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## Selective oxidation of ethylbenzene to acetophenone over Cr(III) Schiff base complex intercalated into layered double hydroxide

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University Grant Commission New Delhi, India, Grant/Award Number: F1-17.1/ 2016-17/RGNF-2015-17-SC-MAD-19994/ SAIII/WeUGC-SAP: No. F.540/13/DRS-I/ 2016 (SAP-I) A new heterogeneous catalyst, Cr(III) Schiff base-containing layered double hydroxide, was synthesized using the intercalation method. The Cr(III) Schiff base complex derived from 2-hydroxy-1-naphthaldehyde and 4-aminobenzoic acid was intercalated into the layered double hydroxide. The synthesized materials were characterized using inductively coupled plasma atomic emission spectrometry, energy-dispersive X-ray analysis, scanning electron microscopy, X-ray diffraction, Brunauer-Emmett-Teller surface area measurement, Fourier transform infrared spectroscopy, thermogravimetric analysis, diffuse reflectance UV-visible spectroscopy and electron paramagnetic resonance spectroscopy. The catalytic activity was investigated for the oxidation of ethylbenzene with tert-butylhydroperoxide as an oxidant under solvent-free conditions as well as with lower chromium concentrations. In the oxidation reaction, ethylbenzene was oxidized to acetophenone and benzaldehyde. The catalyst was recycled ten times without significant loss of catalytic activity. Leaching studies performed with hot filtration experiments showed that the chromium catalyst was heterogeneous in nature and stable under the reaction conditions.

### KEYWORDS

chromium(III) Schiff base complex, ethylbenzene, heterogeneous catalyst, layered double hydroxide, *tert*-butylhydroperoxide

## **1** | **INTRODUCTION**

Side-chain oxidation of saturated hydrocarbons to the corresponding oxygenates is among the most important and challenging reactions in the chemical industry.<sup>[1]</sup> Recently, the selective oxidation of ethylbenzene to acetophenone has drawn immense attention, because acetophenone serves as a crucial platform as an intermediate for the manufacturing of some perfumes, pharmaceuticals, resins, alcohols, aldehydes, etc.<sup>[2]</sup> Conventionally, acetophenone is synthesized by oxidation of ethylbenzene with stoichiometric inorganic oxidants such as permanganate or dichromate.<sup>[3,4]</sup> However, these

reagents also produce huge amounts of corrosive and hazardous wastes.<sup>[5]</sup> In general, chromium-containing catalysts are used in the oxidation of most organic compounds in homogeneous media.<sup>[6,7]</sup> Current industrial processes for the production of acetophenone are based on the liquid-phase oxidation of ethylbenzene by oxygen using homogeneous cobalt-based compounds as catalysts in acetic acid media. This method suffers from its corrosive and environmentally unfriendly nature.<sup>[8]</sup> Hence, there has been an interest in the development of ecofriendly heterogeneous catalysts for the oxidation of ethylbenzene. Heterogeneous catalysts have become very important for ecofriendly industrial processes because

these materials are developed with the objective of performing reactions under milder conditions and without hazardous wastes. Many researchers have used Cr(III)based heterogeneous catalysts for the oxidation of ethylbenzene using various oxidants.<sup>[9-13]</sup> Dapurkar et al.<sup>[9]</sup> have reported catalytic activity of (Cr)MCM-48 for oxidation of ethylbenzene with tert-butylhydroperoxide (TBHP) and achieved 76.3% conversion of ethylbenzene after 12 h. Miao et al.<sup>[10]</sup> have prepared mesoporous transition metal-zirconium oxophosphate composites (M-Cr-ZrPO) for the oxidation of ethylbenzene with TBHP which gave 90% conversion of ethylbenzene with 90% selectivity to acetophenone after 24 h. Selvaraj et al.<sup>[11]</sup> have synthesized a recyclable hexagonally ordered mesoporous CrSBA-15 catalyst for the oxidation of ethylbenzene to acetophenone using TBHP which gave 95.6% conversion of ethylbenzene with selectivity of 98.2% to acetophenone after 10 h of reaction.

Layered double hydroxides (LDHs) are some of the most important inorganic materials with a layered structure, which are anionic clays or hydrotalcite-like compounds.<sup>[14-16]</sup> The structures of LDHs consist of brucitelike (M<sup>II</sup>(OH)<sub>2</sub>) layers with some of the divalent cations (M<sup>II</sup>) substituted by trivalent ions (M<sup>III</sup>). Both divalent and trivalent ions are located at the centre of octahedral (OH<sup>-</sup>) units of the brucite layers. The resulting layers are in an excess of positive charge acquired to balance the intercalated anions. The general formula of LDHs is  $[M_{1}^{II} - M_{x}^{III}(OH)_{2}]^{x+} \cdot (A_{x/n}^{n-}) \cdot mH_{2}O$ , where  $A^{n-}$  is the interlayer anion.<sup>[17,18]</sup> The coefficient x is equal to the molar ratio  $M^{III}/(M^{II} + M^{III})$ , and *m* is the number of water molecules located in the interlayer region together with the anions.<sup>[19]</sup> LDHs have large surface area, good anion-exchange capacity and expansion properties which make them promising materials for the intercalation of anionic metallic complexes.<sup>[20,21]</sup> They have been extensively studied for their intercalation chemistry,<sup>[22-24]</sup> as heterogeneous catalyst precursors and for their ion exchange properties.<sup>[25-28]</sup> LDH-based catalysis is of high interest for green and sustainable chemistry.<sup>[29]</sup> In most cases, LDHs have been prepared using co-precipitation methods.<sup>[25,26]</sup>

Because of our interest in the oxidation of hydrocarbons, in previous studies we have reported layered material-supported recyclable heterogeneous catalysts for the oxidation of hydrocarbons.<sup>[30–35]</sup> In continuation of our work, herein we report the synthesis of a Cr(III) Schiff base complex derived from 2-hydroxy-1-naphthaldehyde and 4-aminobenzoic acid (NAPABA-Cr(III)), which was intercalated into a LDH to afford LDH-[NAPABA-Cr(III)]. Its catalytic behaviour was investigated for the oxidation of ethylbenzene using TBHP as an oxidant. The conditions for maximum conversion of ethylbenzene as well as selectivity for desired product were optimized by varying different parameters such as oxidizing agent, molar ratio of ethylbenzene to TBHP, amount of catalyst and temperature.

