Molybdenum oxide supported on COK-12: A novel catalyst for oxidative dehydrogenation of ethylbenzene using CO₂

Ramudu Pochamoni¹, Anand Narani², Venkata Ramesh Babu Gurram³, Murali Dhar Gudimella³, P. S Sai Prasad Potharaju³, David Raju Burri³ & Kamaraju Seetha Rama Rao³*

¹Catalysis Laboratory, CSIR-Indian institute of Chemical Technology, Hyderabad 500 607, India
Email: ksraramao@iict.res.in
²Chemical Engineering Department, Gayatri Vidya Parishad College of Engineering, Visakhapatnam, India

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P₆m₃-type mesoporous silica (COK-12) prepared at quasi-neutral pH in a buffered medium using sodium silicate as a silica source has been used as a support to prepare a series of MoO₃/COK-12 catalysts with variable MoO₃ loadings by wet impregnation technique. Among these catalysts, 14 wt% MoO₃/COK-12 with small particle size of MoO₃ shows superior activity for the oxidative dehydrogenation of ethylbenzene to styrene in the presence CO₂.

Keywords: Catalysts, Supported Catalysts, Dehydrogenation, Oxidative dehydrogenation, Ethylbenzene, Styrene, Molybdenum oxide, Mesoporous silica, Silica

Selective dehydrogenation of alkanes to the corresponding olefins is an important catalytic process. For reactions limited by thermodynamic equilibrium (e.g., mostly, dehydrogenation reactions), one of the challenge is to achieve a high conversion with high selectivity towards the products. Among the equilibrium constrained dehydrogenation reactions, styrene from ethylbenzene (EB) is important. Styrene is industrially produced by dehydrogenation of ethylbenzene in vapor phase on several iron oxide catalysts promoted with alkaline metal ions, especially K⁺, in the temperature range of 873−974 K. However, presently these catalysts are in disuse as the formation of carbonaceous deposits causes a rapid deactivation. KFeO₂ has been identified as the active phase for the dehydrogenation wherein potassium enhances the activity of iron oxide and reduces the formation of coke deposits that deactivates the catalysts. Co-feeding of steam along with ethylbenzene suppresses the coke formation on the catalyst. An iron oxide-chromium oxide-potassium carbonate based catalyst is used in the industry and improvement of this catalyst is achieved with addition of various metal oxides such as vanadium, cerium, molybdenum, and manganese compounds. Wu et al. indicated that TiO₂−Fe₂O₃, ZrO₂−Fe₂O₃, and TiO₂−Fe₂O₃−ZrO₂ showed higher activities than the conventional K-promoted iron catalysts. Jabarathinam et al. have reported that basic sites and acidic sites present in the spinel oxides containing Ni, Cr, Zn, Cu, Fe, and Al catalysts influence the ethyl benzene conversion.

On the other hand, the catalytic activities of various metal oxides were investigated for the oxidative dehydrogenation of ethylbenzene to styrene. Oganowski et al. reported that the activity of the V-MgO mixed catalysts could be promoted by Cr, Co, and Mo doping. Moran et al. investigated the dehydrogenation of ethylbenzene to styrene using Pt, Mo, and Pt-Mo catalysts supported on clay nanocomposites. Moronta et al. reported that dehydrogenation of ethylbenzene to styrene catalyzed by Co, Mo and Co-Mo catalysts supported on natural and aluminum-pillared clays, gave low conversions (<20%) and cracking products in the dehydrogenation of ethylbenzene. Burri et al. reported the dehydrogenation of ethylbenzene to styrene was carried out by using CO₂ gas over TiO₂-ZrO₂ bifunctional catalyst.

Many research groups are developing new mesoporous materials that have applications as catalysts, adsorbents, or catalyst supports that minimize the deposition of carbon on surface of catalyst and increase the conversion of ethylbenzene as well as styrene selectivity. Burri et al. reported the influence of SBA-15 support on CeO₂-ZrO₂ catalyst for the dehydrogenation of ethylbenzene to styrene under CO₂ flow. Liu et al. have investigated...
the dehydrogenation of ethylbenzene to styrene over LaVox/SBA-15 catalysts in the presence of carbon dioxide. Ohishi et al.\textsuperscript{10} reported dehydrogenation of ethyl benzene with CO\textsubscript{2} over Cr-MCM-41 catalyst. Park et al.\textsuperscript{20} reported the oxidative dehydrogenation of ethylbenzene with carbon dioxide as soft oxidant over zeolite-supported iron oxide catalysts.

