Supporting Information

Direct cyclohexanone oxime synthesis via oxidation-oximization of cyclohexane with ammonium acetate

Ling Peng, Chan Liu, Na Li, Wenzhou Zhong*, Liqiu Mao*, Steven Robert Kirk and

Dulin Yin

National & Local United Engineering Laboratory for New Petrochemical Materials & Fine Utilization of Resources, Key Laboratory of Chemical Biology Traditional Chinese Medicine Research Ministry of Education, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, PR China

*Corresponding authors: Wenzhou Zhong and Liqiu Mao

Fax: +86-731-88872531; Tel.: +86-731-88872576

E-mail: zwenz79@163.com (W. Zhou); mlq1010@126.com (L. Mao)

1. Experimental

1.1 Catalyst preparation

The hollow-structured TS-1 was synthesized under hydrothermal condition by a dissolutionrecrystallization process in tetrapropylammonium hydroxide (TPAOH) solution.¹ First, tetraethyl orthosilicate (TEOS), titanium butoxide (TBOT), TPAOH solution and distilled deionized water were mixed in a 1:0.01:0.4:40 molar ratio forming a clear solution, which was hydrolyzed for 2 h at 60 °C. The obtained gel was transferred to a Teflon-lined stainless steel autoclave and crystallized at 170 °C for 3 days. The white solid was filtrated and washed with large amounts of deionized water and dried at 120 °C for 24 h, followed by calcination at 500 °C for 10 h to remove the residual structure directing reagent. Secondly, the obtained solid TS-1 was treated with H₂SO₄ solution (a weight ratio of the previous calcined TS-1:H₂SO₄:water=10:1.2:140), and the acidtreated solid TS-1 was dispersed in TPAOH solution (a weight ratio of molecular sieve: TPAOH: water=10:1.5:125). The mixture was then recrystallized in a Teflon-lined stainless steel autoclave at 140 °C for 3 days. Filtration of the recrystallized zeolite was washed, dried and finally calcined at 500 °C for 10 h. Silicate-1 was also prepared by an identical procedure, merely without adding titanium.

The hollow-structured Ni-doped TS-1 catalysts were prepared by incipient wetness impregnation of hollow TS-1 with an aqueous solution of nickel acetate to give the final product. The impregnated sample was dried in an oven at 80 °C, followed by calcination at 500 °C in air for 5 h (with heating rate 8 °C/min). By changing the amount of nickel acetate, the hollow-structured Ni/TS-1 composites with 1, 3 and 5 wt. % of Ni were synthesized, labeled by 1% Ni/HTS, 3% Ni/HTS and 5% Ni/HTS, respectively. 3% Ni/Silicalite-1 was also prepared by an identical procedure with using silicate-1 as a support.

1.2 Characterization techniques

The crystalline phase of samples were checked by a Bruker D8 ADVANCE diffractometer operated at 40 kV and 40 mA with $Cu_{K\alpha}$ radiation (λ =1.542 Å). Particle morphology of samples was studied using scanning obtained on a Hitachi S-4800 microscope, while the TEM images were recorded in a JEOL-JEM-2100 microscope operated at 200 kV. The textural properties were measured by N₂ adsorption at -196 °C on a Tristar 3000 sorptometer. Prior to the measurement, degassing was achieved by heating the sample at 200 °C under a reduced pressure of 10⁻⁵ Torr for

3 h. The surface area was determined using the single-point Brunauer-Emmett-Teller (BET) equation, while total pore volume was measured at $P/P_0 = 0.99$. The pore size distributions were determined from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. FT-IR spectra of KBr pellets were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 2 cm⁻¹. UV/Vis diffuse-reflectance spectra were recorded from 200 to 800 nm on a Varian-Cary 5000 spectrometer with BaSO₄ as background standard, using integrating-sphere attachment to assess the nature of Ti and Ni species. The UV-visible spectra of liquid samples are recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). The solvent is measured as a reference/background spectrum. X-ray photoelectron spectroscopy (XPS) was performed in an imaging photoelectron spectrometer (Axis Ultra, Kratos Analytical Ltd.) using Al Ka radiation (1486.7 eV). Binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.8 eV). XPS software was used for curve fitting.

