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THE TRANSFORMATIONS OF 4-*tert*-BUTYLTOLUENE OVER Ce-MODIFIED MORDENITE ZEOLITES

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Abstract

The transformation of 4-*tert*-butyltoluene over Ce-modified H-mordenite with 1 and 4 wt. % of cerium on zeolite prepared by Ce-impregnation of H- mordenite (H-MOR CBV 21A) was studied at 180 °C in the liquid phase. Partial deactivation of external acid sites by Ce-modification has positive effect to suppress dealkylation of *tert*-butyltoluenes and isomerisation of 4-*tert*-butyltoluene to thermodynamically more stable 3-*tert*-butyltoluene.

Key words 4-*tert*-butyltoluene, *tert*-butylation, isomerization, dealkylation, mordenite, zeolites, *Ce- modification, deactivation*

INTRODUCTION

4-*tert*-Butyltoluene is intermediate product for 4-*tert*-butylbenzaldehyde and 4-*tert*-butyl-benzoic acid used in synthesis of fine chemical. [1–4]. 4-*tert*-Butyltoluene is produced by alkylation of toluene in the liquid phase with *tert*-butylation agents, e.g. isobutylene or *tert*-butanol [5] over different catalysts such as $AlCl_3$, sulphuric acid [6], activated clays or silica-alumina [4] and H-MOR, H-Y and H-BEA zeolite catalysts [5].

The problem encountered is that desired 4-*tert*-butyltoluene is a kinetic product and 3-*tert*-butyltoluene is more thermodynamically stable isomer than 4-*tert*-butyltoluene and more, *tert*-butyl group can be cleavaged from aromatic ring forming toluene and isobutylene. The formation of 2-*tert*-butyl-toluene is sterically hindered by the methyl group on the one side and voluminous *tert*-butyl group on the other side. The main alkylation reaction is accompanied by isomerisation of 4-*tert*-butyltoluene to more stable 3-*tert*-butyltoluene and by dealkylation with formation of toluene and isobutylene [5] .

It was published by many authors [7–13] in the study of isopropylation of naphtalene and biphenyl that non-regioselective alkylation and isomerisation of desired 2,6-di-isopropylnaphtalene and

4,4'-di-isopropyl-biphenyl isomers can be decreased by the deactivation of external acid sites of H-mordenite by modification with ceria/cerium. The deactivation of the external acid sites is a characteristic property of cerium [7–9].

The influence of partial deactivation of the external surface of mordenite zeolite by ceria/cerium on the transformations of 4-*tert*-butyltoluene is presented in this paper.

EXPERIMENTAL

Chemicals and Catalysts

4-*tert*-butyltoluene from Aldrich , n-heptane , *tert*-butanol , ethanol , cerium nitrate , all p.a. quality.
H-mordenite (CBV 21 A) from Zeolyst Int. with Si/Al = 10.5 and total acidity (TPDA) = 1.3 mmol/g.
Ce-modified mordenites were prepared by impregnation of H-mordenite with ethanol solution of cerium nitrate, by drying at 60 °C and next by calcination at 500 °C for 6 hours in an air stream.

Table 1. Characteristics of zeolites

zeolite (wt. % of Ce)	S_{BET} (m^2 / g)	V_{micro} , t (cm^3 / g)
Ce (0) H-MOR	468	0.173
Ce (1) H-MOR	494	0.176
Ce (4) H-MOR	417	0.148

Apparatus and Procedure

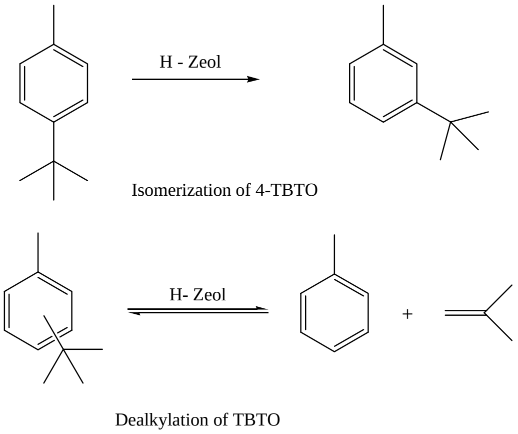
All reactions were carried out in a laboratory autoclave reactor (100 ml). In a typical run (*tert*-butylation of toluene) 40 mmol of toluene, 80 mmol of *tert*-butanol, 70 ml of n-heptane (solvent) and 0.7 g of fresh calcined zeolite kept before adding at 200°C was used. The changes of 4-*tert*-butyltoluene was carried out in the reaction system consisting of 6.7 mmol of 4-TBTO, 70 ml of n-heptane and 0.35 g of fresh calcined zeolite catalyst. All reactions were carried out at the temperature of 180 °C and at autogenous pressure.

