Graphical Abstract

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 byproduct 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 towards EO formation (4304 g EO h^{-1} kg^{-1} Nb). The increased EO productivity either matches or surpasses that 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.

Keywords: Ethylene; Epoxidation; Ethylene oxide; Niobium; TUD-1; mesoporous; Lewis acid.

1. Introduction

The search for alternative EO technology that suppresses CO₂ formation as byproduct 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 CO₂ [1]. Recently, we reported a homogenous catalytic process for ethylene epoxidation that uses methyltrioxorhenium (MTO) as catalyst and H₂O₂ as oxidant providing almost total epoxide selectivity with no CO₂ formation as byproduct [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 CO₂ as byproduct) during liquid phase ethylene epoxidation using H₂O₂ 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 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 incorporated 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 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% H₂O₂ in H₂O), ferroin indicator solution, acetonitrile (AN) (HPLC grade), niobium oxide (Nb₂O₅), niobium(V) chloride (NbCl₅), niobium(V) ethoxide [Nb(OC₂H₅)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 NbCl₅ in ethanol under stirring. To this mixture, a predetermined amount of TEOS was added and the stirring was continued for another 30 minutes. Finally, TEAOH was added dropwise, stirring the mixture vigorously for another 2 h. The resulting gel has the following molar composition: 1 SiO₂: (0.001–0.1) Nb: (0.35–0.5) TEAOH: 1 TEA: 11 H₂O. 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 $-196\text{ }^{\circ}\text{C}$ 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 $550\text{ }^{\circ}\text{C}$ 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 $80\text{ }^{\circ}\text{C}$.

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% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (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:

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

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

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

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

where P_{EO} , S_{EO} , $U_{H_2O_2}$, and $X_{H_2O_2}$ denote EO productivity (g EO h⁻¹ kg⁻¹ metal), EO selectivity, H₂O₂ utilization toward EO formation (also defined as the H₂O₂ utilization efficiency) and H₂O₂ 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-ME} and n_{EG} denote the molar amounts of EO, 2-ME, and EG formed, respectively. $n_{H_2O_2}^0$ and $n_{H_2O_2}$ denote the initial and the final molar amounts of H₂O₂, respectively.

2.5. Elemental analysis

The metal content before and after reactions in the solid catalysts were determined by digesting the catalyst (60 mg) in the presence of HF (2 g), H₂SO₄ (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 ICP-OES technique. With proper calibration using appropriate standards, the ICP-OES analysis provides metal

concentrations in the spent catalyst with high sensitivity (± 1.6 ppm for Nb and ± 0.78 ppm for Si).

2.6 Computational details

Complete geometry optimizations using density functional theory (DFT) of the simplest Nb-incorporated silica frame, its hydroxylated derivative, and their reaction with H_2O_2 were performed using the NWChem 6.5 package [27]. Frequency calculations were carried out to confirm each stationary point as a local minima and obtain zero point vibrational energy (ZPE) corrections to the electronic energies. Different hybrid exchange-correlation functionals were tested for their description of the uncatalyzed ethylene epoxidation reaction (Table S4). Based on these results, which show good agreement with highly correlated methods, and its record of success with transition metals the M06-L hybrid functional [28] was chosen to perform all the calculations. The correlation-consistent polarized basis set with double zeta valence augmented by diffuse functions (aug-cc-pVDZ) [29,30] was used for the first and second row elements. The effective core potential plus double zeta basis set (LANL2DZ) [31] was used for Nb.

3. Results and discussion

The nitrogen sorption results of Nb-TUD-1 samples (Nb wt% = 1.4 – 12.2, Figure 1) reveal type IV adsorption isotherms with H2 type hysteresis loops characteristics of mesoporous amorphous material [23,32]. The BET surface area of Nb-TUD-1 materials varies from 420 m^2/g to 785 m^2/g with an increase in Nb content from 1.4 % to 12.2 % (see Table 1). The corresponding variations in pore volume and average adsorption pore diameter range from 0.67 to 1.22 cm^3/g , and 5 to 20 nm, respectively.