## 2 | EXPERIMENTAL

## 2.1 | Materials and Methods

Zinc(II) nitrate hexahydrate  $(Zn(NO_3)_3 \cdot 6H_2O)$ , aluminium(III) nitrate nonahydrate  $(Al(NO_3)_3 \cdot 9H_2O)$ , chromic chloride  $(CrCl_3 \cdot 6H_2O)$ , 4-aminobenzoic acid, 2hydroxy-1-naphthaldehyde and sodium hydroxide were all of analytical grade and purchased from E. Merck. A 70% commercial aqueous solution of TBHP was also purchased from E. Merck. HPLC-grade ethylbenzene was purchased from SDFCL and its purity was checked using GC to ensure that no oxidation products were present.

A stock solution of TBHP (72% TBHP in ethylbenzene) was prepared by extraction of 55 ml of commercial TBHP (70% in water) into 15 ml of ethylbenzene. Phase separation was promoted by saturation of the aqueous layer with NaCl. The organic layer was dried over MgSO<sub>4</sub>, filtered and stored at 5 °C. The molar ratio of ethylbenzene to TBHP in this solution was 1:3.

Powder X-ray diffraction (XRD) patterns of samples were recorded with a Rigaku diffractometer in the  $2\theta$  range 2–70° using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at a scanning speed of 2° per minute with step size 0.02°. Scanning electron microscopy (SEM) measurements were performed using a JEOL JSM 6100 electron microscope, operating at 20 kV. Fourier transform infrared (FT-IR) spectra were recorded with a PerkinElmer model 1750 in KBr. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer USAA Diamond system in the range 298-973 K, at a heating rate of 10 °C min<sup>-1</sup>. Inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo Electron Iris Intrepid II XSP DUO) was used for estimation of chromium. The electronic spectrum of the solid was recorded with a Varian Cary 5000 spectrophotometer. The electron paramagnetic resonance (EPR) spectrum was recorded with a JES-FA200 ESR X-band spectrometer operated at a microwave frequency of 9.65 GHz at room temperature. The g value is reported relative to a 2,2diphenyl-1-picrylhydrazyl standard with g = 2.0036. N<sub>2</sub> adsorption data, measured at 77 K with a volumetric adsorption set-up (Micromeritics ASAP-2010, USA), were used to determine Brunauer-Emmett-Teller (BET) surface area. Analytical gas chromatography was carried out using a Shimadzu GC-14B with dual flame ionization detector and attached Shimadzu printer having XE-60 ss column. The products were identified by GC-MS (PerkinElmer Clasus 500 column;  $30 \text{ m} \times 60 \text{ mm}$ ).

## 2.2 | Preparation of Catalyst

The Cr(III) complex was synthesized by dissolving 4aminobenzoic acid (10 mmol) into a 50 ml methanolic solution of NaOH (20 mmol) followed by a methanolic solution of 2-hydroxy-1-naphthaldehyde (10 mmol), then immediately CrCl<sub>3</sub>·6H<sub>2</sub>O (5 mmol) was added and the mixture was kept under continuous stirring for 4 h at room temperature. After 4 h, a greenish brown precipitate of NAPABA-Cr(III) complex was formed which was filtered, washed with petroleum ether and dried in air. The obtained complex was characterized using elemental analysis and FT-IR and diffuse reflectance UV (DRUV) spectroscopies. Anal. Found for C<sub>36</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>Cr (%): C, 68.46; H, 3.31; N, 4.38. Calcd (%): C, 68.57; H, 3.52; N, 4.44. FT-IR (KBr pellet, cm<sup>-1</sup>): 3373(br), 1608(m), 1581(m), 1476(w), 1409(m), 657(w), 523(w).

LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] was prepared by a co-precipitation method according to a previously reported procedure with certain modifications.<sup>[36]</sup> Solutions of zinc(II) nitrate hexahydrate (14.82 g) and aluminium(III) nitrate nonahydrate (6.25 g) in decarbonized water were mixed having a Zn/Al molar ratio of 3. To that was added a solution of 4-aminobenzoic acid (10.86 g) and NaOH (7.8 g) in decarbonized water with continuous stirring. Immediately a gel-like mixture was obtained which was digested at 348 K for 48 h. Upon cooling, the product was isolated by filtration, washed with water followed by methanol, and the solid was dried at 333 K overnight.

The ligand was synthesized by mixing LDH-[NH<sub>2</sub>- $C_6H_4COO$ ] (1.0 g) into a methanolic solution of 2-hydroxy-1-naphthaldehyde (0.48 g, 2.77 mmol), the solution instantly becoming yellow due to imine formation. The resulting mixture was refluxed for 3 h with continuous stirring under nitrogen atmosphere. The yellow product was filtered off, washed with methanol followed by acetonitrile and then dried at 333 K overnight.

The LDH-[NAPABA-Cr(III)] catalyst was prepared by incorporation of Cr(III) into the LDH-[NAPABA] ligand. LDH-[NAPABA] (1 g) was suspended in 50 ml of methanol and then a solution of CrCl<sub>3</sub>·6H<sub>2</sub>O (0.26 g) in 50 ml of methanol was added to it with continuous stirring. The WILEY Organometallic 3 of 12

mixture was refluxed for 4 h under nitrogen atmosphere. After cooling, the solid was filtered and wash with methanol. The resulting solid was extracted with methanol followed by acetone and acetonitrile using a Soxhlet extractor to remove excess ligand and metal salt remaining uncomplexed in the host layer as well as on the surface, if any, and dried at 333 K overnight. Scheme 1 illustrates the preparation of the heterogeneous LDH-[NAPABA-Cr(III)] catalyst.

