Abstract

Pollution from motor vehicles is responsible in industrialised nations for ozone forming smog, hazardous carbon monoxide pollution, and other toxic air pollutants. Methyl tert-butyl ether (MTBE) is widely used as an oxygenate for gasoline not only to enhance the octane number but also to make motor vehicle fuel burn more cleanly, replacing toxic additives like lead. Also the synthesis of MTBE offers interesting insights into etherification reactions in general. In the present chapter the catalytic efficiency of transition metal (W, Mo & Cr) modified ceria systems and their sulphated analogues in the gas-phase MTBE synthesis is presented. The effect of various reaction parameters like reaction temperature, flow rate, duration of reaction and methanol to tertiary butanol molar ratio are investigated in detail. The difference in the catalytic activity of the systems has been related to the difference in the surface acidity among them. The performance of the catalytic systems points to its potential in the MTBE technology.
7.1 Introduction

Due to strong environmental concerns about fuel emissions, the use of metal octane enhancers such as tetra-ethyl lead (TEL), tetra-methyl lead (TML), and methyl cyclopentadienyl manganese tricarbonyl (MMT) in gasoline has been phased out in many countries. The concept of reformulated gasoline (RFG) was introduced in the United States to reduce hazardous emissions. The addition of fuel oxygenates to gasoline for increased octane number, higher engine efficiency, and reduction of the polluting components in exhaust gases (such as CO, hydrocarbons, and polynuclear aromatics) has been one of the results of adoption of RFG. Among many potential oxygenated compounds, methyl-tert butyl ether (MTBE) has been widely utilized as a gasoline additive because of its good antiknocking properties, outstanding physical properties such as volatility, miscibility in gasoline, and help in the reduction of hazardous emissions. It also acts as a volume extender, by adding volume to the gasoline pool and by reducing the severity of the naphtha reforming and related conversion operations. MTBE has highly favourable performance qualities from the refiner's perspective, including low sulphur content, acceptable blending vapour pressure, high miscibility in gasoline, moderate boiling point, and stability in storage. Additionally, MTBE's cost, compared to those of other high-octane components, made it the economical choice in the refinery market place.

MTBE was first manufactured commercially in the early 1970s in Europe by Chemische Werke Huls in West Germany and by ANIC in Italy. The current commercial MTBE synthesis is a liquid-phase reaction of methanol and isobutene over sulphonated ion-exchange resins at low temperatures (30-100 °C) and moderately high pressures (usually upto 2.0 Mpa). Although the resin catalysts are very active, they have some major drawbacks such as thermal fragility, sensitivity to methanol-to-isobutene ratios, and corrosive problems. In addition, the deactivated resin catalyst cannot be regenerated and must be properly disposed under current environmental regulations. Another problem concerning MTBE production from isobutene is
that the source of isobutene is limited to catalytic cracking and steam cracking fractions of petroleum refining.

Commercially, MTBE is produced from tert-butyl alcohol (TBA), a chemical produced as a by-product in a number of reaction processes such as the Halcon process (propylene oxide synthesis), where 3.5 kg of tertiarybutanol is produced per kg of propylene oxide\(^{12}\). There are two ways to produce MTBE from TBA, an indirect and a direct method. In the indirect method, TBA is dehydrated to isobutene in the first reactor, followed by reaction of isobutene with methanol to produce MTBE in the second reactor\(^{13}\). In the direct method, MTBE is produced by reacting TBA directly with methanol in one reactor in the presence of an acid catalyst in which water is also formed as a by-product.

Inorganic solid acid catalysts such as microporous zeolites\(^{14-15}\), heteropoly acids (HPA's)\(^{16-18}\) and inorganic oxides such as Nb\(_2\)O\(_5\), TiO\(_2\), ZrO\(_2\), SiO\(_2\)\(^{19}\) are now considered to be potential alternative catalysts for MTBE synthesis and other etherification reactions.

