

A nickel-modified polyoxometalate towards high efficient hydrocarbon selective oxidation

(Supporting Information)

X-ray crystallography

Suitable single crystal with dimensions of $0.12 \times 0.12 \times 0.10$ mm for **1** was glued on a glass fiber. Diffraction intensity data were collected on a Bruker Smart Apex-II CCD diffractometer with Mo K α mono-chromated radiation ($\lambda = 0.71073$ Å) at 296 K. Absorption corrections were applied using the multiscan technique. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the *SHELXL-97* software.¹ All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps. A summary of crystal data and structure refinement for **1** is provided in Table S1. Selected bond lengths and angles are listed in Table S2.

Reference

(1) (a) Sheldrick, G. M. *SHELXS-97*, Program for Crystal Structure Solution. University of Göttingen, Germany, **1997**; (b) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement. University of Göttingen, Germany, **1997**.

Materials and General Methods

All analytical reagents were purchased from commercial sources and used without further purification. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. Scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 scanning electron microscope with acceleration voltage of 20 kV. The IR spectrum was recorded in the range of 4000-400 cm^{-1} on a Nicolet 360 spectrometer with a pressed KBr pellet. The TG-DTA analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA) in N_2 with a heating rate of 10 $^\circ\text{C min}^{-1}$. Powder X-ray diffraction (XRPD) data were collected on an X'Pert-ProMPD (Holand) D/max- γ A X-ray diffractometer with Cu K α radiation in a flat plate geometry. Electrochemical measurements were performed with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China). All electrochemical experiments were carried out at

room temperature. A conventional three-electrode system was used. Ag/AgCl electrode was used as a reference electrode, and a Pt wire was used as a counter electrode. Chemically bulk-modified carbon paste electrode was used as the working electrode. The GC measurements were performed in a Varian 3400 GC column with a cross-linked 5% PhMe silicone column (25 m × 0.20 mm × 0.33 μm) and a FID detector under the following conditions: carrier gas (N₂) at 140 K; temperature program 60 °C, 1 min, 15 °C/min, 180 °C, 15 min; split ratio, 10 : 1; injector, 300 °C; detector, 300 °C.

Catalytic selective oxidation of cyclooctene

The selective oxidation of cyclooctene was carried out in a 50 mL round bottom flask with water condenser and continuous magnetic stirring. 200 mg catalyst and 0.12 g tert-butyl hydroperoxide (TBHP) were put into 10 mL cyclooctene. The mixture was stirred for 48 h at 80 °C. Different samples were collected every 8 hours. After filtering off the catalyst, the conversion of cyclooctene and the selectivity of oxidation products were determined by GC analysis; the variance of values is estimated to be less than ±2%.

Synthesis of [Ni₂(fsa)₇(H₂O)(SiMo₁₂O₄₀)]·H₂O (1): A mixture of Na₂SiO₃·2H₂O (0.03 g), NaMoO₄ (0.3 g), Ni(Ac)₂ (0.3 g), fsa (0.12 g) and distilled water (10 ml) were stirred for 1 h in room temperature. The pH was then adjusted to 1.50 by the addition of 1M HCl. Then the above mixture was transferred into a Teflon-lined stainless vessel (15 ml) and heated to 150 °C for 3 days. The reactor was slowly cooled to room temperature over a period of 16 h. Light yellow crystals of **1** were filtered and washed with distilled water (yield of about 30% based on Mo). Elemental analysis (%) calcd for C₁₁₂H₁₀₉F₁₄Mo₁₂N₂₁Ni₂O₄₂Si₈: C 32.21, H 2.52, N 7.04. Found: C 32.25, H 2.57, N 7.11. IR (KBr pellet, cm⁻¹): 1589, 1504, 1234, 1165, 1106, 958, 905, 793.