Fig. 1. Nitrogen sorption isotherms (left) and pore size distributions (right) of fresh Nb-TUD-1 (Si/Nb) catalysts

Table 1. Physicochemical characteristics of fresh and used Nb-TUD-1 catalysts

Catalyst ^a	Nb (wt %)	S _{BET} ^b (m ² /g)	V _{p, BJH} ^c (cm ³ /g)	d _{p, BJH} ^d (nm)	Total acidity NH ₃ (mmol/g)
Nb-TUD-1(10)	12.2	420	0.67	20	0.42
Nb-TUD-1(20)	6.9	616	0.88	10.3	0.47
Nb-TUD-1(40)	4.0	785	0.87	5.4	0.31
Nb-TUD-1(100)	1.4	627	1.22	11.5	0.17
Used Nb-TUD-1(20) ^e	3.7	437	0.64	7.6	0.14
Nb-TUD-1(200)	0.88	819	1.2	6.6	0.13
Nb-TUD-1(400)	0.42	563	1.0	7.8	0.04
Nb-TUD-1(800)	0.23	705	1.0	6.6	0.03

^aThe number in the parenthesis represents molar Si/Nb ratio, ^bS_{BET} = Specific surface area, ^cV_{p, BJH} = Pore volume, ^dd_{p, BJH} = Average pore diameter, ^eused Nb-TUD-1(20) catalysts recycled after 5 h run

The amorphous and mesoporous nature of Nb-TUD-1 materials are confirmed by HR-TEM micrographs (Figure 2) that show disordered morphology typical of TUD-1 materials [23,32]. A homogeneous distribution of Nb species was also observed in the Nb-TUD-1 samples from elemental mapping profiles obtained with the dual beam FIB/SEM instrument (Figures 3 and S3 respectively). The approximate Nb content estimated from the EDX analysis of small sample regions [5.9 wt% (Fig. 3) and 14.3 wt % Nb (Fig. S3)] are fairly close to those obtained from the more accurate ICP analysis of these samples (6.9 wt.% and 12.3 wt.% Nb, Table 1).

Fig. 2. HR-TEM images of Nb-TUD-1 samples at different Nb loadings from Si/Nb = 10 to 100. The scale bar represents 20 nm.

Fig. 3. SEM image, elemental mapping, and EDX spectrum of Nb-TUD-1(20)

Diffuse reflectance UV-Vis spectra of Nb-TUD-1 samples reveal a well-defined absorption peak around 212-229 nm with a tail extending from 270 nm (Figure 4). The absorption peak is attributed to isolated, well dispersed NbO₄ tetrahedral units whereas the tailing around 270 nm is due to oligomeric NbO₄ units [7, 13, 26, 33, 34]. The absorption in the range of ca. 270-320 nm may also be attributed to the possible exposure of catalyst sample to moisture leading to the presence of penta- or hexa coordinated Nb (V) species. Nevertheless, having some moisture in the gas phase helps mimic the presence of water in the reaction mixture to which the catalyst is exposed. Furthermore, the fraction of such species at 270 nm is relatively low compared to the tetrahedrally coordinated species, and hence any epoxidation activity stemming from them is expected to be low as well. For the commercial Nb₂O₅ powder, two absorption bands, one at 226 nm and a prominent one at 310 nm, are noticed [7, 26]. The lack of these bands in Nb-TUD-1 samples indicates the absence of bulk crystalline Nb₂O₅ in Nb-TUD-1 materials which is also evidenced from wide angle XRD (not shown).

Fig. 4. Diffuse reflectance UV-Vis spectra of Nb-TUD-1 (Si/Nb) catalysts

The total acidity of the Nb-TUD-1 materials from NH_3 -TPD studies, obtained by integrating the desorption areas, is presented in Table 1 and Figure 5. The fresh Nb-TUD-1 samples display similar strength of acid sites compared to Nb-KIT-6 and Nb-KIT-5 materials, as judged from the desorption temperatures. The acidity of Nb-TUD-1 samples increases with Nb loading. A majority of the acid sites occurs in the weak to medium acid strength regions (100–300 °C).

