110th Anniversary: Near-Total Epoxidation Selectivity and Hydrogen Peroxide Utilization with Nb-EISA Catalysts for Propylene Epoxidation

Swarup K. Maiti,† Anand Ramanathan,† and Bala Subramaniam*†‡

†Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66047, United States
‡Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States

Supporting Information

ABSTRACT: The Nb-EISA catalyst with relatively low Nb loadings (∼2 wt %) shows exceptional propylene epoxidation performance with H₂O₂ as oxidant at 30−40 °C, 5−9 bar propylene pressure with nearly total propylene oxide (PO) selectivity (>99%), H₂O₂ utilization (>99%) toward PO formation, high productivity (∼3200 mg/h/g), and mild Nb leaching (3−6%). The predominantly Lewis acidic nature of the Nb-EISA catalysts favors epoxidation while their relatively low Brønsted acidity inhibits H₂O₂ decomposition and Nb leaching. At higher Nb loadings (8−17 wt %), the catalytic performance deteriorates. However, significant performance improvements were achieved when the Nb-EISA materials are calcined in N₂ (instead of air) during synthesis, depositing a carbon layer in the pores. The resulting pore hydrophobicity not only inhibits epoxide ring opening but also increases propylene concentration inside the pores resulting in higher EO productivity and lower H₂O₂ decomposition. The carbonized Nb-EISA materials also show improved stability to leaching.

1. INTRODUCTION
Propylene oxide (PO) is one of the most important chemical intermediates for producing many essential fine chemicals, such as polyurethane plastics, polyglycol esters, unsaturated resins, and surfactants.1−3 The global demand for PO is high, being >10 million metric tons/year in 2012 and growing at an annual rate of 5%.4,5 In general, PO is produced via epoxidation of propylene, an industrially significant substrate. Current commercial routes to PO production are mainly the chlorohydrin process, different hydroperoxide based processes, and the hydrogen peroxide propene oxide (HPPO) process. While the chlorohydrin process suffers from high environmental impact due to much waste generation, the hydroperoxide-based processes depend on stable byproduct (tert-butyl alcohol) value for economic viability. Among these processes, the HPPO process has less environmental impact as it produces only H₂O as byproduct and uses mild operating conditions (40−50 °C and 20−30 bar). The HPPO process provides a maximum PO selectivity of 95% using the titanium silicate (TS-1) catalyst in methanol solvent. While the TS-1 catalyst is active, it is expensive and undergoes deactivation.9 Further, the extent to which H₂O₂ decomposes on the acidic TS-1 catalyst is unknown. Stoichiometric utilization of H₂O₂ toward PO formation with near-complete PO selectivity is vital to making the process economically viable. Hence, there continues to be interest in alternative PO processes using inexpensive and robust catalysts that maximize PO selectivity and H₂O₂ utilization.

Various catalysts have been investigated for propylene epoxidation with hydrogen peroxide, including heteropolyacids,10,11 methyltrioxorhenium (MTO),9 tungsten based homogeneous catalysts,12 and various titanium containing zeolites, viz., Ti-MWW13 and TiCl₄-modified HZSM-5,14 in addition to TS-1.6−8 For example, Xi et al. performed propylene epoxidation10 at 65 °C using in situ formed H₂O₂...
2. EXPERIMENTAL SECTION

2.1. Materials. Triblock copolymer (Pluronic P123, EO20–
PO70–EO20, with an average molecular weight ∼5,800,
Aldrich), ethanol (Absolute, 200 Proof, Acros organics),
methanol (Sigma-Aldrich), tetraethyl orthosilicate (TEOS)
(98% Acros organics), conc. hydrochloric acid (37%, Fisher),
and niobium(V) chloride (Alfa Aesar) were used as received.
Acetonitrile (HPLC grade, 99.9%, Fisher) and H2O2 (50 wt %
in water, Fisher) were used as received for catalytic propylene
ejeroxidation with H2O2. Ferroin indicator solution, ceric sulfate
(0.1 N), and trace metal grade sulfuric acid (99.9 wt %)
were purchased from Fisher Scientific and used as received.
The PO standard, 1-methoxy-2-propanol, and propylene glycol
were purchased from Sigma-Aldrich, whereas 2-methoxy-
1-propanol was purchased from Chem-Bridge Chemical.
Propylene was purchased from Matheson Tri-Gas Co
(polymer grade).