Analytical method

The samples of reaction mixture were withdrawn periodically from the reactor and analyzed on CHROMPACK 9002 gas chromatograph equipped with CP Sil 5 CB column (25m × 0.53 mm) and FID detector. The temperature program was : 60 °C (5 min) from 60 to 220°C with a slope of 5°C/min.

RESULTS AND DISCUSSION

4-*tert*-Butyltoluene and 3-*tert*-butyltoluene are the main alkylation products in tert-butylation of toluene. 2-*tert*-butyltoluene was present in the reaction products only in trace amounts (the influence of steric hindrance of voluminous *tert*-butyl group). The favour-red isomer formed over shape selective zeolites is 4-*tert*-butyltoluene (kinetically favoured) but thermodynamically more stable is 3-*tert*-butyltoluene [6]. The isomerization of 4-*tert*-butyltoluene is one of the secondary reactions in the tert-butylation of toluene. Dealkylation of *tert*-butyltoluenes (the cleavage of *tert*-butyl group) is the next secondary reaction.



Scheme 1. Isomerization of 4-TBTO and dealkylation of TBTO

It is known that diffusion rate of compounds in zeolites is influenced by the ratio of diameters of their molecules and zeolite pores. 4-*tert*-Butyltoluene with kinetic diameter 0.58 nm is the narrowest from all TBTO isomers and has the highest diffusion rate in the mordenite main channels (3-TBTO has lower diffusion rate because it has larger diameter of molecule (0.65 nm) [5] .

The isomerization of 4-TBTO to 3-TBTO runs easier on the external surface , where it is not sterically hindered as in the pores of zeolite. This isomerization can be decreased by deactivation of the acid sites on the external surface of zeolite. One of the methods for deactivation of external surface is impregnation of zeolite with cerium nitrate in ethanol solution and after drying and calcination at 500 °C in the air stream it is ready to use. Cerium is in the form of ceria/cerium [9,13]. This method has been used in this work with the aim to decrease secondary reactions (isomerization and dealkylation) .

Figure 1 and 2 shows the influence of modification of H-mordenite with 4 wt.% of cerium on the conversion of toluene and selectivity to the desired isomer (4-TBTO) in *tert*-butylation of toluene with *tert*-butanol at 180 °C .

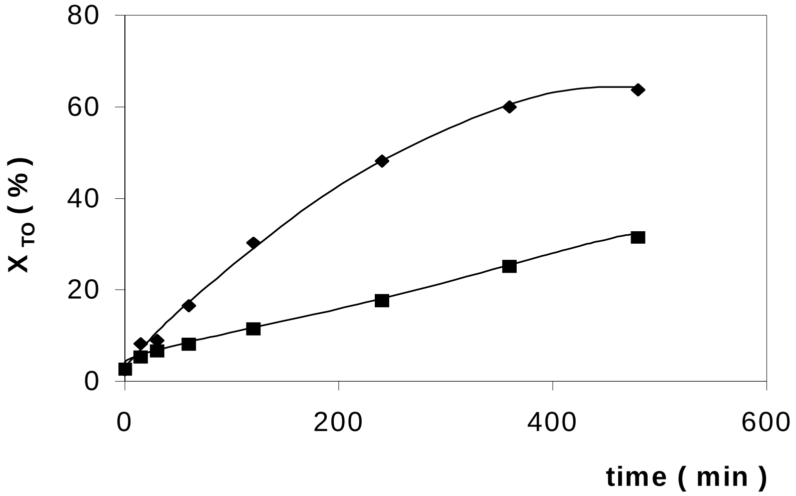


Figure 1. The comparison of H-mordenite and Ce-modified mordenite on toluene conversion (◆-H-mordenite , ■-Ce (4) H-MOR)