Fig. 5. Total acidity of Nb-TUD-1 (Si/Nb) catalysts measured with temperature programmed desorption (TPD) of NH_3

The results of ethylene epoxidation over Nb-TUD-1 are summarized in Table 2. The initial epoxidation rate (R_{EO}) obtained from the slope of the temporal EO formation profile of the most active catalyst was used to quantitatively assess gas-liquid (α_1), liquid-solid (α_2) and intraparticle (η) mass transfer limitations using established criteria. Details of estimating these parameters, including correlations and values of physical properties, are presented in Tables S1- S3. The

estimated values of α_1 , α_2 and η are 1.2×10^{-4} , 1.5×10^{-4} and 2.3×10^{-3} , respectively, indicating that both external and intraparticle mass transfer limitations are insignificant at our reaction conditions.

Negligible EO formation and H_2O_2 decomposition were observed in a blank experiment with siliceous TUD-1 (Table 2, entry 1). Additional blank experiments with homogeneous Nb salts [$\text{Nb}(\text{OC}_2\text{H}_5)_5$ and NbCl_5] (Table 2, entries 2&3) as well as commercial Nb_2O_5 (Table 2, entry 27) show relatively low epoxidation activity and poor H_2O_2 utilization ($\sim 0.5\%$) towards EO formation. However, under similar operating conditions, the Nb-TUD-1 with different Nb contents (1.4 % to 12.2 %) are comparatively very active for ethylene epoxidation (Table 2, entries 4-7). In all experiments, no CO or CO_2 was detected (Fig. S2) confirming negligible burning of ethylene under these conditions. When H_2O_2 was present with the catalyst, the gas phase analysis showed the presence of O_2 , confirming H_2O_2 decomposition.

For similar Nb content, the EO productivity observed with Nb-TUD-1 (342-2539 g EO h^{-1} kg^{-1} Nb) catalysts are higher than those reported previously with Nb-KIT-6 (234-794 g EO h^{-1} kg^{-1} Nb) [17] and Nb-KIT-5 catalysts (273-867 g EO h^{-1} kg^{-1} Nb, Table 2, entries 8-11), and significantly better than Nb-MCM-48 (71-219 g EO h^{-1} kg^{-1} Nb, Table 2, entries 12-15). Further, the EO productivity observed with Nb-TUD-1 catalysts are in the same range as those observed in either the conventional Ag catalyzed process (700-4,400 g EO h^{-1} kg^{-1} Ag) [21] or the methytrioxorhenium catalyzed process (1,610-4,970 g EO h^{-1} kg^{-1} Re) [2]. Even though all the tested catalysts show high activity for ethylene epoxidation, the H_2O_2 utilization efficiency ($U_{\text{H}_2\text{O}_2}$, see Table 2) values on Nb-TUD-1 (6.6-11.8 %), Nb-KIT-5 (7.0-15.8 %), and Nb-MCM-48 (2.9-11.3 %) are quite low. Further, significant Nb leaching (12 – 60.8 % of the initial Nb) was also observed for Nb-TUD-1 during the 5 h run, albeit moderately lower compared to Nb-

KIT-6 (33 – 72%) and Nb-KIT-5 (39 – 48 %). Consequently, recycle runs with Nb-TUD-1 and Nb-KIT-5 catalysts show considerably lower EO productivity (255 – 1471 g EO h⁻¹ kg Nb⁻¹) and 214 – 462 g EO h⁻¹ kg Nb⁻¹, respectively, compared to the previous (first) runs.

Table 2. Ethylene epoxidation activity and selectivity various Nb catalysts [Reaction conditions: MeOH = 624 mmol, H₂O₂=118 mmol, AN = 4.9 mmol, catalyst loading = 500 mg, T = 35 °C, Ethylene P = 50 bar (maintained constant), t = 5 h, 1400 rpm].

