Surface properties and oxydehydrogenation of ethylbenzene over molybdenum doped ceria systems

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Catalytic dehydrogenation of ethylbenzene is of industrial importance in the manufacture of styrene as it is extensively used as an intermediate for the manufacture of polystyrene and numerous thermoplastics. Styrene is commercially manufactured by the catalytic dehydrogenation of ethylbenzene over iron oxide promoted by alkali metal ions. Since this direct dehydrogenation is limited by thermodynamic equilibrium, high temperatures of reactions (>600°C) are required and typical conversions are low. Also, the high temperatures required to give favourable conversion bring about severe cracking of the more complex alkyl benzenes.

The oxydehydrogenation reaction is a potential alternative for the manufacture of styrene at lower temperatures, without thermodynamic restrictions on the yield. Various catalysts have been reported as efficient catalysts for the oxidative dehydrogenation of ethylbenzene. Turco et al. investigated the catalytic properties of zirconium-tin mixed phosphates and observed that mixed zirconium-tin phosphates give much higher ethylbenzene conversion with respect to pure Zr and Sn phosphates, the selectivity to styrene being correspondingly high. They concluded that surface acidity of medium strength plays an important role in the reaction through the formation of a catalytically active coke. Ferrites, a subgroup of spinels, is highly active for the oxydehydrogenation reactions. The catalytic effectiveness of ferrites for many such reactions arises because of the ease with which iron can change its oxidation state between 2 and 3. Rare earth oxides especially CeO$_2$ is used as a component in new catalyst reformulations for the oxidative dehydrogenation of paraffins and ethylbenzene. Hagemeyer et al. have reported a redox process involving the dehydrogenation of ethylbenzene by contact with a catalyst containing a reducible metal oxide (Bi$_2$O$_3$, CeO$_2$ and Cr$_2$O$_3$) in the absence of oxygen and simultaneous reduction of the catalyst, followed by oxidation of reduced catalyst with an oxidizing agent. The present paper deals with oxydehydrogenation activity of molybdenum doped pure ceria and its sulphated analogues.

Materials and Methods
Catalyst preparation
Preparation of pure cerium oxide was achieved by pseudo-template method. An aqueous ammonia solution (25 wt%) was added dropwise over 3 h with constant stirring to a solution of Ce(NO$_3$)$_3$·6H$_2$O containing cetyl trimethyl ammonium bromide as surfactant (the solution was prepared with 58 g of Ce(NO$_3$)$_3$·6H$_2$O and 40 g of surfactant in 2364 mL of distilled water, which represents a 1.2 molar ratio of Ce/surfactant). The pH of the solution was maintained at 11. After precipitation the solution was placed on a thermostatic bath at 90°C for 90 h under continuous stirring. The precipitate was then filtered and dried at
60°C for 24 h. Molybdenum was incorporated using ammonium heptamolybdate solution with 5, 10 and 15% of molybdenum (for 5% molybdenum loading 0.0969 g, for 10% loading 0.2043 g and for 15% loading 0.3248 g of ammonium heptamolybdate per gram of the catalyst was used). Molybdenum promoted sulphated ceria systems were prepared from the hydroxide by a single step impregnation using 0.5 M H₂SO₄ solution (1 mL/g of hydrous cerium oxide) and ammonium heptamolybdate solution with 5, 10 and 15% of molybdenum. The samples were then calcined at temperatures varying from 150 to 500°C and kept at 500°C for 5 h at a heating rate of 12°C/min, with constant air blowing over the samples.

Physico-chemical characterization

The BET surface area and pore volume of the samples were determined by nitrogen physical adsorption at liquid N₂ temperature using a Micromeritics Gemini surface area analyser. XRD patterns were recorded using a Rigaku D-max C X-ray diffractometer using Ni filtered Cu-Kα radiation (λ=1.5406Å). The IR spectra of the samples were recorded on a Nicolet Impact 4000 spectrometer using the KBr pellet method (from 400–4000 cm⁻¹). Diffuse reflectance UV-Vis spectra of the samples were recorded at room temperature between 200–800 nm using MgO as standard in the Ocean Optics-2000 instrument.