2.2. Synthesis of Nb-EISA and Catalyst Character-
ization. The Nb-EISA catalysts were prepared as described
previously.31 Briefly, TEOS was added to the acidified
ethanolic solution containing P123, followed by the required
amounts of niobium(V) chloride predissolved in ethanol. After
stirring the mixture for a couple of hours, it is transferred to a
Pyrex Petri dish, and the solvent is allowed to evaporate for 2–
4 days. The resulting rigid flakes were then calcined in either
flowing air or nitrogen at 550 °C for 5 h at a heating rate of 1.5
°C/min to obtain either Nb-EISA or Nb-EISA, respectively.
The calcined samples were characterized with a comprehensive
suite of complementary analytical techniques including SAXS,
XRD, XRF, N2 physisorption, diffuse reflectance UV–vis
spectroscopy, transmission electron microscopy (TEM, SEM),
NH2-TPD, and FTIR of adsorbed pyridine.31

The metal contents in the fresh and spent solid catalysts
were determined by inductively coupled plasma optical
emission spectrometry (ICP-OES). Prior to analysis, the
catalyst (60 mg) was digested in the presence of HF (2 g),
H2SO4 (3 g), and deionized water (5 g) in an autoclave at 100
°C for 3 h. The resulting solutions were analyzed by the ICP-
OES technique using appropriate calibration standards.
The ICP-OES analysis offers high sensitivity in calculating metal
concentrations in the catalysts (±1.6 ppm for Nb and ±0.78
ppm for Si).

2.3. Volumetric Expansion Studies. When pressurized
propylene is dissolved in methanol, it shows enhanced
solubility resulting in propylene-expanded liquids. A 50 mL
high-pressure Jerguson cell rated to ∼400 bar at 100 °C39
was used for volumetric expansion studies. Either pure methanol
or a methanol + 50% H2O/H2O mixture is placed in the view
cell which is then submerged in a constant temperature bath.
To facilitate the mixing of cell contents, the loaded liquid is
agitated by a piston. Once the desired temperature is attained,
propylene is pumped as a liquid from an ISCO pump into the
cell to the desired pressure. Mixing of the gas and liquid phases
by a piston expedites the attainment of equilibrium (as inferred
from constant P and T). At equilibrium, the volume of a
propylene expanded liquid phase is measured visually on a
calibrated external linear scale.

2.4. Catalytic Epoxidation Studies. The catalysts were
tested for propylene epoxidation in a semibatch mode in a 50 mL
Parr reactor equipped with a magnetically driven stirrer,
pressure transducer, and thermocouple. Reactor details and the
operating procedure are described elsewhere,21 and a
schematic of the reactor unit is given in the Supporting Information (Figure S1). In a typical reaction, a mixture containing a 50% aqueous H₂O₂ (10 mmol) solution, MeOH (625 mmol), acetonitrile (3 mmol) as internal standard, and a solid catalyst (fresh or spent) was loaded into the Parr reactor. A blank experiment using 1,2-dimethoxyethane (DME) as internal standard confirmed the inertness of acetonitrile. The solution was heated with mild stirring to attain the desired temperature (35 °C). Thereafter, propylene was charged from an external reservoir pressurizing the reactor up to 0.9 MPa. The impeller speed was kept at 1400 rpm to eliminate gas–liquid mass transfer limitations. Isothermal semibatch reactions lasting up to 3 h were performed at constant pressure. The liquid-phase reaction mixture was analyzed by online GC to determine the concentrations of the desired product (PO) and the byproducts [1-methoxy-2-propanol (1M2P), 2-methoxy-1-propanol (2M1P), and propylene glycol (PG)]. The following definitions are used in evaluating the performance of the tested catalysts

\[ P_{\text{PO}} = \frac{m_{\text{PO}}}{(\text{batchtime})(m_{\text{metal}})} \]

\[ S_{\text{PO}} = \left( \frac{n_{\text{PO}}}{n_{\text{PO}} + n_{1M2P} + n_{2M1P} + n_{\text{PG}}} \right) \times 100\% \]

\[ U_{\text{H}_2\text{O}_2} = \left( \frac{n_{\text{H}_2\text{O}_2}}{n_{\text{H}_2\text{O}_2} - n_{\text{H}_2\text{O}_3}} \right) \times 100\% \]

\[ X_{\text{H}_2\text{O}_3} = \left( \frac{n_{\text{H}_2\text{O}_3}}{n_{\text{H}_2\text{O}_2} - n_{\text{H}_2\text{O}_3}} \right) \times 100\% \]