#	Catalyst ^a	Nb wt %	<i>P</i> _{EO} (±3%)*	<i>S</i> _{EO} % (±3%)	<i>X</i> _{H₂O₂} % (±3%)	<i>U</i> _{H₂O₂} % (±3%)	Leaching ±5%
1	Si-TUD-1 ^b	0	0	0	0	--	0
2	NbCl ₅	34.4	29.9	100	81.2	0.4	--
3	Nb(OC ₂ H ₅) ₅	29.1	48.1	33.8	78.7	0.5	--
4	Nb-TUD-1(10)	12.2	342	78.5	21.6	11.8	12.0
5	Nb-TUD-1(20)	6.9	667	88.7	21.4	6.6	46.4
6	Nb-TUD-1(40)	4.0	1186	89.1	15.7	8.6	52.5
7	Nb-TUD-1(100)	1.4	2539	87.8	12.8	9.1	60.8
8	Nb-KIT-5(10)	12.3	273	47.8	24.5	13.8	39.8
9	Nb- KIT-5(20)	6.4	446	50.8	17.1	15.8	48.4
10	Nb- KIT-5(40)	3.5	609	62.4	15.6	10.5	42.9
11	Nb- KIT-5(100)	1.4	867	56.1	14.9	7.0	42.9
12	Nb-MCM-48(10)	12.9	71.2	78.8	4.9	11.3	NM ^g
13	Nb- MCM-48(20)	6.8	54.4	75.0	4.2	5.6	NM ^g
14	Nb- MCM-48(40)	3.6	171	89.7	5.7	5.8	NM ^g
15	Nb- MCM-48(100)	1.5	219	81.8	6.4	2.9	NM ^g
16	Nb-TUD-1(10) ^c	10.9	255	80.6	11.5	14.4	NM ^g

17	Nb-TUD-1(20) ^c	3.7	378	99.8	4.6	8.8	NM ^g
18	Nb-TUD-1(40) ^c	1.9	447	99.4	2.4	10.2	NM ^g
19	Nb-TUD-1(100) ^c	0.5	1471	99.6	1.4	15.3	NM ^g
20	Nb-KIT-5(10) ^c	7.4	214	63.8	8.7	13.7	NM ^g
21	Nb- KIT-5(20) ^c	3.3	256	60.8	6.6	10.2	NM ^g
22	Nb- KIT-5(40) ^c	2.0	396	73.8	6.7	7.8	NM ^g
23	Nb- KIT-5(100) ^c	0.8	462	65.6	5.3	5.1	NM ^g
24	Nb/TUD-1 ^d	1.4	2219	96.6	5.1	18.2	87.1
25	Nb/TUD-1 ^e	1.4	1035	96.8	2.8	15.5	92.1
26	Nb/TUD-1 ^f	0.18	1952	100	0.64	13.6	NM ^g
27	Nb ₂ O ₅	69.9	4.38	89.5	4.1	4.0	NM ^g

*± values indicate standard deviations around mean values; ^aThe number in the parenthesis represents molar Si/Nb ratio; ^bBlank run with TUD-1 support as catalyst; ^cUsed catalyst after 5 h run; ^dImpregnation of Si-TUD-1 with NbCl₅ as precursor; ^eImpregnation of Si-TUD-1 with Niobium(V) oxalate as precursor; ^fUsed catalyst from entry 24 after 5 h run. ^gNM = The Nb leaching was not measured due to lower activities compared to fresh Nb-TUD-1 catalysts.

A detailed analysis of the spent Nb-TUD-1(20) catalyst (6.9 wt% Nb) revealed significant changes in surface area, pore volume, and pore size distribution (Table 1 and Figure S4). Further, a decrease in the intensity of the absorption peak around 212-229 nm in the diffuse reflectance UV-Vis (Figure S4) and a drastic decrease [up to 70% for Nb-TUD-1 (20)] in the total acidity (Figure S4) are also consistent with the observed Nb leaching. We also employed two different Nb sources, NbCl₅ and niobium(V) oxalate, to impregnate siliceous TUD-1 with identical Nb wt%. The leaching (~90%) after one cycle on these impregnated materials (Table 2, entries 24&25) is significantly worse than the Nb-TUD-1 material with similar Nb content (Table 2, entry 7) prepared by the sol-gel method.