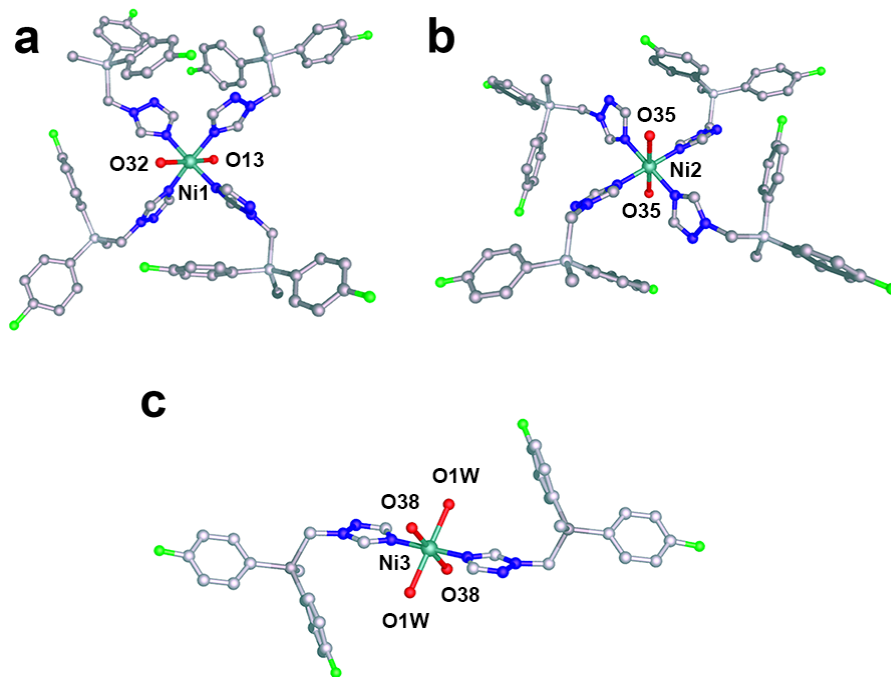


Figure S1. Ball-stick representations of coordination modes of three independent Ni atoms. All H atoms and free lattice water molecule are omitted for clarity.

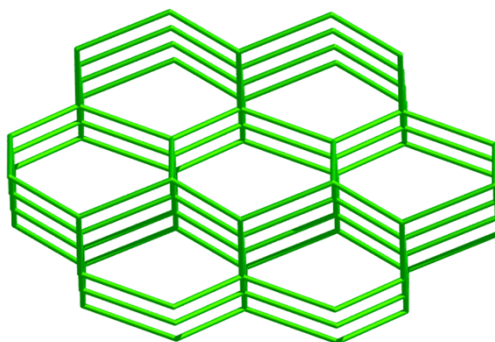


Figure S2. View of the topology of compound 1.

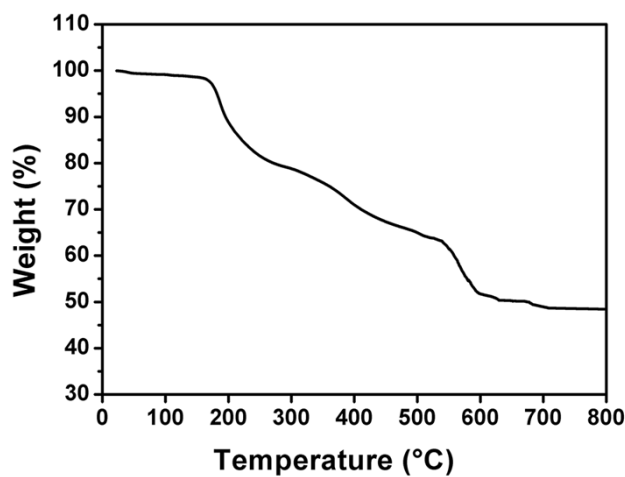


Figure S3. TG curve of compound **1** under N₂ atmosphere.