## 2.3 | Oxidation of Ethylbenzene

Oxidation of ethylbenzene over the LDH-[NAPABA-Cr(III)] catalyst using TBHP as oxidant was carried out under solvent-free conditions in a three-necked roundbottom flask. In a typical run, the flask was loaded with 13 mmol of ethylbenzene, 39 mmol of TBHP (72% in ethylbenzene) and catalyst at the required temperature in an oil bath for 7 h with continuous stirring using a Teflon needle on a magnetic hot plate. After completion of the reaction, the catalyst was filtered off. The catalyst was dried at 333 K for further use. The oxidation products were qualitatively as well as quantitatively analysed using GC-MS and GC, respectively. The GC-MS analysis revealed that the main products were acetophenone and benzaldehyde. Selectivity of products was calculated with respect to the converted ethylbenzene using the internal standard method. The internal standard was dodecane.

## 2.4 | Separation of Acetophenone

Separation of acetophenone was done on the basis of a previously reported method<sup>[37]</sup> after slight modification. The reaction mixture of ethylbenzene oxidation was collected and concentrated under reduced pressure. The concentrated mixture was dissolved in 15 ml of ethanol. Then 1 mmol of Zn granules was added, and the mixture was stirred for 30 min at room temperature. The mixture was filtered and the solvent removed under reduced pressure. This reduced mixture was extracted with saturated NaHCO<sub>3</sub> solution to remove benzoic acid, if any. Then the mixture was washed with water, followed by



SCHEME 1 Synthesis of heterogeneous LDH-[NAPABA-Cr(III)] catalyst

extraction with ether. After removing the aqueous layer, the ethereal layer was dried over anhydrous MgSO<sub>4</sub>. Yellowish oil was obtained which was 90.67% acetophenone with 92% purity. It was characterized using LC–MS and FT-IR analyses. LC–MS: m/z = 21, 57, 77, 105, 121. FT-IR (KBr pellet, cm<sup>-1</sup>): 2978(w), 1690(m), 1263(w).

## 3 | RESULTS AND DISCUSSION

## 3.1 | Characterization of Catalyst

The analytical and physical data including chemical composition of compounds at various stages of the synthesis of the catalyst, namely LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], LDH-[NAPABA-Cr(III)]<sup>b</sup> and LDH-[NAPABA-Cr(III)]<sup>a</sup> (b = before catalytic reaction; a = after catalytic reaction), are given in Table 1. The fresh catalyst, LDH-[NAPABA-Cr(III)]<sup>b</sup>, contains 4.43% chromium, whereas LDH-[NAPABA-Cr(III)]<sup>a</sup> contains 4.38% chromium after ten catalytic cycles, which was determined using ICP-AES. The reduction in the chromium contents may be due to the washing of the catalyst after each cycle.

Figure 1 shows the elemental composition of the catalyst, determined using energy-dispersive X-ray (EDX) analysis. The EDX measurement results for LDH- $[NH_2-C_6H_4COO]$ , LDH- $[NAPABA-Cr(III)]^b$  and LDH- $[NAPABA-Cr(III)]^a$  are presented in Table 1. The presence of carbon, nitrogen, oxygen, zinc, aluminium along with chromium metal in LDH-[NAPABA-Cr(III)] confirms the formation of the heterogeneous catalyst. The ideal formula for LDH-[NAPABA-Cr(III)], based on the elemental content and Zn/Al ratio, is  $[Zn_{0.76}Al_{0.24}(OH)_2]$  [NAPABA-Cr(III)(H<sub>2</sub>O)<sub>2</sub>]<sub>0.12</sub>[NH<sub>2</sub>-

 $C_6H_4COO]_{0.07}$ ·0.47H<sub>2</sub>O. The SEM images in Figure 1 of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] and LDH-[NAPABA-Cr(III)] clearly show that both have similar structures, having flake-like aggregates,<sup>[38]</sup> but with different sizes of the flakes. This clearly indicates the successful intercalation of the chromium Schiff base complex into the LDH host.

Figure 2 shows the XRD patterns of LDH- $[NH_2-C_6H_4COO]$ , LDH- $[NAPABA-Cr(III)]^b$  and LDH- $[NAPABA-Cr(III)]^a$  with the *d*-spacing corresponding to the plane (003). The XRD pattern of LDH- $[NH_2-$ 

 $C_6H_4COO]$  shows the most intense basal reflection at 15.71 Å (003). The characteristic reflections corresponding to (110) plane show atomic distribution density depending on Zn/Al molar ratio. The results are incorporated in Table 2. The basal spacing of (003) plane increases from 15.71 to 22.21 Å in LDH-[NAPABA-Cr(III)]<sup>b</sup>. The gallery height of the catalyst is 17.51 Å when the thickness of the brucite layers (4.7 Å) is subtracted. There was no change in characteristic reflections corresponding to (110) plane after intercalation of the Cr(III) Schiff base complex, which indicates that there was no change in the basic structure of LDH.<sup>[39]</sup> The increase in gallery height clearly indicates successful intercalation of the NAPABA-Cr(III) Schiff base complex in the LDH layers.

Furthermore, particle size of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] support and heterogeneous LDH-[NAPABA-Cr(III)] catalyst was calculated using the Debye–Scherrer equation. The average particle size was calculated for the most intense peak corresponding to the (003) plane of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] and LDH-[NAPABA-Cr(III)] and it was found to be 2.4 and 2.6 nm, respectively. The results are incorporated in Table 2. The increase in gallery height and average particle size of the LDH-[NAPABA-Cr(III)] catalyst clearly indicate the successful intercalation of NAPABA-Cr(III) Schiff base complex into the LDH layers.