An ethylene epoxidation experiment performed with filtered reaction mixture (from the 5 h run corresponding to entry 6, Table 2) containing leached Nb species also showed appreciable EO production activity under operating conditions identical to those used with the fresh catalyst. Interestingly, the EO formation observed during the 5 h run with the fresh catalyst (2.86 mmol corresponding to entry 6, Table 2 based on EO productivity value) is approximately the sum of the EO formation (2.18 mmol) observed with the solution containing the leached Nb species and the EO formation (0.27 mmol) observed with the spent catalyst (following the first 5 h run), all performed under identical operating conditions. Further, another experiment shows that approximately 20% of the Nb species leached out following the first 2 h from the Nb-TUD-1 (40) sample, compared to 52% after 5 h (entry 6, Table 2). This clearly shows that the active Nb species are steadily leached out from the catalyst during the 5 h run, and that the observed EO formation is a result of active Nb species present in both the catalyst and in the leached Nb species. Experiments with Nb₂O₅ as catalyst (entry 27, Table 2) showed a more than fifty-fold lower activity than Nb-TUD-1 catalysts at similar operating conditions, ruling out such dissolved oxides as the active species. The nature of the active Nb species in the leached solution is currently under investigation.

The leaching of Nb depends on various factors including nature of solvent, support (hydrophilicity and hydrophobicity), substrate, and H₂O₂ concentration. As documented in the literature [35], the increased 1-hexene epoxidation activity over titanosilicates with methanol as solvent is attributed to solvent coordination to Ti sites to form the active intermediate Ti species. For a specific substrate (1-hexene), while methanol is preferred solvent over TS-1, acetonitrile is the preferred solvent over Ti-MWW and Ti-Beta owing to the higher epoxidation activity observed with such solvents. Interestingly, a higher H₂O₂ decomposition rate was reported for

Ti-Beta compared to Ti-MWW and TS-1. In our previously reported work on the epoxidation of various substrates using Nb silicates as catalysts and H₂O₂ as oxidant, we observed significantly higher Nb leaching in ethylene/methanol system [20], compared to cyclohexene/acetonitrile system [11]. In other words, while a given solvent may promote epoxidation activity by facilitating the formation of an active intermediate species, it might also give rise to Brønsted acid sites that decompose H₂O₂ and promote metal leaching. In the present work, methanol was chosen as a preferred solvent based on previous literature reports for olefin epoxidations [35, 36].

Table 3. Effect of acidity on H₂O₂ conversion over Nb-TUD-1 catalysts in the absence of ethylene. Reaction conditions: MeOH = 624 mmol, H₂O₂=118 mmol, AN = 4.9 mmol, Catalysts = 500 mg, t = 5 h, 1400 rpm

Nb-TUD-1	Nb content (wt.%)	NH ₃ mmol/g	X _{H₂O₂} %
Si-TUD-1	0	0	0
Nb-TUD-1 (100)	1.4	0.17	2.3
Nb-TUD-1 (40)	4	0.31	7.7
Nb-TUD-1 (10)	12.2	0.39	18.1

No detectable H₂O₂ decomposition was observed over Si-TUD-1 in either the presence or the absence of ethylene under similar operating conditions (Table 3). However, even in the absence of ethylene, approximately 18% H₂O₂ conversion was observed over Nb-TUD-1(10) catalyst implying that the acidity imparted by metal incorporation into the TUD-1 support (Table 3) is a causative factor for H₂O₂ decomposition. Further, it was observed that as the acidity increased, the H₂O₂ conversion increased (Table 3). It is commonly known that homogeneous epoxidation catalysts that are exclusively Lewis acidic (MTO for example) utilize H₂O₂ effectively without

decomposing it [2]. This may suggest that in the case of Nb-TUD-1 and other heterogeneous catalysts, the Brønsted acidity that increases with metal loading (Figure 6) may play a role in decomposing H_2O_2 .