Zeolites have been investigated as efficient catalysts for MTBE formation. A number of papers have been published focusing on the application of zeolites such as H-Y, H-omega, H- mordenite, H-ZSM-5 and H-beta as alternative catalysts for the synthesis of MTBE\(^{20-22}\). Collignon et al. studied MTBE synthesis on a series of zeolites H-Beta with Si/Al ratios ranging from 13 to 194 and found that these materials are significantly more active than all other zeolite types employed. Over zeolites H-Beta with a Si/Al ratio of 25.7, a maximum MTBE yield of ca 50% was obtained at 333 K. This high catalytic activity was explained by a contribution of the large external surface of the zeolites H-Beta used as catalysts\(^{23}\). Investigating the MTBE synthesis on zeolites H-ZSM-5 and H-Y, Kogelbauer et al. observed an increase in the MTBE formation rate and a suppression of by-products after pre adsorption of methanol molecules. This is a hint to the important role of adsorbate complexes formed by adsorption of methanol molecules for the activity of zeolites in MTBE synthesis\(^{24}\).
In the early 1990s, worldwide MTBE production exhibited the highest growth rate of all the commodity chemicals\textsuperscript{25-28}. Further improvements on fuel quality had been expected to make the trend continue beyond 2000. However, concern has been expressed about MTBE as a health hazard. It is currently being banned in California to prevent contamination of ground water\textsuperscript{29,30}. The possible alternatives to MTBE are ethanol, ethyl-tert butyl ether (ETBE), Tert-amyl methyl ether (TAME), and Tert-butyl alcohol (TBA). It is reported that more than 85\% of reformulated gasoline uses MTBE vs. 8\% ethanol. However, these alternatives are less favourable. Gasoline blends have been reported to drastically increase hydrocarbon emissions over MTBE blends\textsuperscript{31}. Moreover, substantially increased use of ethanol as a gasoline additive is likely to result in sharply higher prices for consumers\textsuperscript{32}. Although MTBE may be produced in lesser amounts in the future, its synthesis still offers interesting insights into etherification reactions in general. Thus, it can be thought as a model reaction for understanding the potential use of novel solid acid catalysts for the synthesis of ethers. The synthesis of other ethers will undoubtedly increase as the search intensifies for a replacement of MTBE as a gasoline additive.

In the present work, we have investigated the possibility of using transition metal (W, Mo & Cr) incorporated pure ceria and its sulphated analogues for the vapour phase MTBE synthesis from methanol and tertiary butyl alcohol (TBA). The reaction variables such as temperature of the reaction, time on stream, molar ratio of methanol to tertiary butanol and flow rate were optimised to have maximum conversion. Since, the general mechanism of the reaction suggests that etherification takes place via the intermediate formation of the corresponding tertiary carbocation followed by the nucleophilic attack of the methanol molecules\textsuperscript{33-35}, it is assumed that an enhancement of surface acidity will favour the processes. So, an attempt is also made to correlate the catalytic efficiency of the systems with the surface acidity.

7.2 Methyl tertiary butyl ether synthesis

The vapour phase MTBE synthesis from methanol and tert-butyl alcohol
was carried out in a conventional fixed bed reactor and the experimental procedure is given in section 2.6 of Chapter 2. The product identification was done by the gas chromatographic analysis of the liquid reaction mixture. It was then confirmed by the gas chromatography-mass spectrometer technique. The reaction always yielded MTBE as the major product. The percentage conversion is calculated on the basis of tert-butanol converted into the product.

7.3 Process optimisation

MTBE synthesis was carried out under atmospheric pressure in the presence of nitrogen. The optimisation process was done with 0.5 g of CSW₁₅ catalyst. A detailed investigation on the process optimisation is discussed below.

I. Effect of temperature

Figure 7.1 illustrates the relationship between the conversion of tert-butanol and the reaction temperature in MTBE synthesis over modified ceria systems in the temperature range of 100 to 200 °C. The reactions were carried out at a molar ratio of methanol to tert-butanol of 10:1, and the flow rate was kept as 4 mL/h.