In the present work, the dehydrogenation of ethylbenzene to styrene over MoO\textsubscript{3}/COK-12 catalysts is reported for the first time.

Materials and Methods
Preparation and characterization of the catalysts
The ordered mesoporous SiO\textsubscript{2} (COK-12) was prepared by self-assembly method using a long chain ionic surfactant, i.e., P123, as template and sodium silicate as silica source as reported in an earlier reported method\textsuperscript{21}. In a typical synthesis, COK-12 was prepared by dissolving 4.0 g of the triblock copolymer Pluronic P123 (Sigma Aldrich Chemicals, USA) in 107.5 g water. To this solution, 3.684 g citric acid monohydrate (SD Fine Chem Ltd, India) and 2,540 g trisodium citrate (SD Fine Chem Ltd, India) were added. The resulting solution was stirred for 24 h. Then, sodium silicate (10.4 g) solution (10% NaOH, 27% SiO\textsubscript{2}, Merck, Germany) was diluted with 30.0 g of H\textsubscript{2}O and added to the previous solution. The mixture was stirred for 5 min at 175 rpm with a mechanical stirrer and kept at room temperature without agitation for 24 h. The as-synthesized material was filtered, washed and dried at 333 K overnight. Finally the material was calcined in air in two steps, at 573 K and then at 773 K for 8 h with 1 °C min\textsuperscript{-1} ramps. Different loadings of MoO\textsubscript{3} on COK-12 supported catalysts were prepared by wet impregnation technique, using (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O as the precursor for MoO\textsubscript{3}. All catalysts were calcined in air at 723 K for 5 h with ramping 10 °C min\textsuperscript{-1}. The catalysts were designated as xMC, where x indicates the MoO\textsubscript{3} loading in weight percent.

XRD patterns of the catalysts were recorded on a Rigaku Ultima-IV (Rigaku Corporation, Japan) X-ray diffractometer with Ni-filtered Cu K\textalpha\textsubscript{0} radiation (\(\lambda = 1.5406 \text{Å}\)) at a scan speed of 4° min\textsuperscript{-1} and a scan range of 2–80° at 40 kV and 20 mA. The mesoporous nature of the COK-12 was obtained over a scan range of 0.7–5°. The FT-IR patterns were recorded on a spectrum GX spectrometer (Perkin-Elmer, Germany) in the scan range of 4000–400 cm\textsuperscript{-1}.

Raman spectra were recorded at room temperature in the range of 200–1200 cm\textsuperscript{-1} using a Horiba Jobin-Yvon LabRam HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source with excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were loosely spread onto a glass slide below the confocal microscope for Raman measurements. Temperature programmed reduction (TPR) was performed on a laboratory built equipment containing a programmable temperature controller and a gas chromatograph having a thermal conductivity detector (TCD). About 100 mg of catalyst was taken and pretreated at 573 K for 1 h in Ar flow (60 mL/min). Then the catalyst was exposed to 5% H\textsubscript{2} balance Ar gas for 1 h at 373 K and the temperature of the sample was raised up to 1073 K at a heating rate 10 °C/min. The H\textsubscript{2} gas consumption was monitored with the gas chromatograph using the TCD. Brunauer, Emmett and Teller (BET) equation was used to calculate the surface area, whereas Barret-Joyner-Halenda (BJH) method was used to obtain the pore size distribution of the catalysts\textsuperscript{22}. Prior to N\textsubscript{2} adsorption-desorption experiment on an Autosorb Instrument (Quantachrome, USA), the catalyst was degassed under vacuum at 523 K for 1 h to remove the physisorbed moisture. The morphological features of the catalysts were obtained using a Jeol JEM 2000EXII transmission electron microscope, operating between 160 and 180 kV.

Catalytic activity
Dehydrogenation of ethylbenzene was carried out in a continuous down flow fixed bed reactor operated under atmospheric pressure. In each catalytic run, about 1 g of the catalyst, diluted with an equal amount of quartz grains, was positioned between two layers of quartz wool at the centre of the reactor. The upper portion of the reactor was filled with quartz beads which served both as a pre-heater and a mixer for the reactants. Prior to reaction, the catalyst was exposed to N\textsubscript{2} gas (20 cm\textsuperscript{3}/min) at 873 K for 1 h. After bringing the reactor temperature to the required temperature, ethylbenzene was fed into the reactor through a microprocessor controlled metering pump (Braun, Germany). Along with ethylbenzene, N\textsubscript{2} or CO\textsubscript{2} flow (20 cm\textsuperscript{3}/min) was maintained. The reaction was carried out at 723–923 K. The liquid product mixture was collected every 1 hr in a trap kept at 263 K. The products were analyzed by a flame ionization detector (FID) equipped gas chromatograph, (GC-17A, Shimadzu Instruments, Japan) with an OV-1 capillary column (30 m length,
0.53 mm i.d.) and the components were confirmed by GC-MS, (QP 5050A, Shimadzu Instruments, Japan). Conversion of ethylbenzene and selectivity towards styrene was calculated by Eqs (1) and (2).