where \( P_{\text{PO}} \), \( S_{\text{PO}} \), \( U_{\text{H}_2\text{O}_2} \), and \( X_{\text{H}_2\text{O}_3} \) denote PO productivity (mg PO h⁻¹ g⁻¹ metal), PO selectivity, H₂O₂ utilization toward PO formation, and H₂O₂ conversion, respectively; \( m_{\text{PO}} \) and \( m_{\text{metal}} \) represent the mass of PO formed and the mass of metal in the catalyst, respectively; \( n_{\text{PO}} \), \( n_{1M2P} \), \( n_{2M1P} \), and \( n_{\text{PG}} \) denote the molar amounts of PO, 1M2P, 2M1P, and PG formed, respectively; and \( n_{\text{H}_2\text{O}_2} \) and \( n_{\text{H}_2\text{O}_3} \) denote the initial and the final molar amounts of H₂O₂, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Catalyst Characterization.

Detailed physicochemical characterization of Nb-EISA samples and their carbonized versions (C–Nb-EISA) may be found in the Supporting Information (Figures S2–S9) and elsewhere. Only the salient features are summarized here. The mesoporous nature of Nb-EISA and C–Nb-EISA samples was confirmed by N₂ sorption revealing typical type IV isotherm and H₃ hysteresis. The physicochemical characteristics are summarized in Table 1. For Nb-EISA and C–Nb-EISA samples, the surface area ranges from 615 to 680 m²/g and from 418 to 571 m²/g, respectively, decreasing with increased Nb content (1.6–22.0 wt %). These materials possess an average pore diameter of about 2.7–3.4 nm. Further, the total acidity (0.10–0.31 mmol NH₃/g) was found to be lower compared to other Nb containing mesoporous silicates. Although an increase in the relative amounts of Lewis acid sites was inferred from the FTIR spectra of adsorbed pyridine, relatively low amounts of Bronsted acid sites were observed (Table 1). Further, the weak Bronsted acidity is confirmed by complete desorption of pyridine at mild temperature (250 °C). Diffuse reflectance UV–vis characterization reveals the presence of bands at 200–204 nm attributed to ligand-to-metal charge transfer in isolated Nb₂O₅ tetrahedra and another band at 242–267 nm due to oligomeric Nb₂O₅ tetrahedral. The lack of a band at 290–320 nm implies the absence of bulk Nb₂O₅ species which is also evidenced from powder XRD patterns.

#### 3.2. Volumetric Expansion Studies.

While conventional liquid phases are noncompressible, gas-expanded liquid phases are compressible. The compressibility depends on the extent of gas dissolution in the liquid phase. Hence, volumetric expansion data are important to calculate the propylene concentration in the liquid phase precisely. Such data also facilitate reliable interpretation of the effects of various parameters such as temperature, propylene pressure, and aqueous H₂O₂ concentration on the extent of dissolution of propylene in the liquid phase. As shown in Figure 1, the volume of initial liquid phase containing either pure methanol or a representative reaction mixture (containing methanol and

![Figure 1. Volumetric expansion plot with propylene pressure at 35 °C.](Image)

<table>
<thead>
<tr>
<th>Table 1. Physical Properties of Nb-EISA and C–Nb-EISA Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. catalyst</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>13</td>
</tr>
</tbody>
</table>

a wt % in sample determined by XRF. b wt % in sample determined by TG/DTA. c \( S_{\text{BET}} \) = BET specific surface area from adsorption isotherm at \( P/P_0 \) between 0.05 and 0.30. d \( V_{\text{t}} \) = total pore volume at 0.99 \( P/P_0 \). e \( d_{\text{P}100} \) = average pore diameter calculated from adsorption branch of N₂ isotherms using the BJH model. f Another batch of Nb-EISA (1.9%).

DOI: 10.1021/acs.iecr.9b03461
50% aqueous $\text{H}_2\text{O}_2$) increases with increasing propylene pressure, implying increased propylene dissolution in the liquid phase. At a fixed temperature, the extent of volumetric expansion decreases with increasing $\text{H}_2\text{O}_2$ concentration in the methanol + $\text{H}_2\text{O}_2$ (50% aqueous) mixture. At 35 °C and 9 bar propylene pressure, the volumetric expansion in the case of pure methanol is 29%. In the case of methanol + $\text{H}_2\text{O}_2$ (aqueous) mixtures, the volumetric expansion caused by propylene dissolution at 9 bar and 35 °C is 27%, 23%, and 20% when the $\text{H}_2\text{O}_2$ contents in the mixture are 5, 10, and 15 mmol, respectively. As expected, increased concentrations of polar $\text{H}_2\text{O}_2$ in the liquid phase decrease the solubility of nonpolar propylene. Even though the main product, PO, was not included in the volumetric expansion studies, PO formation during reaction (3 h) constitutes only ≈0.8 wt % of the reaction mixture and, hence, is not expected to alter the propylene dissolution significantly.