From Figure 7.1, it is clear that the reaction is sensitive to slight changes in temperature. A notable increase in tert-butanol conversion is observed in the temperature range 100-150 °C followed by a decay at higher reaction temperatures. The conversion of tertiarybutanol reaches a maximum at 150 °C and it amounts to 52.2%.

The reduction in catalytic activity at higher temperatures can be ascribed to the formation of the co product isobutene either through tert-butanol dehydration or MTBE product de-etherification. Isobutene thus formed will then be lost from the reflux apparatus. Based on thermodynamic equilibrium, the higher temperatures will largely promote side reactions over acid catalysts to produce other hydrocarbons or oxygenates, leading to a linear reduction in the conversion to MTBE with increasing temperatures.
The effect of temperature on conversion in MTBE synthesis.

Catalyst – 0.5 g CSW, molar ratio of methanol to tert-butanol-10:1.
TOS- 2 h, flow rate-4 mL/h

The descending portion of the curve at higher temperatures corresponds to the shift in equilibrium towards a lower yield of MTBE. This type of bell shaped curve is reported in the case of HPW/MCM-41 also, where the HPW/MCM-41 catalysts showed good activity at temperatures close to 100 °C, which make them comparable to that of commercial Amberlyst-15 and thereafter reduction in conversion with rise in temperature was noticed. The effect of temperature on the MTBE synthesis conversion over zeolites has been widely studied which showed that for zeolites such as H-Y and H-ZSM-5, the percentage conversion increased with temperatures below 90 °C, after that it decreases and approaches equilibrium at higher temperatures. The above literature points to the fact that for each catalyst there is an optimal temperature range at which the highest conversion can be obtained. In the present case this optimal temperature is at 150 °C.
II. Effect of flow rate

In the case of gas phase reactions flow rate is an important parameter that has influence on the reactivity. The flow rate alters the contact time of the reactants and products on the catalyst surface. For studying the effect of flow rate on tertiary butanol conversion, four flow rates (3, 4, 5 and 6 mL/h) were selected. The reactions were done at a temperature of 150 °C for 2 hrs. The results obtained are shown in Figure 7.2.

![Conversion vs Flow Rate](image)

Figure 7.2
Influence flow rate in MTBE synthesis.
Catalyst -0.5 g CSW₁₅, temperature-150 °C, tert-butanol to methanol molar ratio- 1:10, TOS-2 h

The results presented in Figure 7.2 indicate that as the flow rate changes from 3 to 5 mL/h, the conversion of tert-butanol increases from 34.9 to 70.7%. Above 5 mL/h, an increase in flow rate decreases the conversion. Brandao et al. investigated the gas phase synthesis of MTBE from methanol and tert-butanol over microporous niobium silicate AM-11 and found that an increase of WHSV has no significant effect on the selectivity for MTBE, whereas the conversion of tertiary butanol decreased markedly. They concluded that longer residence time favoured the yield of MTBE⁴⁵. In the present case also the residence time of the reactants was found to play a decisive role in determining the catalytic activity. At higher flow rates, since
the residence time for the reactants on the catalyst surface is smaller, reduction in the catalytic activity is observed.

III. Effect of molar ratio

To understand the influence of reactant concentration in determining the catalytic activity, a series of experiments were conducted at a reaction temperature of 150°C with flow rate of 5 mL/h. Figure 7.3 depicts conversion levels of tert-butanol with various methanol/tert-butanol molar ratios.