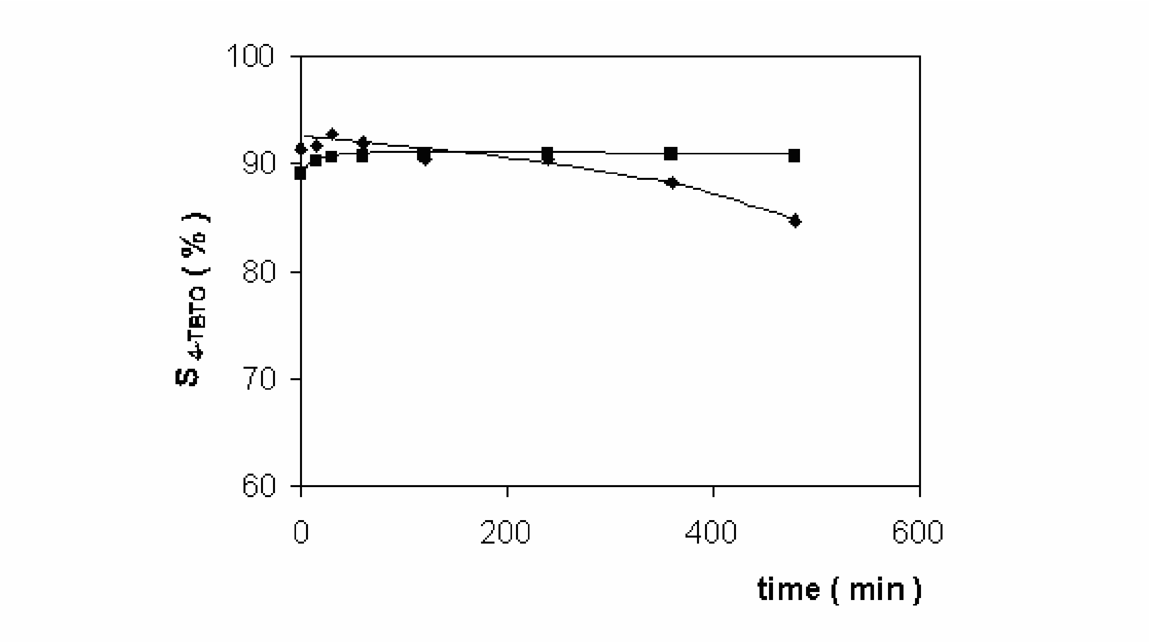


Figure 2. The influence of Ce-modifica-tion of H-mordenite on selectivity to 4-TBTO (◆-H-mordenite, ■-Ce (4) H-MOR)

As can be seen from Figure 2 the Ce-impregnation of H-mordenite (CBV 21A) has positive effect on selectivity to 4-TBTO, which was constant (near 91 %) in comparison with non-modified zeolite (selectivity decreased from 91 to 85 % after 8 hours).

In the next, the transformation of individual 4-*tert*-butyltoluene was studied over H-mordenite and Ce-modified mordenites with 1 and 4 wt. % ceria/cerium at the standard reaction conditions.

Figure 3 shows the influence of Ce-modification of H-mordenite on conversion of 4-TBTO.

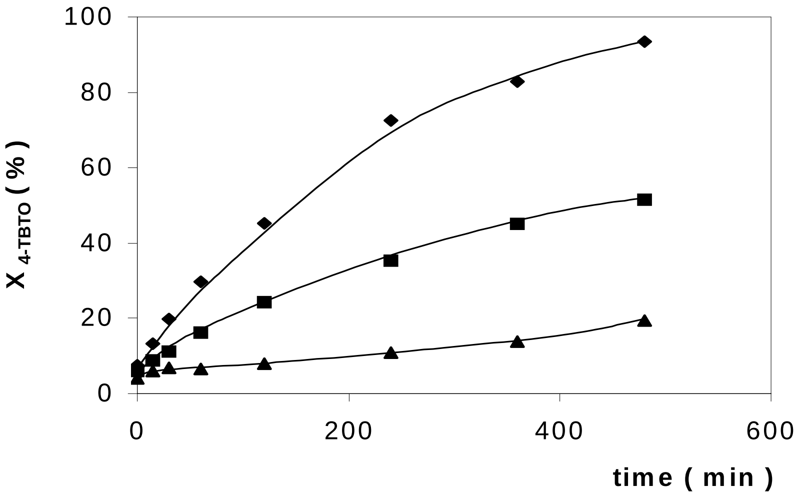


Figure 3. The influence of Ce-modification of H-mordenite on conversion of 4-TBTO at 180 °C (◆ - H-mordenite, ■ - Ce (1) H-MOR, ▲ - Ce (4) H-MOR)

The deactivation of external surface of mordenite with partial deactivation of the external acid sites has significant effect on isomerisation of 4-TBTO. The conversion of this isomer on the H-mordenite was 93.5 % after 8 hours in comparison with 51.5 % (Ce(1) H-MOR) and 19.4 % (Ce(4) H-MOR) at the same time. The results of isomerization and dealkylation reactions of 4-TBTO at the standard reaction conditions are shown in Figure 4 and 5.