Fig. 6. Pyridine FTIR spectra of fresh Nb-TUD-1 catalysts

In order to gain insight into the underlying mechanisms of H_2O_2 decomposition and Nb leaching, we performed DFT calculations on simple model structures, shown in Figure 7, involving the minimal elements of the Nb-TUD-1 catalyst. Tiozzo *et al.* [14] performed diffuse reflectance UV-Vis (DR-UV-Vis) studies of grafted niobium-silica catalysts, and assigned a peak at 245 nm to $\text{O}^{2-} \rightarrow \text{Nb}^{5+}$ transfer which was associated with isolated Nb(V) centers and also proposed that due to the asymmetry of the peak, this peak suggested 2 different coordination geometries: tetrahedral and octahedral. These two coordination sites were further deduced based

on the XANES studies on their niobium-silica catalysts and EXAFS curve fit results were presented to give bond distances and coordination numbers. They proposed oxo-Nb(V) active sites on the catalyst with tetrahedral geometry (with one oxo and 3 bridging oxygens) or octahedral geometry (with one oxo, 3 bridging and two water oxygens [gem-diol]). The DR-UV-Vis spectra of Nb-TUD-1 samples (Figure 5) in the current work, shows a peak around 212-229 nm, which has been attributed to a tetrahedral NbO₄ geometry. The shoulder around 270 nm is due to oligomeric NbO₄ units. The spectra does not indicate a possibility of an octahedral geometry. Based on this current evidence for Nb-TUD-1, the simplest model of the doped silica used in this work is a niobyl silicate (Nb=O) arrangement shown in Figure 7a in which Nb is tetrahedrally coordinated.

Owing to the pentavalent nature of Nb and structural information for Nb-containing silica based catalysts [14, 37, 38], we optimized the niobyl silicate (closed-shell) structure, with a Nb(V) metal center. Three of the tetracoordinated oxygens are present as OH, representative of bridging to the silica framework in this minimalist model, and the fourth oxygen forms a double bond (oxo bond) to Nb(V). The experimental results discussed above and summarized in Tables 2 and 3, indicate that Brønsted acidity due to metal incorporation in Nb-TUD-1 is the likely cause for H₂O₂ decomposition and metal leaching. Based on these findings, we modeled the Brønsted site as the hydroxylated derivative of niobyl silicate (and still a tetrahedral configuration), namely niobium hydroxide (Nb–OH) silicate, as shown in Figure 7b. In this geometry, the niobium is tetravalent and the species is open-shell (doublet) structure with Nb(IV) metal center. The optimized distance parameters for both 7a and 7b are in good agreement with the respective distances as assigned from the experimental EXAFS studies of the grafted niobium-silicate catalysts.

Fig. 7. Optimized model structures of (a) niobyl silicate (Nb=O) and (b) niobium hydroxide (Nb-OH); all distances are in Å. (Cartesian coordinates of these structures are given in Tables S5 and S6).

Fig. 8. Optimized (a) niobyl silicate and (b) niobium hydroxide model structures shown in Figure 7 after H₂O₂ adsorption. (Cartesian coordinates are given in Tables S7 and S8).

The reaction of the niobium silicate structure with H₂O₂ in different orientations (*i.e.*, with the O-O bond parallel and perpendicular with respect to Nb=O bond) was modeled to understand the mechanism of adsorption and potentially H₂O₂ decomposition (Figure 8). In the case of the simplest niobyl silicate, H₂O₂ adsorption in the perpendicular orientation, shown in Figure 8a, is exothermic, with $\Delta H = -9.1$ kcal/mol (-12.4 kcal/mol for the parallel orientation). The H₂O₂

oxygen bound to the Nb is labeled O_α and the other is labeled O_β (and the hydrogens as H_α and H_β , respectively). We were unable to find a pathway for H_2O_2 decomposition when it is bound to niobyl silicate.