\[
\text{Ethylbenzene conv.} = \left( \frac{\text{EB}_{\text{in}} - \text{EB}_{\text{out}}}{\text{EB}_{\text{in}}} \right) \times 100 \quad \ldots (1)
\]

\[
\text{Styrene selectivity} = \left( \frac{\text{Styrene}_{\text{out}}}{\text{Products}_{\text{out}}} \right) \times 100 \quad \ldots (2)
\]

**Results and Discussion**

Low angle X-ray diffraction patterns of the catalysts are displayed in Fig. 1(a). All the samples showed three well resolved diffraction peaks centred at 2\(\theta\) values ~1.02°, 1.76° and 2.04°. These peaks may be indexed to the (100), (110) and (200) planes respectively. These XRD results reveal that even after the impregnation of MoO\(_3\) over COK-12, all the catalysts with different loadings of molybdenum oxides retain the hexagonal symmetry of the support, COK-12. The marginal decrease in XRD peak intensities of COK-12 is noticed with increasing Mo oxides. The decreasing trend in intensities of XRD peaks may be attributed to the lowering of local order, which may be due to the reduction of scattering contrast between the channel walls of the matrices\(^{23, 24}\).

The \(d\)-spacing of COK-12 in all the catalysts are in the range of 8.7–8.8 nm corresponding to a unit cell parameter, \(a=10–10.2\) nm (Table 1), which is in line with the earlier reported value\(^3\).

The wide angle XRD patterns of the MoO\(_3\)/COK-12 samples with different MoO\(_3\) loadings are shown in Fig. 1(b). For comparison, the XRD pattern of pure COK-12 is also shown. The characteristic diffraction peaks of amorphous silica are observed only for the catalysts up to 10 wt% MoO\(_3\) loading, which indicates that the molybdenum species are well dispersed in the catalysts. The characteristic peaks corresponding to molybdenum oxides are noticed for the catalysts with 14 wt% MoO\(_3\) and above loading at 2\(\theta\) values of 12.68°, 23.38°, 25.68° and 27.28° corresponding to the orthorhombic phase of MoO\(_3\)\(^\text{25, 26}\). The MoO\(_3\) particle size determined by Scherrer equation at 14 wt% MoO\(_3\) loading is found to be ~17 nm. Beyond 14 wt% MoO\(_3\) loading, the MoO\(_3\) reflections are clearly visible indicating the formation of bigger MoO\(_3\) particles. XRD studies indicate that the MoO\(_3\) species are highly dispersed in the mesoporous channels of COK-12. XRD signals of MoO\(_3\) have been reported at 15.4 wt% MoO\(_3\) on SBA-15\(^\text{27}\). Another report indicates that MoO\(_3\) XRD reflections started appearing on SBA-15 support from 10 wt% MoO\(_3\) loading onwards\(^\text{28}\). The deviation in Mo loading at which XRD reflections appear depends on the selection of support and method of preparation.

![Fig. 1](image)

**Table 1**—Physico-chemical characterization of MoO\(_3\)/COK-12 catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) ((\text{m}^2/\text{g}))</th>
<th>(V_t) ((\text{cc/g}))</th>
<th>(D_{\text{BJH}}) ((\text{nm}))</th>
<th>(d_{100}) ((\text{nm}))</th>
<th>(a_0) ((\text{nm}))</th>
<th>(t) ((\text{nm}))</th>
</tr>
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<tbody>
<tr>
<td>COK-12</td>
<td>435.06</td>
<td>0.51</td>
<td>3.617</td>
<td>8.832</td>
<td>10.198</td>
<td>6.581</td>
</tr>
<tr>
<td>6MC</td>
<td>300.451</td>
<td>0.35</td>
<td>3.110</td>
<td>8.660</td>
<td>10.000</td>
<td>6.890</td>
</tr>
<tr>
<td>10MC</td>
<td>242.770</td>
<td>0.38</td>
<td>3.750</td>
<td>8.660</td>
<td>10.000</td>
<td>6.250</td>
</tr>
<tr>
<td>14MC</td>
<td>288.25</td>
<td>0.40</td>
<td>4.388</td>
<td>8.658</td>
<td>9.998</td>
<td>5.610</td>
</tr>
<tr>
<td>18MC</td>
<td>169.25</td>
<td>0.23</td>
<td>3.627</td>
<td>8.658</td>
<td>9.998</td>
<td>6.327</td>
</tr>
</tbody>
</table>