### 3.3. Epoxidation of Propylene

#### 3.3.1. Epoxidation of Propylene by Nb-EISA Catalysts

Nb-EISA catalysts with different Nb loadings were screened for propylene epoxidation, and the results are summarized in Table 2 (entries 1–5). The Nb-EISA catalyst with 1.8 wt % Nb loading displayed nearly total $\text{S}_\text{PO}$ (>99%) and $\text{U}_{\text{H}_2\text{O}_2}$ (>99%) with relatively low Nb leaching (3.5%) during a 3 h run. With an increase in Nb loading up to 10.2 wt %, the yield of PO increased and then decreased at the high Nb loading of 22 wt %. $\text{U}_{\text{H}_2\text{O}_2}$ values also decreased with increased Nb loading. The decreases in $\text{P}_{\text{PO}}$ and $\text{U}_{\text{H}_2\text{O}_2}$ values at the higher Nb loadings are attributed to the formation of oligomeric NbOx species that are not as active as the isolated NbOx species for epoxidation. Further, the Bronsted acidic nature of the oligomeric NbOx species also decomposes $\text{H}_2\text{O}_2$, adversely affecting its utilization for PO formation.

We prepared different batches of Nb-EISA materials with similar Nb loadings (1.9–2.0 wt %) and tested for catalyst stability during extended runs (Table 2, entries 6–8). Similar $\text{P}_{\text{PO}}$ was observed for the extended run (10 h) suggesting that the catalyst is stable under the reaction conditions. Further, the decreased Nb leaching (5.7% at 10 h vs 3.5% at 3 h) does not scale with reaction time suggesting that the leaching decreases with time. Additionally, Nb-EISA catalysts prepared in two different batches with almost identical Nb loadings show similar catalytic activities (Table 2, entries 6 and 8) under similar reaction conditions. This indicates that the catalyst synthesis technique is reproducible for similar Nb loadings.

We also tested various mesoporous Nb-silicate catalysts (viz., Nb-KIT-5, Nb-KIT-6, and Nb-TUD-1) that were active for ethylene epoxidation. As shown in Table 3 (entry 1),

| Table 2. Performances of Nb-EISA with Different Nb Loadings and Reaction Times for Propylene Epoxidation$^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>no.</td>
<td>Nb-EISA, Nb wt %</td>
<td>time (h)</td>
<td>$\text{Y}_{\text{PO}}$ (mmol) (±3%)</td>
<td>$\text{P}_{\text{PO}}$ (±3%)</td>
<td>$\text{S}_{\text{PO}}$ % (±3%)</td>
<td>$\text{X}_{\text{H}_2\text{O}_2}$ % (±3%)</td>
<td>$\text{U}_{\text{H}_2\text{O}_2}$ % (±3%)</td>
<td>leaching % (±5%)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.8$^a$</td>
<td>3</td>
<td>0.63</td>
<td>2340</td>
<td>&gt;99</td>
<td>5.3</td>
<td>&gt;99</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>3</td>
<td>1.20</td>
<td>2071</td>
<td>&gt;99</td>
<td>12.7</td>
<td>94.5</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>3</td>
<td>2.84</td>
<td>3050</td>
<td>&gt;99</td>
<td>28.7</td>
<td>96.3</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10.2</td>
<td>3</td>
<td>1.23</td>
<td>777</td>
<td>91.8</td>
<td>22.7</td>
<td>59.0</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>22.0</td>
<td>3</td>
<td>0.84</td>
<td>247</td>
<td>86.6</td>
<td>31.5</td>
<td>31.1</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.0$^a$</td>
<td>10</td>
<td>0.94</td>
<td>3171</td>
<td>&gt;99</td>
<td>9.1</td>
<td>&gt;99</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.0$^a$</td>
<td>3</td>
<td>2.85</td>
<td>2900</td>
<td>&gt;99</td>
<td>27.9</td>
<td>&gt;99</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.9$^a$</td>
<td>3</td>
<td>0.93</td>
<td>3174</td>
<td>&gt;99</td>
<td>9.3</td>
<td>&gt;99</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Different batches with similar Nb loadings. $^b$Reaction conditions: MeOH = 624 mmol, $\text{H}_2\text{O}_2$ = 10 mmol, AN = 3 mmol, catalyst loading = 300 mg, T = 35 °C, propylene $P$ = 9 bar (maintained constant), 1400 rpm.

