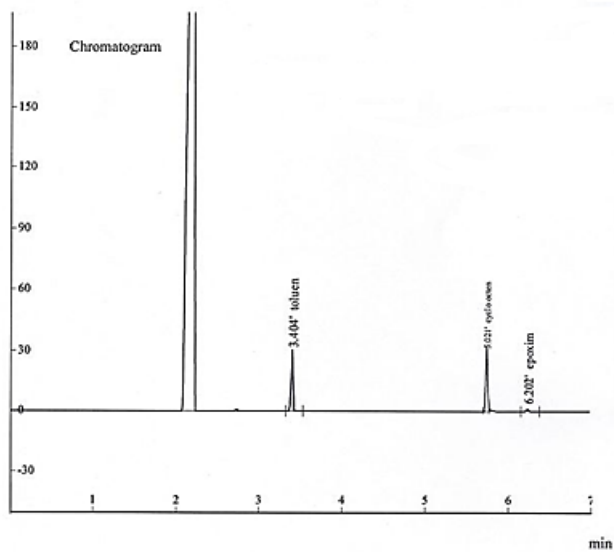
6. Gas chromatograms of standard samples in oxidation of alkenes:

a) 50 mg cyclooctene + 75 mg toluene (internal standard) in 10 mL ethyl acetate



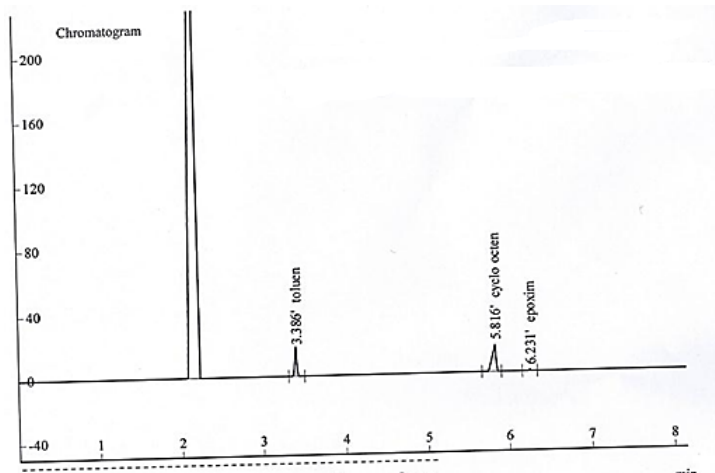
Entry	Time	compound	Area%	Area
1	3.404	toluene	66.82	40417
2	5.809	cyclooctene	32.98	28453
3	6.248	epoxide	0.198	1026

b) 75 mg cyclooctene + 75 mg toluene (internal standard) in 10 mL ethyl acetate



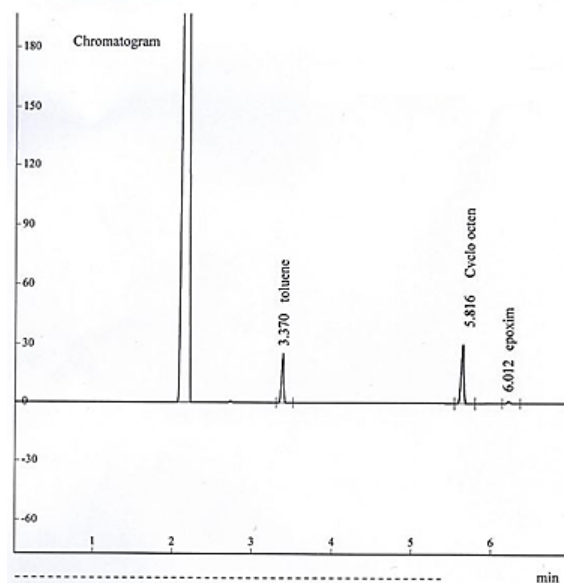
Entry	Time	compound	Area%	Area
1	3.404	toluene	51.17	44172
2	5.021	cyclooctene	48.35	40875
3	6.202	epoxide	0.48	3889

c) 100 mg cyclooctene + 75 mg toluene (internal standard) in 10 mL ethyl acetate



Entry	Time	compound	Area%	Area
1	3.386	toluene	48.04	50634
2	5.816	cyclooctene	51.72	52350
3	6.231	epoxide	0.23	1856