![Figure 7.3](image)

Influence of methanol to tertiary butanol molar ratio in MTBE synthesis. Catalyst – 0.5 g CSW, temperature-150 °C, flow rate-5 mL/h, TOS- 2 h

Methanol to tert-butanol molar ratio is found to exert a positive influence on MTBE formation. As the molar ratio is increased from 1:5 to 1:15, the percentage conversion increase from 52.0 to 76.8%. In all the cases MTBE is formed as the exclusive product. An increase in the concentration of methanol results in an increase in the number of molecules, which in turn results in an increase in the number of effective collisions. Another reason for the increased conversion is the fact that
the excess methanol suppresses the formation and secondary reaction of isobutene and thus promotes the conversion and selective formation of MTBE.

IV. Effect of time on stream

In order to evaluate the stability of the catalytic systems with reaction time, reaction was carried out continuously for 8 hours at 150 °C and the reaction mixture was analyzed at intervals of one hour. The activity profile obtained for CSW₁₅ system as a function of time on stream is given in Figure 7.4.

![Conversion vs. Time on Stream](image)

**Figure 7.4**

Influence of time on stream in MTBE synthesis

Catalyst-1 g CSW₁₅, temperature-150 °C, molar ratio of methanol to tert-butanol-10:1, flow rate-5 mL/h

Figure 7.4 clearly indicates that the reactivity of the catalyst systems increases during the first two hours and remains almost the same up to the fourth hour. Thereafter considerable decrease was noticed, and only 50% conversion was observed after eight hours of reaction. Xia et al. studied the time on stream activity of various mesoporous catalysts like HPW/MCM-41, NaAlMCM-41, HAIMCM-41 and H₂SO₄/
MCM-41 in which the reactions were carried out at the respective optimal reaction temperatures\textsuperscript{37}. They observed that with an increase in time on stream to 110 h and with the exception of H\(_2\)SO\(_4\)/MCM-41, the selective conversion of tertiary butanol to MTBE hardly changes, showing the excellent stability of these catalysts. This is attributed to the relatively small diffusion hindrance over mesoporous catalysts, in which the adsorption-desorption processes readily occur, decelerating the deactivation of the catalysts by coking. The reduction in catalytic activity in the case of H\(_2\)SO\(_4\)/MCM-41 catalyst was ascribed to the leaching of mobile H\(_2\)SO\(_4\) molecules in the gas-liquid stream. The results of present study show that the catalytic system possesses reasonable activity for four hours of reaction run only. The qualitative analysis of the product mixture doesn't show the presence of sulphate ions, which argues against the probability of sulphate leaching. Further the reduction of activity with time may be due to the poisoning of the catalyst by coking or the readsorption of the products on the catalyst surface.

7.4 Catalytic efficiency of different systems

The catalytic activity of three series (W, Mo & Cr doped) of modified ceria catalysts along with their sulphated derivatives is presented in this section. All the reactions were done at a reaction temperature of 150 °C with a methanol to tert-butanol molar ratio of 15:1 and the flow rate was kept as 5 mL/h. Because of the acid catalysed nature of the reaction, the increase in the percentage conversion is correlated with the increase in the surface acidity of the systems as determined by ammonia TPD method.

a) Tungsten incorporated systems

A series of experiments were performed to evaluate the catalytic activity of tungsten modified samples. The results are depicted in Table 7.1. The correlation between the percentage conversion and the total acidity of the systems obtained from ammonia TPD method is given in Figure 7.5.
Table 7.1

Activity of tungsten incorporated systems in the MTBE synthesis

<table>
<thead>
<tr>
<th>Catalytic systems</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.2</td>
<td>100</td>
</tr>
<tr>
<td>SC</td>
<td>31.4</td>
<td>100</td>
</tr>
<tr>
<td>CW\textsubscript{5}</td>
<td>39.7</td>
<td>100</td>
</tr>
<tr>
<td>CW\textsubscript{10}</td>
<td>56.5</td>
<td>100</td>
</tr>
<tr>
<td>CW\textsubscript{15}</td>
<td>58.0</td>
<td>100</td>
</tr>
<tr>
<td>CSW\textsubscript{5}</td>
<td>76.8</td>
<td>100</td>
</tr>
<tr>
<td>CSW\textsubscript{10}</td>
<td>80.1</td>
<td>100</td>
</tr>
<tr>
<td>CSW\textsubscript{15}</td>
<td>77.3</td>
<td>100</td>
</tr>
</tbody>
</table>