The results of BET surface area, pore volume and pore size of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] support and heterogeneous LDH-[NAPABA-Cr(III)] catalyst are incorporated in Table 2. The surface area of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] support is 6.915 m<sup>2</sup> g<sup>-1</sup> whereas surface area of heterogeneous LDH-[NAPABA-Cr(III)] catalyst is 29.93 m<sup>2</sup> g<sup>-1</sup>. The reason for the increase in surface area of the catalyst in comparison to LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] was due to the intercalation of larger complex molecules into the LDH layers which led to an expansion of the layers. This is further supported by the XRD data (the basal spacing increases from 15.71 to 22.21 Å).<sup>[26]</sup> The pore volume of LDH is 0.017 cm<sup>3</sup> g<sup>-1</sup> which increases to 0.121 cm<sup>3</sup> g<sup>-1</sup> in the catalyst while pore size decreases from 100.90 to 36.51 Å in the catalyst. The increase in surface area and pore volume indicates successful intercalation of the Cr(III) Schiff base complex into the LDH layers.

**TABLE 1** Chemical composition and physical data of various compounds

		Metal	EDX data (wt%)					
Catalyst	Colour	content (%)*	Zn	Al	С	0	Ν	Cr
LDH-[NH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> COO]	White	_	26.39	7.73	32.49	29.12	4.27	_
LDH-[NAPABA-Cr(III)] <sup>b</sup>	Brown	4.43	16.41	6.24	45.05	23.17	3.67	5.46
LDH-[NAPABA-Cr(III)] <sup>a</sup>	Brown	4.38	16.30	6.12	44.95	23.14	4.05	5.44

\*From ICP-AES analysis.



 $\label{eq:FIGURE 1} \begin{array}{l} EDX \mbox{ spectra of (a) LDH-[NAPABA-Cr(III)] and (b)} \\ LDH-[NH_2-C_6H_4COO]. \mbox{ SEM images of (c) LDH-[NAPABA-Cr(III)]} \\ and (d) \mbox{ LDH-[NH_2-C_6H_4COO]} \end{array}$ 



**FIGURE 2** XRD patterns of (a) LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], (b) LDH-[NAPABA-Cr(III]<sup>b</sup> and (c) LDH-[NAPABA-Cr(III]<sup>a</sup>

FT-IR spectra of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], The NAPABA-Cr(III) and LDH-[NAPABA-Cr(III)] are shown in Figure 3. In the spectrum of  $LDH-[NH_2-C_6H_4COO]$ (Figure 3a), the broad absorption bands at 3399 and  $3255 \text{ cm}^{-1}$  are attributed to stretching modes of NH<sub>2</sub> and OH groups, respectively. The strong band at 1584 cm<sup>-1</sup> is attributed to C=O stretching vibration. A band at 1445 cm<sup>-1</sup> is due to C=C stretching of aromatic ring.<sup>[40,41]</sup> The bands in the range 428–784  $\text{cm}^{-1}$  are due to stretching vibrations of M–O and O–M–O (M = Zn, Al).<sup>[40,41]</sup> which include translation vibrations of Zn–OH at 637  $\text{cm}^{-1}$  and Al–OH at around 517  $\text{cm}^{-1}$  and deformation vibration of HO-Zn-Al-OH at 428 cm<sup>-1,[42]</sup> which are typical of this class of materials.<sup>[43]</sup> In the spectrum of homogeneous catalyst, NAPABA-Cr(III) (Figure 3b), the broad absorption band at 3373  $\text{cm}^{-1}$  is attributed to stretching modes of  $-NH_2$  group. The band at 1608 cm<sup>-1</sup> is due to C=N stretching of imines while bands at 663 and 499 cm<sup>-1</sup> are due to Cr–N and Cr–O, respectively.

The spectrum of the heterogeneous catalyst, LDH-[NAPABA-Cr(III)] (Figure 3c), shows all the absorption bands corresponding to LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO] along with a band at 1606 cm<sup>-1</sup> due to C=N stretching of imines which was shifted to lower frequency while the bands arising due to Cr–N and Cr–O stretching were shifted to 640 and 426 cm<sup>-1</sup>.<sup>[39]</sup> The presence of these bands clearly indicates the intercalation of NAPABA-Cr(III) into LDH.

The thermal decomposition behaviour of LDH-[NH<sub>2</sub>- $C_6H_4COO$ ] and LDH-[NAPABA-Cr(III)] was evaluated using TGA and the results are shown in Figure 4. The TGA curve of LDH-[NH<sub>2</sub>- $C_6H_4COO$ ] shows a first weight loss from 50 to 170 °C due to the removal of adsorbed water. The second stage corresponds to the degradation of the brucite-like layer and removal of interlayer benzoate anions in the range 200–500 °C. The TGA curve of

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TABLE 2   Texture	al properties o	of support and	heterogeneous	catalyst
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Catalyst	BET surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore size (Å)	d-spacing (Å)	Particle size (nm)
LDH-[NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> COO]	6.915	0.017	100.90	15.71	2.35
LDH-[NAPABA-Cr(III)] <sup>b</sup>	29.93	0.121	36.51	22.21	2.59
LDH-[NAPABA-Cr(III)] <sup>a</sup>	23.73	0.097	29.09	22.20	2.58



**FIGURE 3** FT-IR spectra of (a) LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], (b) NAPABA-Cr(III) and (c) LDH-[LDH-NAPABA-Cr(III)]



FIGURE 4 TGA curves of (a) LDH-[NH $_2\text{-}C_6\text{H}_4\text{COO}]$  and (b) LDH-[NAPABA-Cr(III)]

LDH-[NAPABA-Cr(III)] shows a first weight loss from 50 to 174 °C. A second step in the range 179–340 °C is assigned to partial dehydroxylation of the double hydroxide layers.<sup>[38]</sup> The decomposition of the organic part occurs in the range 343–525 °C.

The DRUV-visible spectra of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], NAPABA-Cr(III) and LDH-[NAPABA-Cr(III)] are shown

in Figure 5. The spectrum of homogeneous complex, NAPABA-Cr(III), shows three bands at 255, 321 and 463 nm. The first band at 255 nm may be assigned to  $\pi \rightarrow \pi^*$  of aromatic rings. The second band at 321 nm is due to  $n \rightarrow \pi^*$  transitions of imine group (C=N). The third band in the range 395–548 nm is assigned to ligand-to-metal charge transfer transition in the metal complex. The absorption above 300 nm also indicates a large conjugated system of the complex. An additional weak and broad band in the range 548–730 nm is due to the d–d transition as reported in the literature.<sup>[39]</sup> All these bands appear in the spectrum of the heterogeneous LDH-[NAPABA-Cr(III)] catalyst with lower intensity due to smaller amount of the homogeneous complex in the layers of LDH.