Surface acidity was evaluated using temperature programmed desorption of ammonia (NH₃-TPD). The tests were carried out in a conventional flow apparatus. The pelletised sample (0.4 g) was activated at 300°C in nitrogen flow for half an hour. After cooling to room temperature, it was saturated with excess ammonia gas in the absence of nitrogen flow and the system was allowed to attain equilibrium. The excess and physically adsorbed ammonia was flushed out by a current of nitrogen. Ammonia was desorbed at different temperatures (100-600°C) with a heating rate of 20°C / minute in the same atmosphere and trapped in H₂SO₄. The amount of ammonia desorbed at each temperature, was determined by back titration with sodium carbonate.

Thermodesorption studies of the samples after adsorption of 2, 6-dimethyl pyridine were performed to know the nature of Bronsted acid sites present in the samples. For this, the activated samples were kept in a desiccator containing vapours of 2, 6-dimethyl pyridine under vacuum for 48 h to allow equilibrium adsorption. It was then subjected to thermal analysis from room temperature to 600°C at a heating rate of 20°C / min.

Catalytic activity measurement

Ethylbenzene from Merck was used as such without further purification. The reaction was carried out in presence of oxygen in a fixed bed tubular glass reactor at 500°C. A soap bubble meter was used to check the flow of air. About 0.5 g of the activated catalyst was placed in the catalyst bed and 15 mL of air flow per minute along with ethylbenzene was passed through the reactor. The products were analysed by gas chromatography (Chemito GC 8610, flame ionisation detector, FFAP column-length 2 m under the following analysis conditions: column temp.: 90°C, injection port and detection port temperatures: 230°C). The influence of temperature, flow rate of ethylbenzene, air flow and time-on-stream were investigated in detail to optimize the reaction conditions. A blank run was carried out at 500°C, which indicated negligible thermal reaction.

Results and Discussion

Catalyst characterization

The surface area values for molybdenum modified pure and sulphated analogues of ceria are presented in Table 1. Pure ceria shows the highest surface area. Incorporation of molybdenum as well as sulphate ions decreases surface area of ceria considerably. The decrease of surface area upon doping can be explained by considering the nature of interaction between the support and the metal oxide, Chen et al.

<table>
<thead>
<tr>
<th>Catalyst no.</th>
<th>Catalyst system</th>
<th>Surface area (m²/g)</th>
<th>Pore vol* (cm³/g)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C</td>
<td>148 203</td>
<td>0.211 8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. SC</td>
<td>44 67</td>
<td>0.122 10.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. CM₅</td>
<td>61 94</td>
<td>0.142 10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. CM₁₀</td>
<td>34 52</td>
<td>0.109 11.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. CM₁₅</td>
<td>26 40</td>
<td>0.085 11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. CSM₅</td>
<td>37 56</td>
<td>0.099 11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. CSM₁₀</td>
<td>22 34</td>
<td>0.078 11.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. CSM₁₅</td>
<td>16 25</td>
<td>0.056 12.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C=pure ceria; SC=sulphated ceria; CM₅, CM₁₀, CM₁₅=ceria with 5, 10 and 15% molybdenum loading respectively; CSM₅, CSM₁₀, CSM₁₅=sulphated ceria with 5, 10 and 15% molybdenum loading respectively.

*Pore volume is measured at a P/P₀ of 0.9782.
have reported several models\textsuperscript{10} for the interactions between molybdena and γ-alumina, which can be tentatively divided into two categories: the dispersed oxide species spread (i) on the top or (ii) incorporated into the surface of the support. This indicates that under appropriate conditions, the dispersed molybdena might cover the support with the formation of a monolayer on the top of the surface, or the dispersed molybdenum ions may be incorporated into the vacant sites on the surface of the support. On the basis of the second concept, the decrease in surface area by molybdenum loading, can be explained as the plugging of the surface vacant sites of ceria by the incorporated molybdenum ions. As a result of this, the pore volume of the modified catalysts are found to be lower than that of the unmodified systems. Another reason for this decrease in surface area is attributed to the agglomeration of the particles upon modification. It has been reported that the crystalline nanoparticles have a tendency to agglomerate and form spherical secondary particles with the addition of either ammonium sulphate or sulphuric acid. The existence of sulphate ions in the acidified solution is responsible for spherical agglomeration of the nanoparticles\textsuperscript{11}. The crystallite size values obtained from XRD measurements using Scherer equation \(t = 0.9 \lambda / \beta \cos \theta\); \(\lambda = \) wavelength of X-ray used, \(\beta = \) FWHM, \(\theta = \) angle of diffraction also shows an increase in crystallite size values with loading. This type of decrease in surface area upon modification has been reported in the case of \(\text{SiO}_2/\text{TiO}_2\) supported molybdena catalysts. Watson et al. observed that from 2-20 wt% loading of molybdena, the catalysts showed a general decrease in surface area with increasing amount of molybdenum added\textsuperscript{12}.