| Table 3. Performances of Different Nb-Silicates for Propylene Epoxidation$^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>no.</td>
<td>catalyst</td>
<td>Nb wt %</td>
<td>$\text{P}_{\text{PO}}$ (±3%)</td>
<td>$\text{S}_{\text{PO}}$ % (±3%)</td>
<td>$\text{X}_{\text{H}_2\text{O}_2}$ % (±3%)</td>
<td>$\text{U}_{\text{H}_2\text{O}_2}$ % (±3%)</td>
<td>leaching % (±5%)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Nb-KIT-5</td>
<td>2.2</td>
<td>2500</td>
<td>88</td>
<td>15.6</td>
<td>70</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nb-TUD-1</td>
<td>3.8</td>
<td>4075</td>
<td>&gt;99</td>
<td>27.1</td>
<td>89.4</td>
<td>20.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Nb-TUD-1$^a$</td>
<td>3.8</td>
<td>3329</td>
<td>&gt;99</td>
<td>26.3</td>
<td>74.6</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Nb-TUD-1</td>
<td>0.8</td>
<td>11680</td>
<td>&gt;99</td>
<td>17.0</td>
<td>80.1</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Bn-Nb-TUD-1</td>
<td>2.7</td>
<td>907</td>
<td>&gt;99</td>
<td>4.1</td>
<td>93.6</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reaction temperature is 40 °C. $^b$Reaction conditions: MeOH = 624 mmol, $\text{H}_2\text{O}_2$ = 10 mmol, AN = 3 mmol, catalyst loading = 300 mg, T = 35 °C, propylene $P$ = 9 bar (maintained constant), t = 3 h, 1400 rpm.
Parametric studies including temperature, propylene pressure, \(H_2O_2\) concentration, and catalyst loading were performed with the Nb-EISA catalyst with 2 wt % Nb, the best-performing catalyst (Table 2). Table 4 summarizes temperature effects. When the reaction temperature is increased from 30 to 35 °C, the PO yield increased approximately 2-fold. Notably, both PO selectivity and \(H_2O_2\) utilization remained high (>99%) at 35 °C. However, at higher temperatures (40 and 45 °C), both PO productivity and \(H_2O_2\) utilization efficiency decreased. The lower activity at higher temperatures (40 and 45 °C) is attributed to the lower propylene dissolution in the gas-expanded liquid phase as well as increased \(H_2O_2\) decomposition, resulting in decreased availability of the two key reactants.

At 35 °C, PO yield increases with propylene pressure. At 35 °C, the PO yields are 0.30, 0.48, and 0.94 mmol at propylene pressures of 5, 7, and 9 bar, respectively (Table 4, entries 2, 5, and 6). Notably, nearly total (>99%) \(S_{\text{PO}}\) and \(U_{\text{H}_2\text{O}_2}\) were achieved in this pressure range, and Nb leaching remained low (within 3–4%). The increased PO yield at higher propylene pressures is attributed to enhanced propylene solubility in the methanolic liquid phase (Figure 2). Given that propylene at 35 °C is below its critical temperature (92.2 ± 0.8 °C), pressurization with \(N_2\) beyond the saturation vapor pressure would cause propylene condensation and dissolution in the liquid phase. For example, when propylene at 9 bar was pressurized with 11 bar of \(N_2\) at 35 °C, the PO yield increased approximately 10% more (Table 4, entries 2 and 7).

The effect of \(H_2O_2\) concentration was also studied. As inferred in Table 4 (entries 2, 8, and 9), PO productivity increased significantly with an increase in \(H_2O_2\) concentration. However, Nb leaching also increased. While negligible \(H_2O_2\) decomposition was observed when 5 or 10 mmol of \(H_2O_2\) was used, significant \(H_2O_2\) decomposition occurred when 15 mmol of \(H_2O_2\) was used.