The EPR spectrum of the heterogeneous LDH-[NAPABA-Cr(III)] catalyst was recorded at room temperature (Figure 6). The EPR spectrum shows a single peak at 320 mT. Also the spectrum gives a g value of 1.947 with  $g_{iso}$  of 2.07. This clearly indicates the presence of chromium metal ion in +3 oxidation state and three unpaired electrons in the d-orbital. The EPR parameters suggest an octahedral geometry for the Cr(III) complex.<sup>[44]</sup> On the basis of EPR analysis an imaginary structure of the catalyst is proposed (Scheme 2).



**FIGURE 5** DRUV-visible spectra of (a) LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], (b) NAPABA-Cr(III) and (c) LDH-[NAPABA-Cr(III)]



**FIGURE 6** EPR spectrum of LDH-[NAPABA-Cr(III)]



**SCHEME 2** Imaginary structure of LDH-[NAPABA-Cr(III)] catalyst

### 3.2 | Catalytic Activity

The oxidation of ethylbenzene was investigated using LDH-[NAPABA-Cr(III)] under solvent-free conditions with TBHP as an oxidant. The products are mainly acetophenone and benzaldehyde and no oxidation products of the aromatic ring are found. Scheme 3 presents the catalytic oxidation of ethylbenzene.

The catalytic activities of LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], LDH-[NAPABA-Cr(III)] and NAPABA-Cr(III) for the oxidation of ethylbenzene were investigated under similar reaction conditions along with blank reactions. The results are presented in Table 3. It was observed that the support, LDH-[NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>COO], was inactive for the



**SCHEME 3** Oxidation of ethylbenzene (EB, ethylbenzene; BZ, benzaldehyde; AP, acetophenone; BA, benzoic acid)

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oxidation of ethylbenzene. It was also observed that no products were formed in blank reactions, when the reaction was carried out in the absence of either catalyst or oxidant. Hence auto-oxidation was ruled out. The heterogeneous LDH-[NAPABA-Cr(III)] catalyst and homogeneous NAPABA-Cr(III) catalyst were found to be active for the oxidation of ethylbenzene and gave acetophenone and benzaldehyde as oxidation products. The catalytic activity of catalyst was assessed on the basis of conversion of substrate and selectivity of products. The percentage conversion of substrate, percentage selectivity of products and turnover number (TON) of the catalysts in the oxidation reaction are calculated as<sup>[34,45]</sup>

Substrate conversion (%) = Substrate converted (mol)/ substrate used (mol)×100

Product selectivity (%) = Product formed (mol)/ substrate used (mol)×100

Turnover number = mmol of products/mmol of catalyst

In order to optimize ethylbenzene oxidation, various parameters, namely effects of oxidant, solvent, concentration of TBHP, concentration of catalyst and reaction temperature, have been studied in detail.

The effect of various oxidants, namely  $H_2O_2$ ,  $O_2$ , 70% TBHP and 72% TBHP in ethylbenzene, was investigated for the oxidation of ethylbenzene. The reaction with  $H_2O_2$  leads to no conversion. The other oxidants effectively oxidize ethylbenzene to acetophenone, benzaldehyde and benzoic acid. The results are presented in Table 3. The conversions of ethylbenzene with  $O_2$ , 70% TBHP and 72% TBHP in ethylbenzene were 23.1, 34.1 and 90.7%, respectively. The oxidant 72% TBHP in ethylbenzene. Hence, it was considered as the best oxidant for our catalytic system.

The effect of various solvents (acetonitrile, acetone, methanol and benzene) on the oxidation of ethylbenzene catalysed by LDH-[NAPABA-Cr(III)] was studied to develop an efficient solvent system. It was observed that the conversion of ethylbenzene decreased in the following order: 52.9% with acetonitrile > 45.2% with benzene > 20.7% with methanol > 16.3% with acetone. The results are given in Table 3. The results indicated that the aprotic solvents favoured the conversion of ethylbenzene in all solvents except methanol was acetophenone. The acetophenone selectivity for the various solvents decreased in the following order: benzene (99.70\%) > acetonitrile (74.55\%) > acetone (52.40\%) > methanol

		Ethylbenzene		Product selectivity (%) <sup>b</sup>		
Catalyst	Oxidant/solvent	conversion (%)	BZ	AP	BA	TON
No catalyst	TBHP <sup>c</sup> /Solvent-free	_	_	_	_	_
LDH-[NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> COO]	TBHP <sup>c</sup> /Solvent-free	_	_	_	_	_
LDH-[NAPABA-Cr(III)]	Ethylbenzene	_	_	_	_	—
NAPABA-Cr(III)	TBHP <sup>c</sup> /Solvent-free	62.0	0.23	99.77	_	563
LDH-[NAPABA-Cr(III)]	H <sub>2</sub> O <sub>2</sub> /Solvent-free	_	_	_	_	_
LDH-[NAPABA-Cr(III)]	70% TBHP/Solvent-free	34.1	0.14	99.75	0.11	310
LDH-[NAPABA-Cr(III)]	O <sub>2</sub> /Solvent-free	23.1	0.63	95.60	3.77	209
LDH-[NAPABA-Cr(III)]	TBHP <sup>c</sup> /Solvent- free	90.7	0.07	99.93	_	825
LDH-[NAPABA-Cr(III)]	TBHP <sup>c</sup> /Acetonitrile	52.9	0.26	74.55	25.19	480
LDH-[NAPABA-Cr(III)]	TBHP <sup>c</sup> /Acetone	16.3	0.68	52.40	46.92	148
LDH-[NAPABA-Cr(III)]	TBHP <sup>c</sup> /Benzene	45.2	0.30	99.70	_	410
LDH-[NAPABA-Cr(III)]	TBHP <sup>c</sup> /Methanol	20.7	0.34	47.78	51.88	188

TABLE 3 Oxidation of ethylbenzene: effect of oxidant, solvent, support, homogeneous and heterogeneous catalyst<sup>a</sup>

<sup>a</sup>Reaction conditions: ethylbenzene (13 mmol); TBHP (39 mmol); catalyst (100 mg); 393 K; 7 h.