X-ray diffraction patterns of the molybdenum loaded catalysts are shown in Fig. 1. The XRD data of the prepared system very closely supports the standard values given in the JCPDS data cards (34-394), thus confirming the fluorite structure of ceria. No characteristic peak of crystalline \(\text{MoO}_3\) is observed. The dispersion capacity of a metal oxide is a critical value, at values lower than which the oxide might become highly dispersed on the support without the formation of its crystalline phase. The results presented in Fig. 1 indicate that the molybdenum loading is below the dispersion capacity, and are finely dispersed. However, it may be possible for \(\text{MoO}_3\) to exist as a microcrystalline material below the XRD detection limit. Ozkan et al. have studied the XRD patterns of a series of \(\text{SiO}_2/\text{TiO}_2\) supported molybdena catalyst with different molybdenum loading. They observed that molybdena species are finely dispersed showing no \(\text{MoO}_3\) diffraction lines up to 15 wt% loading\textsuperscript{12}. Similarly, in the case of \(\text{ZrO}_2\) supported molybdena samples with low \(\text{MoO}_3\) concentration (11 wt%) only tetragonal \(\text{ZrO}_2\) was observed and crystalline \(\text{MoO}_3\) phases were not detected in XRD\textsuperscript{13}.

FT-IR spectra of modified ceria samples show that the absorption bands centred around 1352 and 1057 cm\(^{-1}\) may be assigned to the characteristic peaks of \(\text{CeO}_2\) species\textsuperscript{14}. These peaks are found to shift towards higher wavenumbers upon modification with molybdenum ions. The peaks in the region 1050-900 cm\(^{-1}\) is attributed to terminal Mo=O vibrations and that at 850-700 cm\(^{-1}\) to antisymmetric Mo-O-Mo or O-Mo-O stretching vibrations or both\textsuperscript{15}. The surface hydroxyl groups present in the oxide supports give strong IR bands in the 3000-4000 cm\(^{-1}\) and 1600-1700 cm\(^{-1}\) regions\textsuperscript{16}. The IR bands in the region 3000-4000 cm\(^{-1}\) is due to the –OH stretching frequency and the bands around 1600 cm\(^{-1}\) to the bending vibrations of the –OH group\textsuperscript{9}.

The sulphate loading of the supported system is confirmed by the characteristic peaks in the region 1200-1000 cm\(^{-1}\). The IR spectra of all the sulphated samples show a characteristic peak around 1270 cm\(^{-1}\), which can be ascribed to the bidentate sulphate group coordinated to the metal ion. It was reported that the peak around 1210 cm\(^{-1}\) corresponds to the unsymmetrical vibrations of the chelate bidentate\textsuperscript{17}. The IR

![Fig. 1—XRD patterns of pure and modified ceria samples.](image)
spectra of sulphated metal oxides such as sulphated oxides of ZrO₂, Fe₂O₃ and HfO₂ have been studied in detail for explaining the superacidity of these catalysts. A common feature of all the super acidic sulphated oxides is the presence of a strong band near 1400 cm⁻¹ representing the asymmetric stretching frequency of S=O. The absence of this peak suggests the lack of super acidic properties of the catalytic systems.

UV-vis spectra of the various molybdenum modified ceria systems clearly show the characteristic band arising from CeO₂ species around 300 nm. In the case of simple supported systems, at lower molybdenum loading a small peak in the 230-260 nm region is observed, which is found to disappear at higher molybdenum loading. Also, the band arising from ceria species broadens as the molybdenum loading increases. The surface modification by sulphate anions does not result in strong changes in the UV-vis spectrum, and is characterised by the single peak around 300 nm.