When the catalyst loading is increased by 2-fold (from 150 to 300 mg, entries 10 and 2 in Table 4), the PO yield doubled, resulting in similar PO productivity. However, when the catalyst loading was further increased by 4- and 6-fold (from 150 mg to 600 and 900 mg, entries 10–12), the corresponding increases in PO yield were 2.6× and 3.2×, respectively. These are also reflected in the lower PO productivity at higher catalyst loadings (beyond 300 mg). Thus, lower temperature (~35 °C), lower Nb loadings (~2 wt %), and moderate propylene pressure (~9 bar) are preferred to maximize PO productivity and \(H_2O_2\) utilization while minimizing Nb leaching. Figure 2 compares key performance measures of the Nb-EISA catalyst and its carbonized version at different Nb loadings.

3.3.2. Epoxidation of Propylene by Carbonized Nb-EISA Catalysts (C–Nb-EISA). In order to improve \(H_2O_2\) utilization and epoxide selectivity at higher Nb loadings, the as-synthesized Nb-EISA materials were carbonized by calcination in the presence of \(N_2\) (rather than air) at 550 °C. As expected, the C–Nb-EISA (carbonized version of Nb-EISA) catalysts showed better \(P_{\text{PO}}\), \(S_{\text{PO}}\), \(U_{\text{H}_2\text{O}_2}\), and resistance to metal leaching compared to Nb-EISA with similar Nb loadings (Table 5). For the Nb-EISA catalyst with 10.2 wt % Nb, the values of \(P_{\text{PO}}, S_{\text{PO}}, U_{\text{H}_2\text{O}_2}\), and Nb leaching were 777 mg/h/g, 92%, 59%, and

---

Table 4: Effect of Temperature, Pressure, \(H_2O_2\) Concentration, and Catalyst Loading for Propylene Epoxidation over Nb-EISA (2.0 wt % Nb)4

<table>
<thead>
<tr>
<th>no.</th>
<th>(T) (°C)</th>
<th>(P) (bar)</th>
<th>(H_2O_2) (mmol)</th>
<th>catalyst amt (mg)</th>
<th>(Y_{\text{PO}}) mmol (±3%)</th>
<th>(P_{\text{PO}}) (±3%)</th>
<th>(S_{\text{PO}}) % (±3%)</th>
<th>(X_{\text{H}_2\text{O}_2}) % (±3%)</th>
<th>(U_{\text{H}_2\text{O}_2})% (±3%)</th>
<th>leaching % (±5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>9</td>
<td>10</td>
<td>300</td>
<td>0.48</td>
<td>1618</td>
<td>&gt;99</td>
<td>4.67</td>
<td>&gt;99</td>
<td>5.2</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>9</td>
<td>10</td>
<td>300</td>
<td>0.94</td>
<td>3171</td>
<td>&gt;99</td>
<td>9.08</td>
<td>&gt;99</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>9</td>
<td>10</td>
<td>300</td>
<td>0.83</td>
<td>2809</td>
<td>&gt;99</td>
<td>8.28</td>
<td>97.1</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>9</td>
<td>10</td>
<td>300</td>
<td>0.58</td>
<td>1964</td>
<td>&gt;99</td>
<td>9.04</td>
<td>65.2</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>7</td>
<td>10</td>
<td>300</td>
<td>0.48</td>
<td>1618</td>
<td>&gt;99</td>
<td>4.67</td>
<td>&gt;99</td>
<td>5.2</td>
</tr>
<tr>
<td>6</td>
<td>35</td>
<td>5</td>
<td>10</td>
<td>300</td>
<td>0.30</td>
<td>1032</td>
<td>&gt;99</td>
<td>3.0</td>
<td>&gt;99</td>
<td>4.0</td>
</tr>
<tr>
<td>7</td>
<td>35</td>
<td>20a</td>
<td>10</td>
<td>300</td>
<td>0.97</td>
<td>3323</td>
<td>&gt;98</td>
<td>11.4</td>
<td>86</td>
<td>NMb</td>
</tr>
<tr>
<td>8</td>
<td>35</td>
<td>9</td>
<td>5</td>
<td>300</td>
<td>0.22</td>
<td>733</td>
<td>&gt;99</td>
<td>2.2</td>
<td>&gt;99</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>35</td>
<td>9</td>
<td>15</td>
<td>300</td>
<td>1.41</td>
<td>4776</td>
<td>&gt;99</td>
<td>11.7</td>
<td>80.1</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
<td>9</td>
<td>10</td>
<td>150</td>
<td>0.47</td>
<td>3188</td>
<td>&gt;99</td>
<td>4.5</td>
<td>&gt;99</td>
<td>5.2</td>
</tr>
<tr>
<td>11</td>
<td>35</td>
<td>9</td>
<td>10</td>
<td>600</td>
<td>1.21</td>
<td>2052</td>
<td>&gt;99</td>
<td>11.4</td>
<td>86</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>35</td>
<td>9</td>
<td>10</td>
<td>900</td>
<td>1.54</td>
<td>1760</td>
<td>&gt;99</td>
<td>14.7</td>
<td>&gt;99</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\*a1 bar propylene and 11 bar \(N_2\), \*bNM = not measured. *Reaction conditions: MeOH = 624 mmol, AN = 3 mmol, propylene \(P = \) maintained constant, \(t = 3\ h, 1400\ rpm\).
13.7%, respectively (Table 2, entry 3), compared to 1320 mg/ h/g, >99, 91%, and 8% observed with C–Nb-EISA catalysts with 7.8 wt % Nb (Table 5, entry 3). We hypothesize that carbonization of the silica matrix induces pore hydrophobicity which in turn enhances the propylene concentration in the pores, resulting in higher propylene epoxidation rates. Further, pore hydrophobicity reduces the concentration of polar molecules such as water inside the pores and therefore mitigates the formation of Bronsted acid sites, a causative factor for \( \text{H}_2\text{O}_2 \) decomposition over Nb silicates. The oligomeric species are more susceptible to leaching compared to the isolated NbOx species although the rate of leaching appears to taper off at higher loadings.