\(a\)BET surface area. \(b\)The total pore volume. \(c\)BJH average pore diameter. \(d\)Periodicity derived from low angle XRD. \(e\)The unit cell parameter \((a_0=2d_{100}/\sqrt{3})\). \(f\)The pore wall thickness \((t=a_0-D_{\text{BJH}})\).
The FT-IR spectra (KBr pressed disks) of all the MoO$_3$/COK-12 samples show strong absorptions in the region of 950–1250 cm$^{-1}$, at 808 cm$^{-1}$ and at 472 cm$^{-1}$, which are due to Si-O species in the silica support. In addition, to these major absorptions, the samples with greater molybdenum oxide content (14 wt% MoO$_3$ and above) show additional absorption bands at 990, 864, 820 and 583 cm$^{-1}$. These bands may be attributed to crystalline MoO$_3$(Supplementary Data, Fig. S1).

The laser Raman spectra of MoO$_3$/COK-12 samples with selected MoO$_3$ loadings show that the samples up to 10 wt% MoO$_3$ loadings show no peaks in the Raman spectra. The weak intense peaks noticed at 996 and 819 cm$^{-1}$ for the sample with 12 wt% MoO$_3$ loading may be attributed to Mo=O stretching and Mo–O–Mo stretching of crystalline MoO$_3$. Intensities of these peaks are found to increase with further increase in MoO$_3$ loading$^{30}$ (Supplementary Data Fig. S2).

Figure 2 display N$_2$ adsorption-desorption isotherm of the catalysts. The isotherm shape is of type–IV, which according to the IUPAC classification indicates mesoporous character. The H1–type hysteresis loop, typical for COK-12 materials, is also clearly evident, and the pronounced steep in the adsorption branch of the isotherm indicates a narrow pore size distribution, which is typical of well-ordered mesostructured materials. In the XRD pattern recorded for this sample, high angle reflections are completely missing, except the background signal caused by amorphous silica. This indicates a complete absence of crystalline domains of molybdenum oxide, or if present, the crystal sizes are too small to be detected by X-ray diffraction. All the MoO$_3$/COK-12 materials exhibit mesopore structure.

The reducibility of the molybdenum oxide samples was studied by temperature-programmed reduction (TPR) with hydrogen. The collected TPR profiles are presented in Fig. 3. For the samples with lower MoO$_3$ content (2–12 wt%), only a reduction peak at a higher temperature (1080–1110 K) was observed. The increase in MoO$_3$ content from 14–18 wt% led to the appearance of another reduction peak at 830 K. It is reasonable to speculate that the high temperature peak at 1080–1110 K corresponds to reduction of the monomeric MoO$_3$ species, which may have interactions with COK-12, whereas the reduction peak at 830 K probably arises from the oligomeric MoO$_3$ species or small MoO$_3$ clusters. Further increase in MoO$_3$ content changed the reduction profile significantly. The high dispersion of molybdenum on the silica support causing the reduction of Mo$^{6+}$ ions begins at a temperature as low as ~823 K for majority of the MoO$_3$ catalysts$^{27}$.

TEM images recorded for COK-12 and 14MC samples show well-ordered hexagonal arrays of mesoporous even after incorporation of MoO$_3$ (Fig. 4).

Influence of MoO$_3$ loading under N$_2$ atmosphere

The dehydrogenation of ethylbenzene activity (carried out under vapor phase conditions at atmospheric pressure under inert gas N$_2$ flow) over various MoO$_3$/COK-12 catalysts against reaction temperature has been shown in Fig. 5. The conversion
of ethylbenzene increases with increase in loading of molybdenum oxide till 14 wt%, beyond which it decreases. However, the selectivity to styrene decreases marginally with increase in MoO$_3$ loading. The molybdenum species are isolated or are highly dispersed at lower molybdenum loadings which may be responsible for increasing the activity till 14 wt% MoO$_3$ loading. Further increase in molybdenum oxide loading leads to the formation of bulk and oligomeric molybdenum oxides on the surface, which may be responsible for the decreasing activity. In general, the conversion of ethylbenzene increases with increasing temperature from 723−923 K and all catalysts followed a similar trend. At 873 K, the EB conversion under N$_2$ flow over 14 wt% MoO$_3$/COK-12 (30%) was always greater than that reported in literature for Mo/MCM-41 catalyst (6%).

