Aerobic oxidative desulfurization coupling of Co polyanion catalysts and p-TsOHbased deep eutectic solvents through a biomimetic approach

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^b Collaborative Innovation Center for Light Hydrocarbon Transformation and Utilization, College of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, Shandong, China Figure S1. The IR spectrum of $(NH_4)_3Co(OH)_6Mo_6O_{18}$.

Figure S2. UV-vis spectrum of the (NH₄)₃Co(OH)₆Mo₆O₁₈.

Figure S3. The XRD pattern of the (NH₄)₃Co(OH)₆Mo₆O₁₈

Figure S4. The XPS spectrum of the (NH₄)₃Co(OH)₆Mo₆O₁₈

Figure S5. The infrared spectroscopy of p-TsOH, PEG4000 and p-TsOH/PEG4000

Figure S6. FT-IR spectrum for the sulfur compounds before and after desulfurization reaction.

Figure S7. Infrared spectroscopy of DBT、 p-TsOH/PEG4000 and the mixture of p-TsOH/PEG4000 and DBT.

Figure S8. The GC–MS analysis of oil phase (a) and the DES phase (b).

Experimental

Preparation of the DESs and Catalyst

All the chemicals were of analytical grade and used as received. The $(NH_4)_3Co(OH)_6Mo_6O_{18}$ was prepared according to the procedure reported in literature ^{1,2}. The eutectic mixtures were formed by stirring the two components at 80 °C until a homogeneous colorless liquid was formed ^{3,4}. Model diesel (S:500 ppm) was prepared by dissolving one of the model sulfur compounds, BT, DBT, or 4,6-DMDBT in Decalin.

Oxidation and desulfurization of the model diesel

In a typical run, a mixture, containing 20 mL model diesel, 4 mL DESs and 20mg catalyst, was stirred vigorously at 60 °C by bubbling molecular oxygen. The upper phase (model diesel) was periodically sampled and analyzed. The sulfur contents of the samples were determined by gas chromatography using tetradecane as the internal standard with flame ionization detection (FuLi 9750, HP-5). The oxidized S-compound was characterized by GC–MS (Agilent 7890/5977B- GC/MSD; PONA).

Oxidation and desulfurization of the commercial diesel

Oxidation of the commercial diesel was carried out as follows. The mixture, containing 10 mL of the commercial diesel (24 ppm), 10 g of DESs and catalyst 20 mg, was stirred vigorously at 60 °C by bubbling molecular oxygen for 4 h. The oxidized diesel was analyzed by gas chromatography coupled with flame photometric detection (GC-FPD) (Agilent 7890B; HP-5, 50 m×0.25 mm i.d. ×0.25 μ m; FPD:

Agilent). The sulfur content in the original diesel and in the desulfurization diesel was determined by microcoulometry (detection limit, 0.1 ppm).

Characterization

The infrared spectroscopy of sample was recorded on Shimadzu IRAffinity-1S FT-IR spectrometers using KBr pellets. UV-vis diffuse reflectance spectroscopy was recorded on a TU-1901 (Beijing General Analytical Instrument Ltd Co., China). The scanning patterns were recorded at 200-800 nm in a step-scan mode with a step of 5 nm. The crystal structure of the sample was recorded by X-ray diffraction (XRD, Rigaku, Smart Lab3) with Cu K α radiation. X-ray photoelectron spectroscopic (XPS) measurements were conducted on an AXIS-ULTRA DLD-600 W spectrometer with Al K α irradiation and the binding energies were calibrated by using the C 1s peak of contaminant carbon at 284.5 eV as an internal standard.

Results and Discussion

Characterization of (NH₄)₃Co(OH)₆Mo₆O₁₈ and p-TsOH/PEG4000

The IR spectrum of $(NH_4)_3Co(OH)_6Mo_6O_{18}$ is shown in Fig. S1. The spectrum polyoxometalate discloses the characteristic peaks of bridged Mo-O-Mo around 577, 655 cm⁻¹, The peaks at 895 and 940 cm⁻¹ are ascribed to the terminal group of Mo=O peak and the peak at 451 cm⁻¹ is attributed to central Mo-O-Co modes ^{1,5,6}. There are two broad bands at 1400 and 3179 cm⁻¹ derived from the stretching vibration of NH_4^+ . The results are good in agreement with the structural analysis. UV–vis spectrum (Fig. S2) was also used to detect the structure of Co polyanion

 $(NH_4)_3Co(OH)_6Mo_6O_{18}$. The absorption in the range of 200–330 nm is attributed to the feature of the polymer Mo-O-Mo structure in the polyanion ^{1,5,6}. The two bands at 411 and 609 nm are the characteristic of Co³⁺ in the spectrum of Co polyanion ⁵.