### 3.3. Catalyst Stability

Recycle tests with the Nb-EISA catalyst with 1.9 wt % Nb loading were carried out up to four cycles (Table 6, entries 1–5). Notably, a slightly improved PO productivity \( (P_{\text{PO}}) \) was achieved in the first recycle run compared to the first run with a fresh catalyst. Interestingly, after the first recycle run, \( P_{\text{PO}} \) remained almost unchanged during the subsequent recycle runs. Nearly total PO selectivity and \( \text{H}_2\text{O}_2 \) utilization were observed with steady but low Nb leaching (~6 wt %) during the recycle runs. The increased PO productivity during the first recycle run may be attributed to the leaching of extra framework NbOx species that are not as active as the framework Nb species. The carbonized version, C–Nb-EISA with 1.55 wt % Nb loading, showed similar trends during four recycle runs (Table 6 entries 6–10), confirming that both Nb-EISA and its carbonized version are recyclable catalysts.

During allyl alcohol epoxidation with hydrogen peroxide, both Ti-MCM-41 and Ti-SBA-15 showed Ti leaching as well as partial collapse of the mesoporous structure. The fresh Nb-EISA and C–Nb-EISA catalysts along with the corresponding spent catalysts after the fourth recycle run and after a 10 h extended run were analyzed by the N\(_2\) physisorption method. As inferred from Table 1 (entries 9–12), no significant changes between the fresh and spent catalysts were observed in the nitrogen physisorption isotherms and pore size distribution, confirming that the catalysts are structurally stable under reaction conditions. Further, no evidence of Si leaching was observed in the spent reaction mixtures providing complementary evidence that the Nb leaching is not due to a loss of the structural integrity of the siliceous support during the reaction. These observations thus clearly demonstrate that inducing hydrophobicity in the pores not only enhances epoxidation rates but also inhibits leaching. This provides guidance for future work in developing new catalyst synthesis methods to achieve optimum hydrophobicity that minimizes catalyst leaching to practically viable levels.

### 3.4. Proposed Mechanism for Propylene Epoxidation

Recently, our group and collaborators conducted mechanistic investigations of liquid phase ethylene epoxidation by aqueous hydrogen peroxide catalyzed by niobium silicate. Density functional theory calculations were used to investigate catalytic pathways and probable reasons for hydrogen peroxide decomposition and potential metal leaching. In the present work, the propylene epoxidation was performed under reaction conditions similar to ethylene epoxidation using a similar type of Nb incorporated mesoporous silicate as catalyst. We therefore hypothesize that the ethylene epoxidation mechanism can be extended to propylene epoxidation as well. Scheme 1 shows plausible mechanistic pathways for propylene epoxidation based on previous studies.