The position of ligand to metal charge transfer (O²⁻→Ce⁴⁺) spectra depends on the ligand field symmetry surrounding the Ce center. The electronic transitions from oxygen to cerium require higher energy for a tetra coordinated Ce⁴⁺ than for a hexa-coordinated one. It was reported in the case of Ce-MCM-41 samples that the absorption band centered at 300 nm is due to the presence of Ce⁴⁺ species in the tetra-coordinated environment, whereas in the case of a silica and ceric oxide mixture and Ce-exchanged MCM-41 samples, two distinct bands, at 300 and 400 nm are observed, corresponding to two different types of Ce⁴⁺ species. The absorption at higher wavelength (~ 400 nm) may be assigned to hexa-coordinated Ce⁴⁺ species. Li et al. have studied the UV-vis spectra of molybdate species dispersed on γ-alumina and reported that the band at 230-260 nm is the characteristic absorption of Mo=O bond of tetrahedral molybdate and the band at about 320 nm is due to the Mo-O-Mo bridge bond of octahedral species. On the basis of the above, it may be assumed that in the present case the band around 300 nm originates from CeO₂ species in the tetrahedral environment. The absence of band at 400 nm suggests that octahedral CeO₂ species is not present in the catalyst. Moreover, the band at 230 nm present in the case of CM₅ and CM₁₀ system may be assigned to the absorption of Mo=O bond of tetrahedral molybdate. The fact that this band disappears at higher molybdenum loading points to the possibility of overlap with the ceria bands. The broadening of the band corresponding to ceria species supports the above possibility.

Table 2 gives acid strength distribution of molybdenum incorporated pure and sulphated ceria systems. The distribution pattern can be classified into weak (desorption at 100-200°C), medium (201-400°C) and strong (401-600°C) acid sites. Pure ceria possesses low surface acidity. Upon modification with molybdenum ions, there is enhancement in the strength and amount of acid sites in the weak, medium and strong regions. Among the simple supported catalysts maximum acidity is possessed by the CM₅ system. The TPD data of the modified sulphated systems indicates considerable enrichment in the surface acidity as compared to the sulphated ceria catalyst. In both cases surface acidity does not show a regular rise with increase in molybdenum concentration.

Thermodesorption study of adsorbed basic molecules is a popular method for the determination of acid amount of solid catalyst as well as acid strength, as it is an easy and reproducible method. 2, 6-dimethylpyridine (2, 6-DMP) is a sterically hindered molecule which can be used for the selective determination of Brønsted acid sites. Though it adsorbs strongly on Brønsted acid sites, it also forms weak bonds with Lewis acid site at low temperatures. So an appropriate purging temperature is essential for the selective determination of Brønsted acid sites by 2, 6-DMP. Satsmua et al. reported that the coordinatively adsorbed 2, 6-DMP on Lewis acid sites can be eliminated by employing a purging temperature above 300°C. In the present study, for the selective determination of the Brønsted acid sites the adsorption temperature was kept at 300°C. The number of mmols of 2, 6-DMP desorbed per g of the catalyst is

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of ammonia desorbed (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak (100-200°C)</td>
</tr>
<tr>
<td>C</td>
<td>0.17</td>
</tr>
<tr>
<td>SC</td>
<td>0.36</td>
</tr>
<tr>
<td>CM₅</td>
<td>0.51</td>
</tr>
<tr>
<td>CM₁₀</td>
<td>0.36</td>
</tr>
<tr>
<td>CM₁₅</td>
<td>0.48</td>
</tr>
<tr>
<td>CSM₅</td>
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</tr>
<tr>
<td>CSM₁₀</td>
<td>0.54</td>
</tr>
<tr>
<td>CSM₁₅</td>
<td>0.66</td>
</tr>
</tbody>
</table>

*May include small amounts of physisorbed ammonia too.
catalyst in the temperature range 301-600°C has been divided into weak (301-400°C), medium (401-500°C) and strong (501-600°C) acid sites. The results are given in Table 3. The results clearly show that incorporation of molybdenum ions reduces the Brønsted acidity of pure ceria. Among the simple supported systems, CM_10 shows maximum Brønsted acidity. In the case of sulphated systems, CSM_10 and CSM_15 possess Brønsted acidity comparable to pure ceria.

Catalytic activity measurement

Oxidative dehydrogenation of ethylbenzene

Oxidative dehydrogenation of ethylbenzene proceeds efficiently over molybdenum doped pure as well as sulphated ceria systems. Since the reaction conditions play an important role in determining the catalytic activity and selectivity towards different products, an attempt was made to optimize reaction conditions such as temperature, flow rate of ethylbenzene, airflow and time-on-stream.