The XRD pattern (Fig. S3) revealed the presence of highly crystalline planes of the prepared Anderson polyoxometalate based on JCPDS 04-0226. The XPS analysis was carried out to clarify the oxidation state of the elements present in the (NH₄)₃Co(OH)₆Mo₆O₁₈. The survey spectrum of the Anderson-type polyoxometalate is illustrated in Fig. S4 (A) and it is mainly composed of elements of N, O, Co and Mo. The peak deconvolutions for N 1s, O 1s, Co 2p and Mo 3d are listed in Fig. S4(B-E). The XPS spectrum of N 1s (Fig. 4(B) shows the binding energy at 398.3 and 401.3 eV, assigning to N-H and N-C (small amounts of carbon may originate from the characterization process) ^{7,8}. The peak of O 1s (Fig. S4(C)) can be separated into three peaks located at 530.4, 531.4 and 532.7 eV, which are contributed by Mo-O, Co-O and peroxo groups of polyoxometalate ^{8–10}. The peak of the Mo (Fig. S4(D)) located at 232.8 eV is attributed to Mo 3d^{5/2} corresponding to the Mo (VI) oxidation state in the catalyst ^{1,11}. The XPS spectrum of Co 2p^{3/2} can be resolved curve-fitting into three peaks with binding energies of about 781.3, 784.1 and 786.8 eV, attributable to the Co(\mathbb{II}), Co(\mathbb{II}) and satellite of Co(\mathbb{II}) (Fig. S4(E)) ¹²⁻¹⁴.

The infrared spectroscopy of p-TsOH, PEG4000 and p-TsOH/PEG4000 were employed to study their interaction (Fig. S5). Comparing p-TsOH with p-TsOH/PEG4000, the peak of SO₂OH (1200, 1130, 1042 and 1013 cm⁻¹) was vanished, indicating the strong interaction between p-TsOH and PEG4000. Besides, In contrast with PEG4000 with p-TsOH/PEG4000, the peaks at 1103, 1037, 945 and 842 cm⁻¹ of PEG4000 became weaker and wilder, suggesting that hydrogen bonds might be formed ¹⁵.



Figure S1. The IR spectrum of (NH₄)₃Co(OH)₆Mo₆O₁₈.



Figure S2. UV-vis spectrum of the (NH₄)₃Co(OH)₆Mo₆O₁₈.



Figure S3. The XRD pattern of the (NH₄)₃Co(OH)₆Mo₆O₁₈



Figure S4. The XPS spectrum of the (NH₄)₃Co(OH)₆Mo₆O₁₈



Figure S5. The infrared spectroscopy of p-TsOH, PEG4000 and p-TsOH/PEG4000



Figure S6. FT-IR spectrum for the sulfur compounds before and after desulfurization reaction.



Figure S7. Infrared spectroscopy of DBT、 p-TsOH/PEG4000 and the mixture of p-TsOH/PEG4000 and DBT.

Infrared spectroscopy was also used to study the mechanism of AODS in DESs. Fig. S7 shows the IR spectra in the range from 600 to 1000 cm⁻¹ of p-TsOH/PEG4000, DBT and their mixture at molar ratio 2:1. The three weakening or fading bands (at 963, 744 and 701 cm⁻¹) of DBT in their mixture imply that there is a strong interaction between DESs and S-compounds, making the weaken of aromaticity of DBT and resulting in the promotion of oxidation reaction reactivity.



Figure S8. The GC–MS analysis of oil phase (a) and the DES phase (b).

In addition, GC–MS analysis was applied to determine the sulfur species in model oil phase and reaction products in DES phase. After reaction, the upper oil phase was separated from the DES phase by a plastic dropper and measured directly. Subsequently, the DES phase was extracted with trichloromethane (CHCl₃), the resulting trichloromethane phase were analyzed by GC–MS. The GC–MS spectrograms of oil and DES phase in 30 min and 4h were drawn in Fig. S8. When in 30 min, only DBT was detected in oil phase while both DBT and DBTO₂ were found in DES phase. Due to the removal of DBT was 99% in 60 min, the residual DBT was almost undetectable in oil phase after reaction while only DBTO₂ presented in DES phase, indicating that DBTO₂ was the only oxidation product. Based on the GC–MS results, we could speculate probable catalytic oxidative mechanism that the sulfur compounds such as DBT were extracted into DES phase firstly, and then was oxidized to DBTO₂.

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