A five-step cycle is proposed. The initial steps consist of adsorption of hydrogen peroxide to the Nb center followed by coordination of propylene to the \( \text{H}_2\text{O}_2 \), resulting in the formation of \( \text{Nb}-\text{hydroperoxide} \). The \( \text{H}_2\text{O}_2 \) coordinated propylene then undergoes epoxidation via an oxygen atom transfer from the hydroperoxide moiety to the \( \text{C}==\text{C} \) bond of propylene via a transition state. The epoxidation proceeds preferentially as a direct attack of the nucleophilic olefin on an
electrophilic peroxo oxygen center via a transition state of spiro structure (Sharpless mechanism). Propylene epoxidation follows an electrophilic mechanism in which the π* bond of the alkene transfers electrons to the σO−O* peroxo antibond of the Nb-hydroperoxide intermediate and accepts electrons from the π* orbital of peroxo oxygen into its (alkene’s) π* orbital. This electron donation process elongates the O−O bond and eventually leads to its cleavage to form the corresponding epoxide. The epoxidation step to form propylene oxide is the rate-limiting step. The subsequent steps involve desorption of the propylene oxide product followed by dehydration to regenerate the catalyst. If methanol is used as solvent, the propylene oxide can further undergo hydrolysis and solvolysis reactions to form the corresponding byproducts, propylene glycol and isomers of methoxy propanol, respectively. The extent of byproduct formation depends on the Brønsted acidity of the catalyst and the process conditions. In general, higher Brønsted acidity, temperature, and water content enhance byproduct formation.

It is noteworthy that the reaction of the niobium silicate structure with H₂O₂ was modeled in different orientations in order to understand the mechanism of H₂O₂ adsorption (step 1 in Scheme 1), potential H₂O₂ decomposition, and metal leaching. The computational model suggested that Brønsted acidity can induce H₂O₂ decomposition and metal leaching. According to the model, when H₂O₂ is adsorbed on a Lewis acidic site (Nb=O, niobyl silicate model, compound 1 in Scheme 1) in the perpendicular orientation, the process is less exothermic with ΔH = −9.1 kcal/mol (−12.4 kcal/mol for the parallel orientation). However, the model could not predict a pathway for H₂O₂ decomposition when it is bound to niobyl silicate indicating that Lewis acidic sites show no H₂O₂ decomposition.

In contrast, when H₂O₂ is adsorbed on a Brønsted acidic site (Nb−OH, niobium hydroxide model, compound 1a in Scheme 1), it readily undergoes decomposition in a highly exothermic process (ΔH = −52.0 kcal/mol), breaking the O₁−O² bond and forming water through extraction of the hydroxyl proton to O²⁻ (compound 2a, Scheme 1). This process transfers H¹ proton from the O²⁻ of H₂O₂ to the bridging oxygen (O₆). Dissociation of the O₆−Nb bond (via bond elongation) leads to Nb leaching. Clearly, the ideal catalyst should display predominant Lewis acidity to favor epoxidation and minimal Brønsted acidity to reduce H₂O₂ decomposition and metal leaching. In order to reduce the Brønsted acidity, we hypothesized that catalysts with relatively low Nb content should have more isolated Nb sites (Lewis acid sites) with reduced Brønsted acid sites. A catalyst synthetic technique such as the Evaporation Induced Self-Assembly (EISA) method has been reported to provide improved metal dispersion with relatively low Brønsted acidity. The fact that the Nb-EISA catalysts with enhanced Lewis acidity and reduced Brønsted acidity clearly improves epoxidation yield with reduced leaching lends credence to this proposed mechanism.

4. CONCLUSIONS

Nb-EISA catalysts with low Nb loadings (<2 wt %) exhibit excellent activity for propylene epoxidation displaying virtually total PO selectivity and H₂O₂ utilization toward PO formation with much reduced Nb leaching compared to Nb silicates prepared by impregnation and/or hydrothermal synthesis techniques. This excellent performance is attributed to the
presence of predominantly Lewis acid sites with significantly lower Brønsted acid sites. However, on Nb-EISA catalysts with higher Nb loadings (>3.7 wt %), the PO selectivity and H₂O₂ utilization decreased with increased Nb leaching. This deterioration in performance is attributed to increases, albeit low, in Brønsted acidity at reaction conditions. Carbonized versions of the Nb-EISA improve the performance of such catalysts by increasing pore hydrophobicity that enhances propylene concentration in the pores while inhibiting polar molecules, especially water and the resultant formation of Brønsted acid sites. The Nb-EISA and its carbonized version are both stable and recyclable catalysts. These insights pave the way for rational design of improved propylene epoxidation catalysts.

**REFERENCES**