1.3 DFT calculations

The geometrical structure of the T9 cluster models with active sites, $Si_8TiO_{24}H_{12}$ and $Si_7TiNiO_{24}H_{12}$, was optimized using the B3LYP method of DFT with 6-311++G(d, p) basis set. Natural bond orbital (NBO) analyses were performed by the B3LYP method on the optimized structure to gain insight into the electronic distribution and bonding patterns of these models. All the calculations were conducted using the Gaussian-09 version C02 package with tight self-consistent field (SCF) convergence and ultrafine integration grids. Models have been considered where one Ti-(O-Si)₄ or (Si-O)₃-Ti-O-Ni bridging site on the surface was constructed with a Ni atom, representing the surface modification of HTS with Ni species. In both cases, the unsaturated bonds are saturated by hydrogen atoms.

1.4 Catalytic reactions

Selective oxidation-oximization of cyclohexane was carried out in a Teflon-lined 100 ml stainless-steel autoclave equipped with a magnetic stirrer. Typically, 0.15 g of cyclohexane, 1.21 g of 30% H₂O₂ aqueous solution, 2.47 g CH₃COONH₄, 7.5 ml mixed solvent and 0.08 g of catalyst were charged to the autoclave in one lot, the autoclave was closed and submerged in a thermostatically controlled oil bath at reaction temperature for different periods of time. After the reaction, the reaction mixture was dissolved in ethanol and the catalyst was immediately separated from the suspension by filtration. The components of the liquid phase such as unreacted

cyclohexane, cyclohexanol, cyclohexanone, cyclohexyl nitrite and cyclohexanone oxime were identified by GC-MS and quantitatively analyzed by Shimadzu 2014 gas chromatograph with a HP-5 polysiloxane capillary column ($30m \times 0.32 \text{ mm} \times 0.50\mu\text{m}$) and a flame ionization detector using n-octanol as the internal standard. Both the injector and detector temperature were 250 °C, and the column temperature was 80 °C. Conversion (%) based on cyclohexane substrate = {1-[(concentration of substrate left after reaction) × (initial concentration of substrate)-1]} × 100. Product selectivity = content of this product/(adding cyclohexane amount (mmol)-the amount of cyclohexane recovered (mmol)) × 100%.

1.5 In situ Fourier transform IR measurements

In situ Fourier transform IR measurements were carried out using React ATR-Probe IN350-TEX equipment (BRUKER) with a light conduit and diamond insertion probe. The system of MCT (Mercury cadmium telluride) was cooled using liquid N₂. FTIR spectra were collected in the wave number range between 3000 and 650 cm⁻¹. The experiments were performed at 80 °C in a 250 mL, 4-necked flask with a condenser, thermometer, and magnetic stirrer. The temperature was maintained by using an appropriately adjusted water bath. The molar ratio of each substance was cyclohexane:H₂O₂:CH₃COONH₄ = 1:1:2.5. 150 ml mixed solvent and 1.6 g of catalyst were used The cyclohexane level was 0.036 mol, and H₂O₂ was added. The ReactIR15 probe was stretched into the liquid system and scanned every 15 s. Because the 2250–1950 cm⁻¹ region for the diamond is the infrared shielding area, we selected the 1800–600 cm⁻¹ region for the analysis of spectra.



Scheme S1 Comparison of current industrial process and one-step method presented herein for preparation of cyclohexanone oxime.

Sample	$S_{BET}(m^3/g)^a$	$V_p(cm^{3/g})$	$D_p(nm)^b$
1%Ni/HTS	307	0.249	3.25
3%Ni/HTS	322	0.252	3.13
5%Ni/HTS	291	0.234	3.22
3%Ni/Silicalite-1	299	0.255	3.41

Table S1 The BET surface area, pore volume and pore size of samples.

^aBET surface area.

^bThe pore-size distribution determined by the BJH method.

Ammonium salts	Structural optimization ^a	N-H bond distance ^b (Å)	NBO charge ^c (e)
HCOONH ₄	نې خ	1.753	-1.056
CH ₃ COONH ₄	્રં	1.768	-1.069
NH ₄ HCO ₃	چې کې د	1.704	-1.064
NH4Cl	÷>	1.726	-1.035
(NH ₄) ₂ SO ₄	چ	1.651	-1.054

 Table S2 Structural optimization of the molecular structure for ammonium salts by DFT investigation.

