Facile Preparation of Haggite by Redyction V_2O_5 in Guaiacol/Methanol Solution

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Experimental Section

Materials: The chemicals were purchased from commercial suppliers and used as received. AR reagent grade chemicals including guaiacol, anisole, methanol, ethanol, n-propanol, n-butanol and isopropanol were purchased from Guangfu Inc. Divanadium pentaoxide were purchased from Fangzheng Inc.

Reduction of V₂O₅: The reduction of V₂O₅ in guaiacol/methanol solution was carried out in an autoclave (Parr Instruments, 300 mL). In a typical experiment, the reactor was loaded with 0.5 g V₂O₅, 1.0 g guaiacol, 60 mL methanol, sealed and purged with N₂ five times. The reactor was heated to the reaction temperature (240–300 °C) within 1.5 h and kept at this temperature for the desired reaction time with stirring at 500 rpm. Then the reactor was rapidly cooled down by immersing the reactor into a cold water bath. The reactions without guaiacol were performed in an autoclave (Anhui Kemi Machinery Technology Co., LTD., 300 mL) following the abovementioned procedures. However, 0.625 g V₂O₅ and 75 mL solvent were loaded into the reactor because 75 mL was the least amount for stirring in this reactor.

The post-reaction liquid and solid were separated by filtration. The liquid was analyzed by an Agilent Technologies 6890N GC equipped with a HP-5 MS capillary column (Agilent, 30 m \times 0.25 mm \times 0.25 µm) and a FID detector with anisole as the internal standard. The GC parameters used for analysis were as follows: inlet temperature 280 °C, detector temperature 300 °C, split ratio 1:50. The oven temperature ramps from an initial temperature of 45 °C to a final temperature of 250 °C at 10 °C min⁻¹ and then is held at the final temperature for 2 min. Liquid products were identified using a mass selective detector (MSD, Agilent Technologies, model 5973). The fragmentation pattern acquired on the MS was compared with those in the NIST Mass Spectral Library to identify the structure of each product.

The yield of every alkylphenol was calculated according to Eqs (1). The total yield of alkylphenols was calculated according to Eqs (2). In these equations, n presents the amount of the species in moles. The yield and total yield were determined by averaging the data measured in three times.

 $Yield_{i} = \frac{n_{product \, i}}{n_{initial \, guaiacol}} \times 100\% \tag{1}$

 $Total yield of alkylphenols = \sum_{i=Alkylphenol} Yield_i$ (2)

Characterizations: X-ray diffraction (XRD) patterns of the samples were recorded at room temperature using a Rigaku D/max 2500 v/pc instrument (Rigaku Corp. Japan) and a Rigaku D/max-IIIA diffractometer with Cu K_a radiation, 40 kV and 200 mA, at a scanning rate of 6 °/ min. The surface morphology of materials was observed with a Hitachi S-4800 scanning electron microscope (SEM) and a JEOL JSM-6301F SEM. To analyze the V-2p state of the spent catalyst, X-ray photoelectron spectroscopy was recorded using a PHI1600 XPS system with Al-K_a radiation. Liquid samples were mixed with CDCl₃ (1:1 v/v) and then analyzed with nuclear magnetic resonance (NMR,Varian inova 500 MHz).



Figure S1. The oxidation products obtained in the reduction of V_2O_5 in different solvents detected by GC-MS. Note: the oxidation states of solvents and the produced acetals are given.



Figure S2. ¹H-NMR spectrum of the liquid obtained from the reduction of V_2O_5 in methanol at 280 °C for 1.5 h. Note: the signal of methanol is suppressed.



Figure S3. ¹H-NMR spectrum of the liquid obtained from the reduction of V_2O_5 in isopropanol at 280 °C for 1 h. Note: the signal of isopropanol is suppressed.



Figure S4. (a) Proposed reaction paths of methanol (b) The oxidation states of carbons involved in oxidation reactions.