The effect of airflow on the conversion of ethylbenzene and product distribution over CSM_5 was studied. In the absence of airflow very little conversion of ethylbenzene was noticed. With an increase in the concentration of oxygen from 5 to 15 mL/min, the percentage conversion increased from 10.3 to 20.2. At the same time, styrene selectivity increased initially and then showed a small decrease at 15 mL/min. A styrene selectivity of 90.4% was noticed at airflow of 10 mL/min.

The presence of oxygen is found to enhance the catalytic activity towards oxidative dehydrogenation of ethylbenzene. This enhancement in the presence of oxygen is due to the fact that the additional air supply re-oxidises the reduced catalyst thereby providing the oxygen needed for hydrogen abstraction. The increased availability of oxygen found to enhance the formation of C-oxides.

The effect of temperature on the conversion and product selectivity was studied in the range of 350-550°C. As the temperature of the reaction increased, an appreciable increase in the conversion of ethylbenzene was observed. A rise in temperature from 350 to 550°C resulted in an increase of conversion from 9.2 to 34.6%. However, styrene selectivity increased initially in the temperature range 350-450°C and thereafter decreased. Maximum styrene selectivity was observed at 450°C, when ethylbenzene conversion was about 20.2%. A satisfactory conversion of ethylbenzene and styrene selectivity was observed at 500°C. As the temperature was increased further to 550°C, the styrene selectivity decreased from 84.8 to 78.5%, with a simultaneous enhancement in the selectivity of toluene and benzene. The selectivity to C-oxides was found to decrease with increase in temperature.

Turco et al.² investigated the influence of reaction temperature in the oxidative dehydrogenation of ethylbenzene over zirconium-tin mixed phosphates and found that with an increase of temperature from 400 to 500°C, ethylbenzene conversion increases from 16 to 64%. It was reported in the case of sulphated tin oxide modified with CeO_2, that as temperature increased from 450 to 500°C, an increase in ethylbenzene conversion occurred, but the selectivity to styrene increased initially and then decreased. The selectivity to C-oxides was found to decrease in this case also.³ Bokade et al.⁶ studied the oxidative dehydrogenation of ethylbenzene over Cu_2(Fe),Co,Fe_2O_3, and observed that styrene selectivity increased first in the temperature range of 375 to 425°C and thereafter decreased because of the increased rate of side reactions like disproportionation and dealkylation reaction at high temperatures. In the present case, since an increase in temperature from 500 to 550°C, resulted in a decrease of styrene selectivity, 500°C was taken as the optimum reaction temperature of the reaction.

Figure 2 clearly shows the effect of flow rate of ethylbenzene on conversion and product selectivity. The percentage conversion of ethylbenzene is found to be maximum at low flow rates. As the flow rate of ethylbenzene increased from 3 to 5 mL/h, the conversion of ethylbenzene decreased from 33.2 to 14.4%. Regarding styrene selectivity, with an increase in flow rate of ethylbenzene from 3 to 5 mL/h, selectivity was found to increase from 76.7 to 90.9%. Thereafter,
selectivity decreased with increase in flow rate of ethylbenzene. Toluene and C-oxide selectivities were found to decrease with an increase in feed rate.

The decrease in conversion with increase in flow rate of ethylbenzene may be due to the less contact time of the reactants with the catalyst surface. At higher feed rates, the reactants do not get enough time to get adsorbed on the catalyst surface, which eventually leads to decrease in conversion. A similar trend has been reported by Vrieland\(^{26}\) in the case of oxydehydrogenation of ethylbenzene to styrene over cerium pyrophosphate, where a decrease in flow rate of ethylbenzene (increase in reactant concentration) was found to increase ethylbenzene conversion from 67.2 to 73.2%.

To study the nature of deactivation of the catalytic systems, the reaction was carried out continuously for 6 h at 500°C. The flow rate of ethylbenzene and air were kept as 5 mL/h and 15 mL/min. The analysis of the reaction mixture was carried out at regular intervals of 1 h. Results show that even though there is a small drop in catalytic activity for the second hour, in subsequent hours the activity is nearly constant. Same trend was seen regarding styrene selectivity also. The maximum conversion obtained was 24.5%, and the styrene selectivity was 86.9%. Selectivity to benzene and toluene was found to increase with time. Deactivation studies show that the catalytic system possesses reasonable stability even after 6 h of reaction run. The decrease in activity during the initial stage of the reaction is due to the reduction of the metal ions present on the catalyst surface. These ions are further re-oxidized by the external supply of air thus providing long-term catalytic stability to the systems.