Amount of Catalyst-0.5 g, temperature-150 °C, time on stream -2 h, molar ratio of methanol to tert-butanol-15:1, flow rate-5 mL/h

From Table 7.1, it is evident that pure ceria gives the lowest conversion under the specified reaction conditions. Enhancement in catalytic activity was observed with modification. Comparing the catalytic activity of simple as well as sulphated systems, it was observed that sulphate modification has a positive influence on the catalytic activity of supported systems towards the reaction. Among the sulphated systems maximum activity is shown by CSW\textsubscript{10} system, and it amounts to 80.1%.

From the Figure 7.5, it is clear that total acidity is lowest for pure ceria which in turn gives the lowest conversion. As the tungsten loading increases the total acidity of the systems was found to increase. This paved way for their higher conversion. Among the sulphated systems, CSW\textsubscript{10} possess maximum number of acid sites, which gives the highest conversion.
Catalysis by nanocrystalline ceria modified with transition metals

The catalytic activity of different systems is found to be in accordance with the surface acidity possessed by them. Xia et al. studied the catalytic activity of MCM-41 supported 12-tungstophosphoric acid (HPW) catalysts with various HPW loading for the gas-phase synthesis of MTBE. They observed that the surface acidity of HPW/MCM-41 catalysts was enhanced stepwise by increasing the HPW loading. In agreement to the acidity values the catalytic activity of the systems also increased with HPW loading.

b) Molybdenum incorporated systems

The catalytic efficiencies of molybdenum incorporated ceria systems as well as their sulphate modified series in MTBE synthesis are presented in Table 7.2. The tert-butanol conversion is correlated with total acidity as obtained from ammonia TPD (Figure 7.6)
Table 7.2
Activity of molybdenum incorporated systems in the MTBE synthesis

<table>
<thead>
<tr>
<th>Catalytic systems</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.2</td>
<td>100</td>
</tr>
<tr>
<td>SC</td>
<td>31.4</td>
<td>100</td>
</tr>
<tr>
<td>CM5</td>
<td>75.6</td>
<td>100</td>
</tr>
<tr>
<td>CM10</td>
<td>42.1</td>
<td>100</td>
</tr>
<tr>
<td>CM15</td>
<td>49.7</td>
<td>100</td>
</tr>
<tr>
<td>CSM5</td>
<td>56.4</td>
<td>100</td>
</tr>
<tr>
<td>CSM10</td>
<td>36.3</td>
<td>100</td>
</tr>
<tr>
<td>CSM15</td>
<td>78.6</td>
<td>100</td>
</tr>
</tbody>
</table>

Amount of Catalyst-0.5 g, temperature-150 °C, time on stream -2 h, molar ratio of methanol to tert-butanol-15:1, flow rate-5 mL/h

From Table 7.2, it is clear that ceria in the pure form is less active in the MTBE synthesis than the supported catalysts. In the case of molybdenum impregnated systems, a sharp decrease in percentage conversion is observed as we move from CM5 to CM10 system, although a slight increase is noticed for CM15 system. Among the sulphated series, maximum activity is shown CSM15 system.

Figure 7.6 illustrates that the activity pattern in the case of molybdenum doped systems is in agreement with surface acidity values obtained from TPD of ammonia. Among the molybdenum systems surface acidity is the highest for CSM15 system. Since the activity is related to the surface acidity, this system gives the maximum conversion. According to Xia, Hidajat and Kawi, who studied the catalytic activity of various mesoporous catalysts like HPW (50%)/MCM-41, H2SO4/MCM-41, HAIMCM-41, NaAlMCM-41 and SiMCM-41, the catalytic activity towards MTBE synthesis corresponds to the surface acidity possessed by them. The relative
Concentrations of the total acid sites in these mesoporous catalysts is in the decreasing order HPW (50%)/MCM-41>H₂SO₄/MCM-41>HaAlMCM-41>NaAlMCM-41>>Si-MCM-41. The activity of these catalysts was found to increase in the same order, thus pointing to the involvement of total number of acid sites in MTBE synthesis.