<sup>b</sup>AP, acetophenone; BZ, benzaldehyde; BA, benzoic acid.

<sup>c</sup>72% TBHP in ethylbenzene.

(47.78%). The selectivities of benzaldehyde and benzoic acid were favoured in protic solvents while the selectivity of acetophenone was favoured in aprotic solvents.<sup>[46]</sup> These results indicate that dipole moments of the solvent may play an essential role in the oxidation of ethylbenzene. However, the reaction under solvent-free conditions gave higher selectivity and more catalytic activity than in the presence of a solvent (protic and aprotic). This was probably due to competition for the active sites of the metal centre of the catalyst between substrate and solvent molecules, resulting in reduction of effective collision between two substrate molecules.

The effect of concentration of TBHP was studied by considering three different molar ratios (1:1, 1:2 and 1:3) of ethylbenzene to TBHP in the oxidation of ethylbenzene under solvent-free condition at 393 K for 7 h.

The results are presented in Table 4. It was observed that the conversion of ethylbenzene gradually increases with increasing ethylbenzene-to-TBHP molar ratio from 1:1 to 1:2, i.e. from 48.3 to 78.5%. On further increasing the molar ratio to 1:3, the conversion increases to 90.7%. The conversion of ethylbenzene was increased by 12.3% when ethylbenzene-to-TBHP molar ratio changed from 1:2 to 1:3. The selectivity of benzaldehyde decreased from 4.34 to 0.07% with increasing molar ratio of ethylbenzene to TBHP from 1:1 to 1:3 while the selectivity of acetophenone increased from 95.67 to 99.93% with increasing molar ratio of ethylbenzene to TBHP from 1:1 to 1:3. At all molar ratios, acetophenone was the major product. The TON of the catalyst also increased from 438 to 825 with increasing molar ratio of ethylbenzene to TBHP from 1:1 to 1:3 because at high TBHP

TABLE 4 Ethylbenzene oxidation of over LDH-[NAPABA-Cr(III)] under various conditions

	Substrate:	Catalyst	Temperature	Conversion		Selectivity of p		
Entry	oxidant ratio	amount (mg)	(K)	Time (h)	(%)	BZ	AP	TON
1	1:1	100	393	7	48.3	4.34	95.7	438
2	1:2	100	393	7	78.5	0.22	99.8	713
3	1:3	100	393	7	90.7	0.07	99.3	825
4	1:3	75	393	7	76.7	0.14	99.9	924
5	1:3	50	393	7	69.1	0.17	99.8	1256
6	1:3	100	373	7	77.9	0.12	99.9	708
7	1:3	100	353	7	66.6	0.14	99.9	605

<sup>a</sup>BZ, benzaldehyde; AP, acetophenone.

concentration a greater amount of nascent oxygen is provided by the oxidant. Thus, a molar ratio of ethylbenzene to TBHP of 1:3 was considered as optimum.

The effect of catalyst concentration on the oxidation of ethylbenzene was studied by considering three different concentration of catalyst (50, 75 and 100 mg) at 393 K for 7 h. The results are presented in Table 4. It was observed that when the concentration of catalyst increases from 50 to 100 mg, the conversion of ethylbenzene increases from 69.1 to 90.7%. The selectivity of benzaldehyde decreases from 0.17 to 0.07%, while the selectivity of acetophenone increases from 99.83 to 99.93% with increasing catalyst concentration from 50 to 100 mg. The conversion and selectivity were low at lower catalyst concentration due to the insufficient active sites of the catalyst,<sup>[47]</sup> while the conversion and selectivity increased when the catalyst concentration reached to 100 mg. This was probably due to the active sites releasing a greater amount of nascent oxygen, which ultimately led to a vigorous oxidation reaction. Acetophenone was the major product at all catalyst concentrations. However, the TON of the catalyst decreased from 1256 to 825 with increasing catalyst concentration from 50 to 100 mg. Similar observations have been reported by various researchers.<sup>[4,48]</sup> Thus, 100 mg of catalyst is considered as optimum.

The temperature plays an important role in catalytic reactions; hence we studied the oxidation of ethylbenzene at three different temperatures (353, 373 and 393 K). The results are presented in Table 4. It was observed that when temperature increases from 353 to 393 K conversion of ethylbenzene increases from 66.5 to 90.7%. The selectivity of benzaldehyde decreases from 0.14 to 0.07%, while the selectivity of acetophenone increases from 99.86 to 99.93% with increasing temperature from 353 to 393 K. Acetophenone was the major product at all reaction temperatures. The TON of the catalyst also increases from 605 to 825 with increasing temperature from 353 to 393 K. Thus 393 K is considered optimum. Clearly, the [LDH-NAPABA-Cr(III)] catalyst was a highly active

catalyst and selective for oxidation of ethylbenzene to acetophenone; therefore the subsequent research was devoted to this catalyst. Thus the optimum conditions for obtaining maximum conversion of ethylbenzene are a molar ratio of ethylbenzene to TBHP of 1:3, 100 mg of catalyst and temperature of 393 K.

Table 5 compares the results of the present work with those for previously reported catalysts.<sup>[9–13]</sup> The catalyst and method applied in the present case have advantages in terms of heterogeneous nature and better conversions, selectivity and reusability of the catalyst and separation of acetophenone.