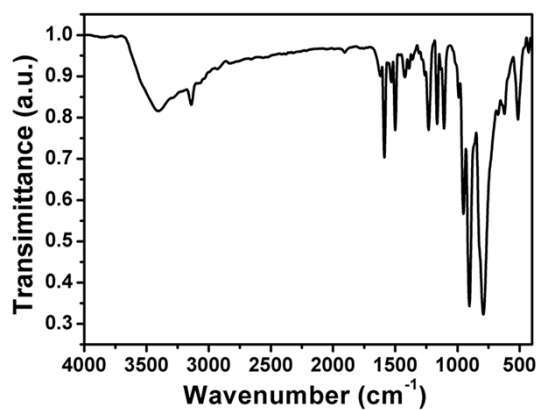


Figure S4. FT-IR spectrum of compound **1**. Characteristic bands at 958, 905, and 793 cm⁻¹ are attributed to $\nu(\text{Si-O})$, $\nu(\text{Mo=O})$, and $\nu(\text{Mo-O-Mo})$ vibrations, respectively.¹⁻³ Moreover, the characteristic bands in the regions of 1589–1106cm⁻¹ can be regarded as features of the fsa ligands.⁴

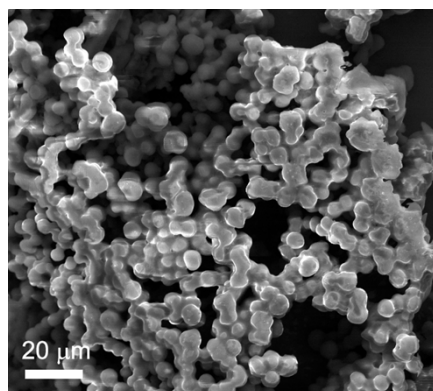


Figure S5. The SEM image of the compound **1**.

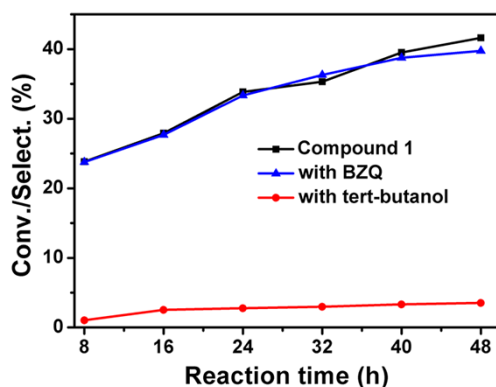


Figure S6. Catalysis activities of compound **1** in reactive species trapping experiments with two types of reactive species scavengers.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{112}H_{109}F_{14}Mo_{12}N_{21}Ni_2O_{42}Si_8$
Formula weight	4180.59
T /K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	24.369(5)
b (Å)	24.336(4)
c (Å)	25.550(5)
α /°	90.00
β /°	107.319(4)
γ /°	90.00
V (Å ³)	14465(5)
Z	4
D_c (g/cm ³)	1.918
μ (mm ⁻¹)	1.423
GOF	0.994
Reflections collected	73009
Independent reflections	25217
Parameters	1903
R_{int}	0.1485
R_1^a [$I > 2\sigma(I)$]	0.0818
wR_2^b [all data]	0.2224

$$^{[a]}R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad ^{[b]}wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

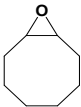

Table S2. Selected bond lengths (Å) and angles (°) for compound **1**.