**Influence of MoO$_3$ loading under CO$_2$ atmosphere**

The MoO$_3$/COK-12 catalysts exhibit higher activity in ethylbenzene dehydrogenation in CO$_2$ atmosphere, especially towards selectivity of styrene. XRD results of catalysts samples containing 6, 10 and 14% MoO$_3$ show the presence of MoO$_3$ in amorphous state, implying that the MoO$_3$ species are in a highly dispersed state. The conversion of ethylbenzene and selectivity of styrene over 14 wt% MoO$_3$ catalyst either in N$_2$ and CO$_2$ flow is higher than those on V-MgO catalysts under air and H$_2$O environments. At low loading of MoO$_3$, the conversion of ethylbenzene is very low, and with increase in MoO$_3$ loading, conversion of ethylbenzene increases in presence of both inert (N$_2$) and soft oxidant (CO$_2$). The increasing trend is observed up to 14 wt% MoO$_3$ loading and thereafter, conversion of ethylbenzene decreases due to formation of bulk MoO$_3$ species on the surface of the COK-12. The XRD results show that up to 14 wt% MoO$_3$ loading the MoO$_3$ phase is in amorphous state and beyond this loading, it is crystalline due to the formation of bulk MoO$_3$ species (Fig. 1b and Table 1). Li. & others have calculated the theoretical MoO$_3$ loading to form a monolayer on MCM-41 and found it to be 0.26 wt/wt of MoO$_3$ on MCM-41. In the present case, the theoretical MoO$_3$ amount to form a monolayer on COK-12 is found to be ~50 wt% MoO$_3$, which is very high compared with the value of 14 wt% MoO$_3$ obtained from XRD results. This is possible when a patchy MoO$_3$ layer is formed on the surface of the support. A similar observation has been made on MoO$_3$/SBA-15 catalysts. The selectivity of styrene is higher under a soft oxidant (CO$_2$) as compared with an inert flow (N$_2$). It is well known that in the absence of CO$_2$ as oxidant, the dehydrogenation reactions lead to non-selective products and facilitate faster deactivation of the catalyst. If CO$_2$ is introduced deactivation of the catalyst drops drastically and selectivity of the products increases over prolonged times. These observations can be used as a good basis to explain the better performance of the present catalysts. However, with an increase in reaction temperature (above 873 K), the selectivity of styrene decreased considerably due to thermal cracking of ethylbenzene to other products.

At higher temperatures, formation of higher amounts of toluene and benzene occurs and leads to severe fall in the styrene selectivity. In order to assess the potential role of CO$_2$ in directing the styrene formation and maintaining the selectivity, further investigations are necessary.
catalyst stability, 14 wt% MoO₃/COK-12 catalyst was studied for ethylbenzene dehydrogenation at 923 K both in N₂ and CO₂ flows separately against time-on-stream (Supplementary Data, Fig. S3). The conversion of ethylbenzene in presence of N₂ is very high for the first hour (~81%), but decreases drastically with time and reaches a low of conversion at 9 h. Also, selectivity towards styrene is very low (~60%). Formation of coke may be the reason for decrease in the conversion. In the presence of CO₂ as oxidant, both ethylbenzene conversion (65–60%) and selectivity (95–90%) towards styrene was fairly stable during time-on-stream study. Significant difference in the styrene selectivity and catalyst stability in CO₂ and N₂ feed gases is mainly due to the occurrence of simple dehydrogenation of ethylbenzene in N₂ flow (Eq. 3), whereas in the presence of CO₂, the reverse water gas shift (RWGS) reaction coupled with the simple dehydrogenation takes place as shown in Eq. (4).

\[
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 + \text{H}_2 \quad \ldots \text{(3)}
\]

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \ldots \text{(4)}
\]

**Conclusions**

The MoO₃/COK-12 catalysts prepared by wet impregnation show excellent stability in the dehydrogenation of ethylbenzene in presence CO₂. The maximum activity exhibited by 14 wt%MoO₃/COK-12 catalyst is due the formation of patchy MoO₃ monolayer on COK-12.

**Supplementary Data**

Supplementary data associated with this article, i.e., Figs S1-S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(4-5) 493-498_SupplData.pdf.

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