## 3.3 | Recycling of Catalyst

The reusability of a heterogeneous catalyst is an important factor from commercial and economic points of view. In order to check the reusability of the catalyst, a recycling experiment was performed under the optimized reaction conditions. After completion of the reaction, the catalyst was separated from the reaction mixture by filtration and



FIGURE 7 Recycling of catalyst

<b>TABLE 5</b> Comparisons of present work with previous studies for oxidation of ethyl	benzene
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Catalytic system	T (°C)/solvent	Oxidant	Time (h)	Conversion (%)	Product <sup>a</sup>	Selectivity (%)	Ref.
(Cr)MCM-48	120/chlorobenzene	TBHP	12	76.30	AP	82.90	[9]
M-Cr-ZrPO	80/acetonitrile	TBHP	24	91.60	AP	87.0	[10]
CrSBA-15	120/chlorobenzene	TBHP	10	95.6	AP	98.20	[11]
Cr-MPO1	100/acetonitrile	O <sub>2</sub>	6	8.5	AP	69.40	[12]
CuCr <sub>2</sub> O <sub>4</sub>	70/acetonitrile	$H_2O_2$	6	68.5	AP	78.0	[13]
Present work	120/solvent-free	TBHP	7	90.74	AP	99.93	

<sup>a</sup>AP, acetophenone.

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washed several times with methanol, acetonitrile and acetone. The washed catalyst was dried at 333 K overnight to remove the adsorbed solvent molecules from the catalyst surface and then it was further subjected to consecutive catalytic runs. The LDH-[NAPABA-Cr(III)] catalyst was recycled ten times for the oxidation of ethylbenzene. The conversion of ethylbenzene decreased from 90.7 to 87.1% after the tenth cycle (Figure 7).

The conversion of ethylbenzene was reduced by 3.6% from first to tenth cycle. The recycling results indicate that the catalyst was stable during the catalytic reaction. There was no significant loss of catalytic activity, showing



FIGURE 8 Results of quenching experiment

that the LDH-[NAPABA-Cr(III)] catalyst could be recycled ten times in the liquid-phase oxidation of ethylbenzene. The recycled catalyst was further characterized using ICP-AES, BET surface area, XRD and EDX. It was observed that no significant changes occur in metal content, composition and surface area of regenerated catalyst after the tenth cycle, which also confirm the stability of the catalyst. Only a small loss in metal content (0.05%) was observed after the tenth cycle. However, metal leaching is observed in several catalytic systems on the basis of conversion.<sup>[10,11]</sup>

# 3.4 | Probable Mechanism for Ethylbenzene Oxidation

The mechanism for ethylbenzene oxidation was investigated using a quenching experiment with radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a quenching reagent. The reaction was carried out under optimized reaction conditions. After completion of 1 h of reaction, BHT was added and the reaction was continued for a further 7 h (Figure 8). GC analysis showed no further increase in conversion of ethylbenzene after the addition of BHT. This clearly indicates that oxidation of ethylbenzene by TBHP appears to be a radical process because addition of BHT, a radical scavenger, inhibited the formation of any product in the oxidation reaction. Thus, oxidation of ethylbenzene with TBHP catalysed by LDH-[NAPABA-Cr(III)] probably proceeds via a free radical mechanism (Scheme 4). In the first step, the metal centre of LDH-



**SCHEME 4** Probable free radical mechanism for oxidation of ethylbenzene with TBHP catalysed by LDH-[NAPABA-Cr(III)]

[NAPABA-Cr(III)] catalyst acts as an initiator in the homolytic cleavage of TBHP into free (*t*-BuO<sup>•</sup>) alkoxy and (*t*-BuOO<sup>•</sup>) alkylperoxy radicals (initiation step). In the second step, alkylperoxy radicals attack ethylbenzene to convert it into 1-*tert*-butylperoxyethylbenzene. In the next step, 1-*tert*-butylperoxyethylbenzene leads to the formation of acetophenone, benzaldehyde and benzoic acid. Acetophenone is formed by dehydration while benzaldehyde by loss of methanol from 1-*tert*-butylperoxyethylbenzene. Benzaldehyde on further oxidation gives benzoic acid.

#### 3.5 | Hot Filtration Experiment

The heterogeneity of the catalyst was investigated for the oxidation of ethylbenzene using a hot filtration experiment. The catalytic reaction was carried out under optimized reaction conditions, and during the reaction the catalyst was filtered off after 1 h in the first cycle at 393 K to avoid re-adsorption of leached chromium onto the catalyst surface. The filtrate collected after 1 h of the first cycle was placed again into the reaction flask and the reaction was continued for a further 7 h. GC analysis showed no further increase in conversion of ethylbenzene. The reaction mixture did not exhibit any colour, indicating the absence of chromium, which was estimated using ICP-AES. This suggested that no chromium leaching occurred during the catalytic reaction. This observation indicates that the catalyst is heterogeneous in nature.

### 4 | CONCLUSIONS

A heterogeneous catalyst, LDH-[NAPABA-Cr(III)], was synthesized by intercalation of a Cr(III) Schiff base complex into LDH and characterized using ICP-AES, EDX, SEM, XRD, BET surface area measurement, FT-IR, TGA, EPR and DRUV-visible techniques. Its catalytic activity was studied for the liquid-phase selective oxidation of ethylbenzene with TBHP under solvent-free conditions. In the oxidation reaction, ethylbenzene was oxidized to acetophenone and benzaldehyde. A maximum conversion of ethylbenzene of 90.7% with 99.93% selectivity of acetophenone was observed under optimized reaction conditions. Acetophenone was the major product and can be isolated from the reaction mixture with 92% purity. Essentially pure acetophenone was isolated in 90.67% product. The catalyst was heterogeneous and stable and could be recycled up to ten times without significant loss of catalytic activity.

