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Mechanistic insights for enhancing activity and stability of Nb-incorporated silicates for selective ethylene epoxidation

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ABSTRACT

Significant ethylene epoxidation activity was observed over niobium (Nb) incorporated mesoporous silicate materials Nb-KIT-5, Nb-MCM-48, and Nb-TUD-1, with hydrogen peroxide (H_2O_2) as oxidant and methanol (MeOH) as solvent under mild operating conditions (35 °C and 50 bars). No CO_2 as by-product was detected at these conditions. The measured ethylene oxide (EO) productivity over Nb-TUD-1 materials (342–2539 g EO h^{-1} kg^{-1} Nb) spans a greater range than those observed with Nb-KIT-6 (234–794 g EO h^{-1} kg^{-1} Nb), Nb-KIT-5 (273–867 g EO h^{-1} kg^{-1} Nb) and Nb-MCM-48 (71–219 g EO h^{-1} kg^{-1} Nb) materials at similar operating conditions. However, significant H_2O_2 decomposition and Nb leaching were observed in all cases. Computational studies employing minimal models of the catalytically active sites, suggest how the Brønsted acidity may lead to these detrimental pathways. Indeed, lowering the metal loading to significantly reduce the Brønsted acidity results in a dramatic increase in H_2O_2 utilization toward EO formation (4304 g EO h^{-1} kg^{-1} Nb). The increased EO productivity either matches or surpasses what was observed on the conventional Ag-based heterogeneous catalyst (with O_2 as oxidant) as well as a Re-based homogeneous catalyst (with H_2O_2 as oxidant). These results are paving the way for further computational and experimental investigations aimed at the rational design of improved epoxidation catalysts that reduce H_2O_2 decomposition and metal leaching to practically viable levels.

1. Introduction

The search for alternative EO technology that suppresses CO_2 formation as by-product and thereby conserves feedstock continues to receive attention. During the last several decades, the traditional Ag-based catalysts have undergone significant improvement to increase EO selectivity to values reaching 90% with the remaining product being CO_2 [1]. Recently, we reported a homogenous catalytic process for ethylene epoxidation that uses methyltrioxorhenium (MTO) as catalyst and H_2O_2 as oxidant providing almost total epoxide selectivity with no CO_2 formation as by-product [2]. Detailed economic analysis indicates that the use of less expensive and earth-abundant catalytic materials (compared to Re) could improve process economics and practical viability [3]. This motivated us to explore such alternative epoxidation catalyst candidates.

Niobium-based heterogeneous catalysts have been receiving increased attention as epoxidation catalysts [4–13]. Various Nb-containing catalysts have been shown to exhibit excellent catalytic activities for the epoxidation of cyclic alkenes [5,6,11,14–17], oils [10,12] and propylene [18], as well as fine chemical substrates such as limonene, carveol, isopulegol, carvone, and squalene [8,19]. During cyclohexene oxidation with Nb containing MCM-41 and MCM-48 catalysts, similar conversion activities are reported; however, significantly higher epoxide selectivity is reported on Nb-MCM-48 albeit at lower Nb loading [16]. In contrast, NbSM-2, a material synthesized following a procedure similar to TUD-1, showed higher activity for cyclohexene epoxidation compared to NbMCM-41 [17]. In previous studies, we showed that Nb-KIT-6 [20] promotes selective EO formation (without any CO_2 as by-product) during liquid phase ethylene epoxidation using H_2O_2 as oxidant. The observed EO productivity (234–794) g EO h^{-1} kg Nb^{-1} is lower but of the same order of magnitude as that reported for the conventional Ag-based gas phase ethylene epoxidation process that uses dioxygen as oxidant [21,22]. However, Nb leaching, anywhere from 30% to 75% depending on loading, was observed during

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5 h batch runs. In addition, significant H_2O_2 decomposition was also observed, possibly due to the Brønsted acidity imparted by Nb incorporation in the silicate framework [20].

Encouraged by the activity displayed by Nb-KIT-6 catalysts, we decided to investigate Nb incorporation in other mesoporous supports such as TUD-1, KIT-5, and MCM-48. TUD-1 is an amorphous mesoporous silicate that has several advantages such as ease of preparation, wide pore size distribution, high thermal stability, and environmentally benign synthesis protocol [23]. Further, it was shown that metal leaching was minimal when Co-TUD-1 was used as catalyst for the aerobic oxidation of cyclohexane [24]. We prepared Nb-KIT-5 and Nb-MCM-48 materials, following the procedures reported elsewhere [7,25]. In addition to EO productivity, performance measures such as activity, metal leaching and H_2O_2 utilization efficiency were also assessed to evaluate relative performance and practical viability. Guided by mechanistic insights from computational studies, the catalysts were rationally redesigned to improve H_2O_2 utilization and reduce metal leaching. These efforts are guiding the quest for the continued development of practically viable catalysts characterized by high activity, total epoxidation selectivity, maximized H_2O_2 utilization, and stability to metal leaching.

2. Experimental

2.1. Materials

Methanol (MeOH), employed as solvent, was used as received without further purification. Ceric sulfate (0.1 N) and trace metal grade sulfuric acid (99.9 wt.%) were purchased from Fischer Scientific. Ethylene (high purity grade) was purchased from Matheson Tri-Gas Co. H_2O_2 (50 wt.% H_2O_2 in H_2O), ferroin indicator solution, acetonitrile (AN) (HPLC grade), niobium oxide (Nb_2O_5), niobium(V) chloride ($NbCl_5$), niobium(V) ethoxide [$Nb(OC_2H_5)_5$], triethanolamine (TEA), tetraethylammonium hydroxide (TEAOH, 35%), tetraethyl orthosilicate (TEOS), 2-methoxyethanol (2-ME) and anhydrous ethylene glycol (EG) were purchased from Sigma–Aldrich and used without further purification. The EO standard was purchased from Supelco Analytical.