The catalytic efficiencies of molybdenum supported catalysts in oxidative dehydrogenation of ethylbenzene are given in Table 4. Most of the molybdenum doped systems show remarkable styrene selectivity in oxidative dehydrogenation reaction as compared to the pure systems. In the case of CM\(_{10}\) system however, styrene selectivity was lower than pure ceria. In all the cases, styrene was formed as the major product with small amounts of benzene, toluene and carbon oxides. Among molybdenum supported simple systems, maximum activity was shown by CM\(_3\) system, whereas CSM\(_{15}\) gave maximum conversion among the sulphated systems. Similar trend was seen regarding styrene selectivity also.

The correlation between ethylbenzene conversion and surface acidity is presented in Figure 3. From the literature there is evidence that surface acidity plays a direct\(^{27}\) or an indirect\(^{28}\) role in the oxidative dehydrogenation of ethylbenzene. Tagawa et al. studied silica alumina, tin oxides and phosphates and concluded that moderate acid strength is the key factor\(^{26}\). Removal of strong acid sites by addition of sodium acetate improved the selectivity but excessive sodium deactivated the catalyst. A similar conclusion was reached by Fiedorow et al.\(^{27}\) with alumina where small amounts of sodium ion did not affect activity even though strong acid sites would have been removed. Echigoya et al.\(^{29}\) found that introducing acidity into silica by addition of either magnesium or zirconium correlated well withoxydehydrogenation activity. Pyridine in the feed, which would adsorb on

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>Conversion (%)</th>
<th>Styrene</th>
<th>Toluene</th>
<th>Benzene</th>
<th>C-oxides</th>
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<tbody>
<tr>
<td>C</td>
<td>26.2</td>
<td>89.0</td>
<td>6.2</td>
<td>3.4</td>
<td>1.4</td>
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<tr>
<td>SC</td>
<td>18.6</td>
<td>87.1</td>
<td>7.1</td>
<td>3.9</td>
<td>1.9</td>
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<tr>
<td>CM(_3)</td>
<td>37.5</td>
<td>92.7</td>
<td>3.7</td>
<td>2.0</td>
<td>1.6</td>
</tr>
<tr>
<td>CM(_{10})</td>
<td>23.8</td>
<td>87.6</td>
<td>4.5</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>CM(_{15})</td>
<td>26.5</td>
<td>91.5</td>
<td>4.2</td>
<td>2.2</td>
<td>2.1</td>
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<td>CSM(_3)</td>
<td>28.9</td>
<td>90.9</td>
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<tr>
<td>CSM(_{10})</td>
<td>26.6</td>
<td>94.1</td>
<td>3.1</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>CSM(_{15})</td>
<td>30.6</td>
<td>92.6</td>
<td>2.3</td>
<td>1.1</td>
<td>4.0</td>
</tr>
</tbody>
</table>
strong acid sites at these temperatures, did not affect the oxidation reaction.

Figure 3 clearly indicates that in the present case also medium acid centres play a vital role in determining the catalytic activity. Among molybdenum doped pure ceria systems, the catalytic activity decreased as the molybdenum loading increased to 10% and thereafter increased. Similar trend was seen in the case of sulphated ceria systems also. A one-to-one comparison of the catalytic activity with the amount of acid sites indicates that this trend is in accordance with the amount of medium acid sites.

Conclusions
Molybdenum doped pure as well as sulphated ceria systems show same structural patterns as that of the parent forms. XRD patterns reveal the characteristic fluoroite phase of cerium oxide in all the catalytic systems. In FT-IR spectra of the catalysts there are definite bands showing the presence of surface hydroxyl groups, Mo-O vibrations, sulphate bidentate groups and Ce$\text{O}_2$ species. The UV-vis spectra of the catalytic systems reveal that the Ce$\text{O}_2$ species are present in a tetrahedral environment and in the low loaded samples, there is the formation of tetrahedral molybdate species. Enhancement in acid structural properties is evident from TPD of ammonia although the Brönsted acidity of the catalysts decreases with molybdenum incorporation. In the oxydehydrogenation of ethylbenzene, all the catalytic systems show high selectivity to the formation of styrene. There is good correlation between the catalytic activity of the different systems and the amount of medium acid sites possessed by them. Deactivation studies establish high thermal stability of the catalysts with respect to ethylbenzene conversion and styrene selectivity even after 6 h of reaction run.

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References