^a Ammonium salts were optimized using the B3LYP method of DFT with 6-311++G(d, p) basis set. ^b The N–H bond distance of the NH⁴⁺ connecting a acid anion.

^c Natural bond orbital (NBO) analyses were performed by the B3LYP method on the optimized structure.

	5			2		2
			Sel. (%)			
Entry	Solvents	Conv. (%)	ОН	 o		OH N
1	Acetonitrile	6.8	57.3	15.2	9.6	17.8
2	Ethanol	2.1	38.9	48.4	5.6	7.4
3	t-Butanol	1.6	44.51	37.4	18.1	-
4	Ethyl acetate	7.6	66.3	13.5	20.2	-
5	Acetic acid	4.0	39.1	14.5	20.5	25.1
6	Propionic acid	1.6	40.8	26.5	9.7	23.0
7	Trifluoroacetate	3.4	15.4	35.6	28.00	21.0
8	CH ₃ CN-CH ₃ COOH	13.6	31.2	3.2	14.9	50.7
9	CH ₃ CN-CF ₃ COOH	11.1	37.3	5.8	20.6	36.3

Table S3 Effect of solvent over cyclohexane conversion and cyclohexanone oxime selectivity.^a

^a Conditions: 0.08g catalyst, cyclohexane 0.15 g (1.78 mmol), CH₃COOH/CH₃CN (7.5 ml, V=1:4), ammonium acetate as an ammonium source, cyclohexane: ammonium acetate =1:18 (molar ratio), cyclohexane:H₂O₂ = 1:6 (molar ratio), reaction time 4 h at 110 °C. ^b Conversion (%) based on cyclohexane substrate = $\{1-[(\text{concentration of substrate left after reaction}) \times (\text{initial concentration of substrate})-1]\} \times 100$. ^c Product selectivity = content of this product/(adding cyclohexane amount (mmol)-the amount of cyclohexane recovered (mmol)) × 100%.

			Sele. (%) ^c			
Entry	Substrate	Conv. (%) ^b	—он	 0	⟨N ^{OH}	Others
1 ^d	Cyclohexane	57.7	49.4	43.9	-	6.7
2 ^d	Cyclohexanol	58.9	-	68.5	-	31.5
3	Cyclohexanol	15.5	-	30.9	64.6	4.5
4	Cyclohexanone	75.7	-	-	95.3	4.7

Table S4 Control experiments for the reaction mechanisms.^a

^aConditions: 0.08g 3%Ni/HTS catalyst, substrate 0.15 g (1.78 mmol), CH₃COOH/CH₃CN (7.5 ml, V=1:4), ammonium acetate as an ammonium source, substrate: ammonium acetate =1:18 (molar ratio), substrate:H₂O₂ = 1:6 (molar ratio), reaction time 4 h at 110 °C. ^b Conversion (%) based on cyclohexane substrate = {1-[(concentration of substrate left after reaction) × (initial concentration of substrate)-1]} × 100. ^c Product selectivity = content of this product/(adding substrate amount (mmol)-the amount of substrate recovered (mmol)) × 100%. ^d Without using ammonium acetate.



Fig. S1. XRD patterns of samples



Fig. S2 FT-IR spectra of different catalysts.



Fig. S3 XPS spectra of different catalysts.



Fig. S4 Electronic structure of optimized models for the different active (A) and (B).



Fig. S5 UV-Vis spectra of the solvents in cyclohexane solution (A) and cyclohexanone oxime in different solvents (B).



Fig. S6 Electronic structure of optimized models for the CH₃COOH molecule in different solvent environment (using the B3LYP method of DFT with 6-311++G(d, p) basis set and the PCM solvation model, dispersion interactions with the Grimme D3 method and natural bond orbital (NBO) analyses on the optimized structure).



Fig. S7 Geometrical optimization of the molecular structure by DFT investigation (using the B3LYP method of DFT with 6-311++G(d, p) basis set).



Fig. S8. The three-dimensional plot of the *in situ* FT-IR spectra of the oxidation-oximation reaction (A with cyclohexane, B without cyclohexane).



Fig.S9 Proposed tandem catalysis scheme consistent with observations.

References

G. Zou, W. Zhong, L. Mao, Q. Xu, J. Xiao, D. Yin, Z. Xiao, S. R. Kirk and T. Shu, *Green Chemistry*, 2015, **17**, 1884-1892.