2.2. Synthesis of Nb-TUD-1

Nb-TUD-1 materials were synthesized following a procedure similar to that for siliceous TUD-1 [23]. In a typical synthesis, a mixture of TEA and deionized water was added to a solution of $NbCl_5$ in ethanol under stirring. To this mixture, a predetermined amount of TEOS was added and the stirring was continued for another 30 min. Finally, TEAOH was added dropwise, stirring the mixture vigorously for another 2 h. The resulting gel has the following molar composition: 1 SiO_2: (0.001–0.1) Nb: (0.35–0.5) TEAOH: 1 TEA: 11 H_2O. This gel was aged at room temperature for 24 h followed by drying at 100 °C for 24 h. The resulting solid was then transferred into a Teflon lined autoclave for hydrothermal treatment at 180 °C for 6 h. Finally, the template was removed by calcination in air at 600 °C for 10 h with a heating rate of 1 °C/min. The samples with varying Si/Nb ratios are named as Nb-TUD-1(x) where x represents the Si/Nb atomic ratio.

2.3. Catalyst characterization

Mesoporous Nb-incorporated catalytic materials used in this study were characterized in detail as reported elsewhere [7,26]. Briefly, nitrogen adsorption–desorption isotherms were measured at −196 °C on a Quantachrome NOVA 2000e sorption analyzer. Diffuse reflectance UV–Vis spectra were recorded under ambient conditions with a Perkin Elmer Lambda 850 instrument equipped with diffuse reflectance integrating sphere, with Spectralon as the reference. Temperature programmed desorption of ammonia (NH_3-TPD) spectra were measured on a Micromeritics Autochem 2910 instrument equipped with a Thermal Conductivity Detector (TCD) after treating the sample at 550 °C in a flow of He. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images [with energy dispersive X-ray (EDX) spectra] were obtained on a Technai F20 G2 X-Twin Field Emission STEM instrument operating at 200 kV and a Versa 3D dual beam Scanning Electron Microscope/Focused Ion Beam instrument (FEI, Hillsboro, OR, USA) with a silicon drift EDX detector, respectively. FTIR spectra of adsorbed pyridine were obtained on a Tensor-27 instrument with Pike diffuse reflectance accessory. Prior to analysis at room temperature, the samples were equilibrated with pyridine. Subsequently, any physisorbed pyridine was removed by evacuation at 80 °C.

2.4. Catalytic epoxidation studies

Ethylene epoxidation reactions were conducted in a semi-continuous mode in a 50 mL Parr reactor equipped with a magnetically driven stirrer, pressure transducer, and thermocouple. Details of the reactor and its operation are given elsewhere [20]. A schematic of the reactor setup is provided in the supplementary materials (Fig. S1). Briefly, a solution containing 50% H_2O_2/H_2O (118 mmol), MeOH (624 mmol) and internal standard AN (4.9 mmol) was charged into the reactor. Ethylene was injected from an external reservoir pressurizing the reactor up to 50 bar. The inertness of AN was confirmed experimentally via blank runs. The reactor pressure was held constant by continuously replenishing the consumed ethylene from the external ethylene reservoir. The reactor temperature was maintained at 35 °C. The impeller speed was kept at 1400 rpm to ensure the absence of mass transfer limitations. Isothermal, constant pressure semi-batch reactions last up to 5 h. A Sample GC/FID chromatogram and gas phase (TCD) analysis of the ethylene epoxidation reaction mixture is given in Fig. S2.

The following definitions are used in assessing the performance of the tested catalysts:

$$P_{\mathrm{EO}} = \frac{m_{\mathrm{EO}}}{(\text{batch time})(m_{\mathrm{metal}})}$$

$$S_{\mathrm{EO}} = \left(\frac{n_{\mathrm{EO}}}{n_{\mathrm{EO}} + n_{2\text{-}\mathrm{ME}} + n_{\mathrm{EG}}}\right) \times 100\%$$

$$U_{\mathrm{H_2O_2}} = \frac{n_{\mathrm{EO}} + n_{2\text{-}\mathrm{ME}} + n_{\mathrm{EG}}}{n^0_{\mathrm{H_2O_2}} - n_{\mathrm{H_2O_2}}} \times 100\%$$

$$X_{\mathrm{H_2O_2}} = \frac{n^0_{\mathrm{H_2O_2}} - n_{\mathrm{H_2O_2}}}{n^0_{\mathrm{H_2O_2}}} \times 100\%$$

where P_{EO}, S_{EO}, $U_{\mathrm{H_2O_2}}$, and $X_{\mathrm{H_2O_2}}$ denote EO productivity (g EO h^{-1} kg^{-1} metal), EO selectivity, H_2O_2 utilization toward EO formation (also defined as the H_2O_2 utilization efficiency) and H_2O_2 conversion, respectively. m_{EO} and m_{metal} represent the mass of EO formed and the mass of metal in the catalyst, respectively. n_{EO}, $n_{2\text{-}\mathrm{ME}}$ and n_{EG} denote the molar amounts of EO, 2-ME, and EG formed, respectively. $n^0_{\mathrm{H_2O_2}}$ and $n_{\mathrm{H_2O_2}}$ denote the initial and the final molar amounts of H_2O_2, respectively.

2.5. Elemental analysis

The metal content before and after reactions in the solid catalysts was determined by digesting the catalyst (60 mg) in the presence of HF (2 g), H_2SO_4 (3 g) and DI water (5 g) in an autoclave at 100 °C for up to 5 h and the resulting solution was analyzed by