Catalytic activity correlated with the total acidity obtained from ammonia TPD.

c) Chromium incorporated systems

To study the catalytic efficiencies of chromium doped ceria and sulphated ceria systems, a set of reactions were performed under optimised reaction conditions. The results are presented in Table 7.3. The difference in catalytic activity among the systems is correlated with the difference in surface acidity possessed by these catalysts, as depicted in Figure 7.7.
Table 7.3
Activity of chromium incorporated systems in the MTBE synthesis

<table>
<thead>
<tr>
<th>Catalytic systems</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.2</td>
<td>100</td>
</tr>
<tr>
<td>SC</td>
<td>31.4</td>
<td>100</td>
</tr>
<tr>
<td>CCr5</td>
<td>39.7</td>
<td>100</td>
</tr>
<tr>
<td>CCr10</td>
<td>33.4</td>
<td>100</td>
</tr>
<tr>
<td>CCr15</td>
<td>34.2</td>
<td>100</td>
</tr>
<tr>
<td>CSCr5</td>
<td>35.8</td>
<td>100</td>
</tr>
<tr>
<td>CSCr10</td>
<td>38.4</td>
<td>100</td>
</tr>
<tr>
<td>CSCr15</td>
<td>41.4</td>
<td>100</td>
</tr>
</tbody>
</table>

Amount of Catalyst-0.5 g, temperature-150 °C, time on stream -2 h, molar ratio of methanol to tert-butanol-15:1, flow rate-5 mL/h

From Table 7.3, it is noticeable that all the systems show remarkable activity towards the reaction. Among the chromium doped systems, as the percentage of chromium increases, the catalytic activity decreases from CCr5 to CCr10, and a small increase is noticed for CCr15. An enhancement in catalytic activity is observed for sulphated as well as chromium incorporated ceria systems. Among the chromium incorporated sulphated systems highest percentage conversion is given by CSCr15, which amounts to 41.4%.

From Figure 7.7, the total acidity of the supported systems is found to decrease as the percentage of chromium is increased from 5 to 10, thereafter a small increase is noticed. As far as sulphated systems are considered, a gradual increase in surface acidity is seen with modification. The catalytic activity of the systems was found to be in agreement with the surface acidity.
Catalysis by nanocrystalline ceria modified with transition metals

192

1.4 %°

E

E

3

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o 204 -0.6o E

E

0 . . 0.2 E0 O <

(D

CCr10 ­ CCr15 ­ CSCr5 ~

CSCr10 1 CSCr15

-0- Total acidity (mmol/g) -0- Conversion ( % )

Figure 7.7

Catalytic activity correlated with the total acidity obtained from ammonia TPD

7.5 Conclusions

The following are the key points derived from this study:

* Transition metal promoted (W, Mo & Cr) ceria systems and their sulphated analogues are found to catalyse the vapour phase methyl tertiary butyl ether synthesis with considerable activity.

* The reaction gives 100% selectivity to methyl tertiary butyl ether over all the systems.

* Study about the reaction parameters such as temperature of the reaction, reaction time, methanol to tertiary butanol molar ratio and flow rate suggest that these parameters play an important role in determining the catalytic activity and each has a specific value for maximum conversion.

* The agreement between the catalytic activity and the surface acidity points to the fact that the difference in catalytic activity among the systems can be related to the difference in the surface acidity possessed by them.
REFERENCES

20. A. Kogelbauer, M. Öcal, A. A. Nikolopoulos, J.G. Goodwin Jr and G. Marcelin,
Catalysis by nanocrystalline ceria modified with transition metals