In contrast, when H_2O_2 adsorbs on the Brønsted site represented by the niobium hydroxide, it readily decomposes in a highly exothermic process ($\Delta H = -52.0$ kcal/mol) through breaking of the $O_\alpha-O_\beta$ bond and formation of water through extraction of the hydroxyl proton to O_β . This is accompanied by the transfer of H_α from the O_α of H_2O_2 to the bridging oxygen (O_b) and dissociation of the O_b-Nb bond, as shown in Figure 8b. These results suggest that the H_2O_2 decomposition is associated with the presence of Brønsted acid sites, particularly Nb-OH. The decomposition mechanism, indicated by these electronic structure calculations, involves the formation of water, addition of an oxygen atom to the Nb, and transfer of H to the bridging oxygen. This last feature suggests that H_2O_2 decomposition and metal leaching may be directly linked as the decomposition reaction severs a connection of the Nb to the silica framework. These calculations provide only a first-order picture of H_2O_2 decomposition and metal leaching.

Structural rigidity of the silica framework can affect the acidity of metal dopants by imposing geometrical constraints that increase the electron deficiency of the metal. The smaller structure studied above does not include such geometrical constraints, though no significant rearrangement of the structure is observed upon H_2O_2 adsorption. However, in order to examine such effects, we have performed calculations on a larger system by replacing the OH groups bound to the Si and Nb centers in structures 7a and 7b with $OSiH_3$ groups to form $(OSiH_3)_2(OH)Si-O-NbO(OSiH_3)_2$ and $(OSiH_3)_2(OH)Si-O-Nb(OH)(OSiH_3)_2$ models (Structures S7a and S7b respectively in Fig. S7, Tables S9 and S10). To model the rigidity of a silica framework, the $OSiH_3$ groups are first optimized in the bare cluster and then constrained in subsequent modeling

of H₂O₂ adsorption. We observe negligible differences in the bond distances involving the active metal center (δR of 0.01 Å for Nb=O, Si-O_b and Nb-O_b in S7a and δR of 0.01 Å for Si-O_b and no change for Nb=O and Nb-O_b in S7b). Moreover, small geometrical changes (δR of 0.01 Å for Nb=O and δR of 0.02 Å for Si-O_b and Nb-O_b in S8, Tables S11) were noted upon H₂O₂ adsorption on the structurally rigid niobyl active site. These results indicate that the acidity of the Nb center relevant to interactions with H₂O₂ in structure 7a is not strongly influenced by constraints imposed by the silica framework.

H₂O₂ adsorption on the niobyl (OSiH₃)₂(OH)Si-O-NbO(OSiH₃)₂ structure (Fig. S8) has ΔE (bare electronic energy change upon binding) of -14.5 kcal/mol while the smaller niobyl (OH)₂(OH)Si-O-NbO(OH)₂ structure (8a, Fig. 8) has ΔE = -13.6 kcal/mol. The small changes in geometry on introducing structural rigidity to the smaller model as well less than 1 kcal/mol energy difference on H₂O₂ adsorption between the flexible and the larger constrained model justify the use of the minimalistic model to represent the niobium-based silica catalyst. These studies point to directions for further study that would include the effect of the structural rigidity of the silica framework, multiple decomposition reactions at the same Nb site, and the role of other components of the reaction mixture such as water.

To reduce the Brønsted acidity, we hypothesized that catalysts with low Nb content (typically Nb = 0.015-0.5 wt.%) should have isolated Nb sites (Lewis acid sites) with much reduced if not total elimination of Brønsted acid sites. Indeed, Nb-TUD-1 catalysts with Nb loadings in the 0.23 - 0.88 wt% range displayed progressively lower acidity at decreased metal loading (Table 4, Figure 9). These materials also exhibit type IV adsorption isotherm with H₂ hysteresis, typical of TUD-1 type mesoporous structures (Figure S5). Their surface areas range from 649 – 735 m²/g, pore volumes from 1.0 to 1.17 cm³/g and average adsorption pore diameter from 6.5 to 10.8 nm