Ni(1)-O(32)	2.307(9)	Ni(1)-N(1)	2.001(10)
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Ni(1)-N(4)	2.007(11)	Ni(1)-N(7)	2.011(11)
Ni(1)-N(10)	2.003(11)	Ni(2)-O(35)	2.366(9)
Ni(2)-O(35)#1	2.366(9)	Ni(2)-N(13)#1	2.073(12)
Ni(2)-N(16)#1	1.971(12)	Ni(2)-N(13)	2.073(12)
Ni(2)-N(16)	1.971(12)	Ni(3)-O(1W)	2.254(10)
Ni(3)-O(38)#2	2.068(9)	Ni(3)-N(19)#2	1.950(11)
Ni(3)-N(19)	1.950(11)	Ni(3)-O(1W)#2	2.254(10)
Ni(3)-O(38)	2.068(9)	N(1)-Ni(1)-O(32)	87.4(4)
N(1)-Ni(1)-N(4)	91.7(4)	N(1)-Ni(1)-N(7)	175.2(4)
N(1)-Ni(1)-N(10)	91.0(4)	N(4)-Ni(1)-O(32)	88.1(4)
N(4)-Ni(1)-N(7)	89.7(5)	N(7)-Ni(1)-O(32)	97.2(4)
N(10)-Ni(1)-O(32)	92.9(4)	N(10)-Ni(1)-N(4)	177.1(5)
N(10)-Ni(1)-N(7)	87.5(4)	O(35)#1-Ni(2)-O(35)	180.0(6)
N(13)-Ni(2)-N(13)	180.0(10)	N(13)#1-Ni(2)-O(35)	85.3(4)
N(16)-Ni(2)-O(35)	92.0(4)	N(16)#1-Ni(2)-O(35)	88.0(4)
N(16)-Ni(2)-N(13)#1	90.0(5)	N(16)-Ni(2)-O(35)#1	88.0(4)
N(16)#1-Ni(2)-N(13)	90.0(5)	N(16)#1-Ni(2)-N(13)#1	90.0(5)
N(16)#1-Ni(2)-N(16)	180.0(9)	N(16)-Ni(2)-N(13)	90.0(5)
O(38)#2-Ni(3)-O(1W)	91.9(4)	O(1W)#2-Ni(3)-O(1W)	180.0(7)
O(38)#2-Ni(3)-O(1W)#2	88.1(4)	O(38)-Ni(3)-O(1W)	88.1(4)
O(38)-Ni(3)-O(38)#2	180.0(6)	O(38)-Ni(3)-O(1W)#2	91.9(4)
N(19)#2-Ni(3)-O(1W)#2	89.9(4)	N(19)-Ni(3)-O(1W)#2	90.1(4)
N(19)-Ni(3)-O(1W)	89.9(4)	N(19)#2-Ni(3)-O(1W)	90.1(4)
N(19)-Ni(3)-O(38)#2	91.4(4)	N(19)#2-Ni(3)-O(38)#2	88.6(4)

Symmetry transformations used to generate equivalent atoms: #1 1-X,-Y,-Z; #2 -X,-Y,-Z.

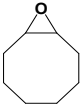
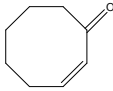
Table S3. Effect of variety of reaction time on selective oxidation of cyclooctene using compound **1** as catalyst.

Reaction time (h)	Product Selectivity (%)		Conversion (%)	$\Sigma_{\text{sel}}\text{C}_8^{\S}$
				
0	0	0	0	0
8	84.53	15.47	23.81	100
16	86.08	13.79	27.92	99.87
24	91.38	8.27	33.86	99.65
32	93.15	6.21	35.33	99.36
40	95.83	3.14	39.52	98.97
48	97.21	1.64	41.63	98.85

Reaction conditions: Compound **1** (200 mg), cyclooctene (10 mL), TBHP (0.12 g), 80 °C. \S Total selectivity to C₈ partial oxidation products.

Table S4. Effect of different materials as catalysts on selective oxidation of cyclooctene.

catalysts	Product Selectivity (%)	Conversion (%)	$\Sigma_{\text{sel}}\text{C}_8^{\S}$
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Compound 1	97.21	1.64	41.63	98.85
Ni(Ac) ₂	83.97	13.39	15.14	97.36
SiMo ₁₂	72.34	24.88	5.43	97.22

Reaction conditions: catalysts (200 mg), cyclooctene (10 mL), TBHP (0.12 g), 80 °C. §Total selectivity to C₈ partial oxidation products.

References in Supporting Information

1. T. Ueda, J.-i. Nambu, H. Yokota and M. Hojo, *Polyhedron*, 2009, **28**, 43-48.
2. M. Nakayama, T. Ii, H. Komatsu and K. Ogura, *Chem. Commun.*, 2004, 1098-1099.
3. C. Rocchiccioli-Deltcheff, M. Fourer, R. Frank and R. Thouvenot, *Inorg. Chem*, 1983, **22**, 207.
4. H. Itoh, H. Kajino, T. Tsukiyama, J. Tobitsuka, H. Ohta, Y. Takahi, M. Tsuda and H. Takeshiba, *Bioorgan. Med. Chem.*, 2002, **10**, 4029-4034.