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#### REFERENCES

- R. A. Sheldon, J. K. Kochi, Metal-Catalyzed Oxidation of Organic Compounds, Academic Press, New York 1981.
- [2] C. L. Hill, Activation and Functionalization of Alkanes, John Wiley, New York 1989 372.
- [3] D. Lee, U. A. Spitzer, J. Org. Chem. 1969, 34, 1493.
- [4] I. C. Chisem, K. Martin, M. T. Shieh, J. Chisem, J. H. Clark, R. Jachuck, D. J. Macquarrie, J. Rafelt, C. Ramshaw, K. Scott, Org. Process Res. Dev. 1997, 1, 365.
- [5] J. H. Clark, A. P. Kybett, P. Landon, D. J. Macquarrie, K. J. Martin, Chem. Soc. Chem. Commun. 1989, 1355.
- [6] G. Canielli, G. Cardillo, Chromium Oxidation in Organic Chemistry, Springer, Berlin 1984.
- [7] J. Muzart, Chem. Rev. 1992, 92, 113.
- [8] T. Maeda, A. K. Pee, D. Haa, Japanese Patent, JP 7.196573, 1995.
- [9] S. E. Dapurkar, A. Sakthivela, P. Selvam, New J. Chem. 2003, 27, 1184.
- [10] Z. Miao, H. Zhao, J. Yang, J. Zhao, H. Song, L. Chou, New J. Chem. 2015, 39, 1322.
- [11] M. Selvaraj, D. W. Park, I. Kim, S. Kawi, C. S. Ha, Dalton Trans. 2012, 41, 14204.
- [12] A. P. Singh, N. Torita, S. Shylesh, N. Iwasa, M. Arai, *Catal. Lett.* 2009, 132, 492.
- [13] S. S. Acharyya, S. Ghosh, R. Bal, Ind. Eng. Chem. Res. 2014, 53, 20056.
- [14] D. Carriazo, M. del Arco, E. García-López, G. Marcì, C. Martín,
   L. Palmisano, V. J. Rives, *Mol. Catal. A* 2011, *342–343*, 83.
- [15] W. T. Reichle, Solid State Ionics 1986, 22, 135.
- [16] D. Carriazo, M. del Arco, C. Martín, V. J. Rives, *Appl. Clay Sci.* 2007, *37*, 231.
- [17] V. Rives, M. A. Ulibarri, Coord. Chem. Rev. 1999, 181, 61.

## 12 of 12 WILEY-Organometallic

- [18] D. Y. Wang, F. R. Costa, A. Vyalikh, A. Leuteritz, U. Scheler, D. Jehnichen, U. Wagenknecht, L. Haussler, G. Heinrich, *Chem. Mater.* 2009, 21, 4490.
- [19] A. A. A. Ahmed, Z. A. Talib, M. Z. J. Hussein, *Phys. Chem. Solids* **2012**, 73, 121.
- [20] J. Feng, Y. He, Y. Liu, Y. Du, D. Li, Chem. Soc. Rev. 2015, 44, 5291.
- [21] B. Monteiro, S. Gago, S. S. Balula, A. A. Valente, I. S. Goncalves, M. J. Pillinger, *Mol. Catal. A* 2009, *312*, 23.
- [22] A. Aguzzi, V. Ambrogi, U. Costantino, F. J. Marmottini, Phys. Chem. Solids 2009, 68, 808.
- [23] R. Marangoni, L. P. Ramos, F. J. Wypych, *Colloid Interface Sci.* 2009, 330, 303.
- [24] N. Wang, J. Sun, H. Fan, S. Ai, Talanta 2016, 148, 301.
- [25] X. Wang, G. Wu, X. Liu, C. Zhang, Q. Lin, Catal. Lett. 2016, 146, 620.
- [26] K. M. Parida, M. Sahoo, S. J. Singha, Mol. Catal. A 2010, 329, 7.
- [27] Z. P. Xu, J. Zhang, M. O. Adebajo, H. Zhang, C. Zhou, *Appl. Clay Sci.* 2011, 53, 139.
- [28] K. M. Parida, M. Sahoo, S. Singha, J. Catal. 2010, 276, 161.
- [29] C. H. Zhou, Appl. Clay Sci. 2011, 53, 87.
- [30] S. Khare, R. Chokhare, P. Shrivastava, J. S. Kirar, S. Parashar, Porous Mater. 2017, 24, 855.
- [31] S. Khare, R. Chokhare, P. Shrivastava, J. S. Kirar, S. Parashar, Indian J. Chem. Sect. A 2016, 55, 1449.
- [32] S. Khare, P. Shrivastava, J. S. Kirar, S. Parashar, Indian J. Chem. Sect. A 2016, 54, 403.
- [33] S. Khare, R. Chokhare, P. Shrivastava, J. S. Kirar, *Indian J. Chem. Sect. A* 2015, 54, 1032.
- [34] S. Khare, P. Shrivastava, J. Mol. Catal. A 2016, 411, 279.
- [35] S. Khare, P. Shrivastava, Catal. Lett. 2016, 146, 319.

- [36] S. Bhattcharjee, J. A. Anderson, Catal. Lett. 2014, 95, 119.
- [37] B. Gutmann, P. Elsner, D. Roberge, C. O. Kappe, ACS Catal. 2013, 3, 2669.
- [38] S. Bhattacharjee, K. E. Jeong, S. Y. Jeong, W. S. Ahn, New J. Chem. 2010, 34, 156.
- [39] G. Wu, X. Wang, J. Li, N. Zhao, W. Wei, Y. Sun, *Catal. Today* 2008, 131, 402.
- [40] M. Mamat, E. Kusrini, A. H. Yahaya, M. Z. Hussein, Z. Zainal, *Int. J. Technol.* 2013, 1, 73.
- [41] P. Ding, B. J. Qu, Colloid Interface Sci. 2005, 291, 13.
- [42] F. Li, L. Zhang, D. G. Evans, C. Forano, X. Duan, *Thermochim. Acta* 2004, 424, 15.
- [43] Y. Feng, D. Li, Y. Wang, D. G. Evans, X. Duan, Polym. Degrad. Stab. 2006, 91, 789.
- [44] S. Praveen Kumar, R. Suresh, K. Giribabu, R. Manigandan, S. Munusamy, S. Muthamizh, V. Narayanan, *Spectrochim. Acta* A 2015, 139, 431.
- [45] S. Khare, R. Chokhare, Mol. Catal. A 2012, 353-354, 138.
- [46] D. Habibi, A. R. Faraji, C. R. Chim. 2013, 16, 888.
- [47] V. Raji, M. Chakraborty, P. A. Parikh, Ind. Eng. Chem. Res. 2012, 51, 5691.
- [48] R. Xie, G. Fan, L. Yang, F. Li, Catal. Sci. Technol. 2015, 5, 540.

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