(Table 5). Also, the number of Brønsted sites decreases with metal loading as evidenced from the FTIR spectra of adsorbed pyridine (Figure 6). The acidity of Nb-TUD-1 with a Nb loading of 0.23 wt% is 0.03 NH₃ mmol/g, almost identical to the acidity of the SiO₂ framework. The ethylene epoxidation with these low Nb content catalysts (Table 4) show high activity (1041-4304 g EO h⁻¹ kg Nb⁻¹) and EO selectivity (87.8-99.9 %) with increased H₂O₂ utilization (20.6-78.7 %), supporting our hypothesis that a reduction in Brønsted acidity is beneficial to effective H₂O₂ utilization in EO formation.

Table 4. Evaluation of lower metal loading on the performance of Nb-TUD-1 catalysts for ethylene epoxidation. [Reaction conditions: MeOH = 624 mmol, H₂O₂=118 mmol, AN = 4.9 mmol, Catalysts = 300 mg, Ethylene P = 50 bar (maintained constant), t = 5 h, 1400 rpm]

Catalyst ^a	Nb wt %	P _{EO} (±3%)	S _{EO} % (±3%)	X _{H2O2} % (±3%)	U _{H2O2} % (±3%)	Total acidity NH ₃ (mmol/g)	Leaching ±5%
Nb-TUD-1(200)	0.88	4304	91.7	5.8	20.6	0.13	62.2
Nb-TUD-1(400)	0.42	2783	94.5	0.8	45.5	0.04	80.5
Nb-TUD-1(800)	0.23	1041	99.9	0.09	78.7	0.03	88.7

Fig. 9. Acidic properties of Nb-TUD-1 catalysts with low metal loading (Nb = 0.23-0.88 wt%), measured from NH₃-TPD profiles

A maximum in EO productivity was observed with respect to Nb content. As the Nb loading is decreased (from 6.9 wt.% to 0.88 wt.%), the number of Brønsted acid sites decreases resulting in (a) lower H₂O₂ decomposition and higher H₂O₂ utilization [from 6.6 % at 6.9 wt.% (Table 2, entry 4) to 20.6 % at 0.88 wt.% (Table 4, row 1)], and (b) increased EO productivity [from 667 at 6.9 wt.% (Table 2, entry 4) to 4304 g EO h⁻¹ kg⁻¹ Nb at 0.88 wt.% (Table 4, row 1)]. However, at extremely low Nb loadings (< 0.88 wt.%), even though the H₂O₂ decomposition is further curtailed, the EO productivity is also decreased (Table 4, rows 2 and 3) due to limited availability of Lewis acid sites responsible for the EO formation activity. On the other hand, even at lower acidities, significant metal leaching occurs implying that the remaining Brønsted acid sites, even though significantly reduced, are detrimental to catalyst performance.

4. Conclusions

Nb-incorporated TUD-1 materials are shown to epoxidize ethylene using H_2O_2 as oxidant with excellent activity and EO selectivity under mild reaction conditions (35 °C, 50 bars) with *no* CO_2 formation as byproduct. The observed EO productivity on low Nb loaded TUD-1 catalysts [1041-4304 g EO h^{-1} kg Nb $^{-1}$] are significantly higher than those observed with Nb-KIT-5, Nb-MCM-48, and Nb-KIT-6 catalysts. However, drastic H_2O_2 decomposition and metal leaching are major impediments that must be overcome for these catalysts to have practical viability. Complementary DFT-based computational studies using minimalist models of the catalytically active metal site and their reaction with H_2O_2 suggest that a reaction mechanism involving Brønsted acid sites, particularly niobium hydroxide sites, could contribute to H_2O_2 decomposition and metal leaching. Indeed, Nb-TUD-1 catalysts prepared with lower metal loadings significantly reduce the Brønsted acidity and display markedly higher H_2O_2 utilization and EO productivity. These results provide valuable guidance for future computational and experimental investigations aimed at developing stable and practically viable catalysts.

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