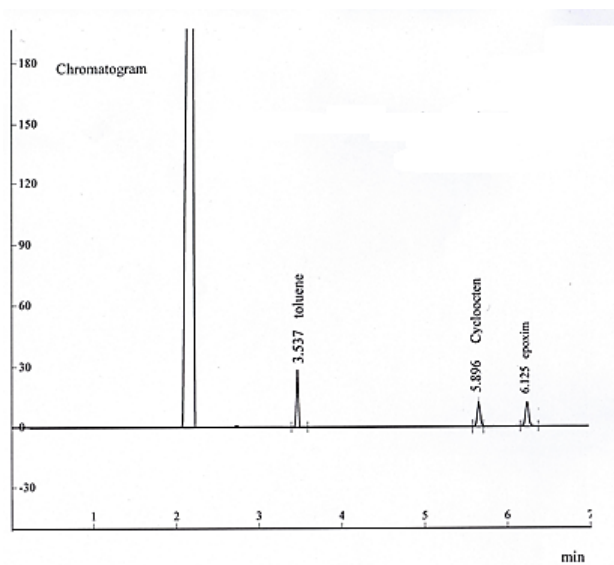
d) 125 mg cyclooctene + 75 mg toluene (internal standard) in 10 ml ethyl acetate



Entry	Time	compound	Area%	Area
1	3.370	toluene	30.44	44172
2	5.816	cyclooctene	69.35	10875
3	6.012	epoxide	0.21	2089

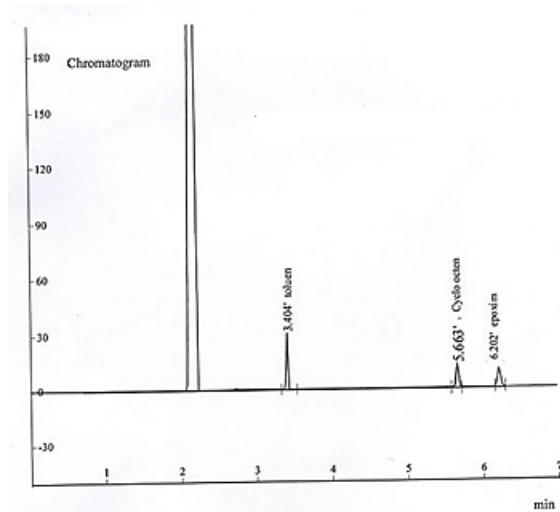
9. Gas chromatogram of epoxidation reaction mixture

a) Epoxidation of cyclooctene by $\text{Mo}_{72}\text{Cr}_{30}$ after 1h reaction



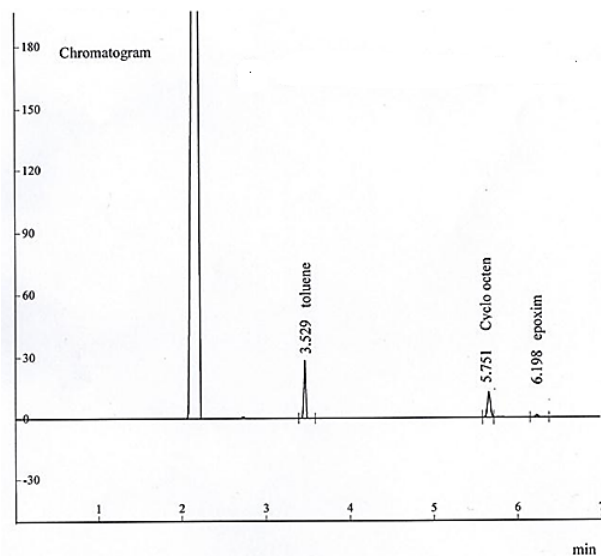
Entry	Time	compound	Area%	Area
1	3.537	toluene	41.17	98125
2	5.896	cyclooctene	31.35	67582
3	6.125	epoxide	26.48	52556

b) Epoxidation of cyclooctene by $\text{Mo}_{72}\text{V}_{30}$ after 1h reaction



Entry	Time	compound	Area%	Area
1	3.404	toluene	44.17	68128
2	5.663	cyclooctene	34.35	59752
3	6.202	epoxide	21.48	32819

c) Epoxidation of cyclooctene by $\text{Mo}_{72}\text{Fe}_{30}$ after 1h reaction



Entry	Time	compound	Area%	Area
1	3.404	toluene	57.17	91125
2	5.663	cyclooctene	41.35	67582
3	6.202	epoxide	0.96	3505

References

1. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman and F. Peters, *Angew. Chem. Int. Ed.*, 1998, **37**, 3360–3363.
2. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, Sh. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein and V. Schünemann, *Angew. Chem. Int. Ed.*, 1999, **38**, 3238–3241.
3. A.M. Todea, A. Merca, H. Bögge, J. V. Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry and A. Müller, *Angew. Chem. Int. Ed.*, 2007, **119**, 6218–6222.