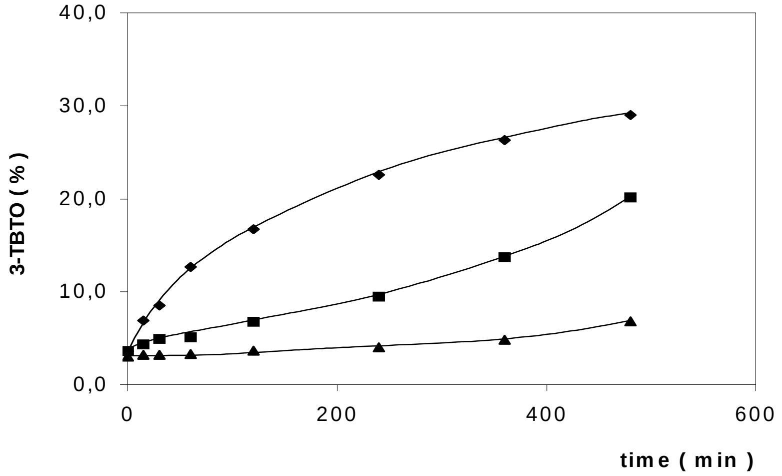


Figure 4. The influence of Ce-modification of H-mordenite on formation of 3- TBTO (◆ - H-mordenite, ■ - Ce (1) H-MOR, ▲ - Ce (4) H-MOR)

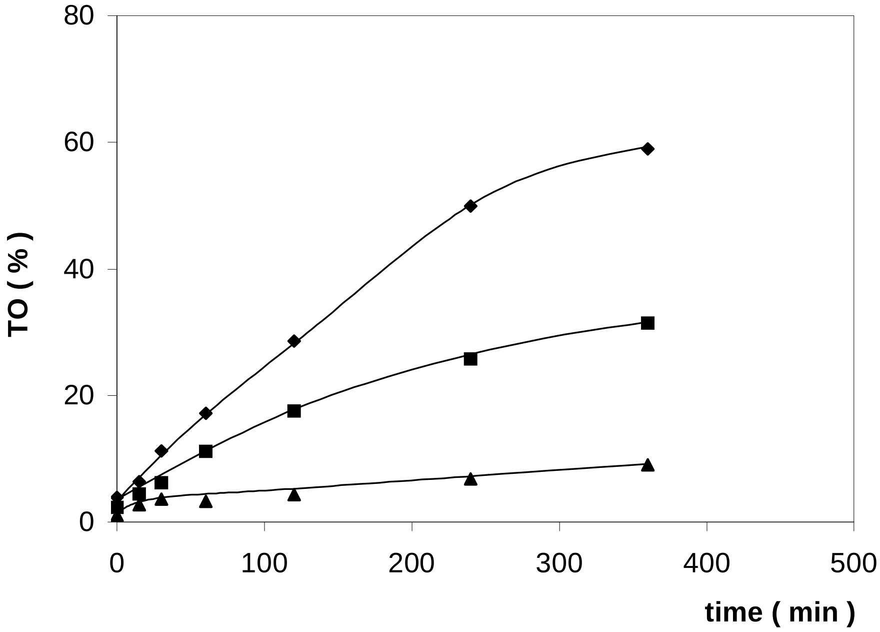


Figure 5. The influence of Ce-modification of H-mordenite on dealkylation of 4-TBTO (◆ - H-mordenite, ■ - Ce (1) H-MOR, ▲ - Ce (4) H-MOR)

It can be seen from these results that the most important secondary reaction is dealkylation of 4-TBTO to toluene and isobutylene.

Dealkylation of 4-TBTO can be carried out on both acid sites in the pores of zeolite and on external acid sites. Isomerization of 4-TBTO to 3-TBTO is prefered on the external surface of zeolite. These results are in good accordance with results of many authors [7-13] in alkylations of naphtalene and biphenyl over mordenite zeolites modified with cerium impregnation.

It is evident that partial deactivation of external surface of mordenite with ceria/cerium has important effect on the decrease of 4-TBTO dealkylation and isomerization as non-desired secondary reactions in the *tert*-butylation of toluene.

CONCLUSION

Modification of H-mordenite with ceria/cerium by impregnation method and next calcination is one of the simple methods for deactivation of acid sites on the external surface. The influence of partial deactivation of external acid sites by Ce-modification on conversion of 4-*tert*-butyltoluene was studied. 4-*tert*-Butyltoluene is changed in the process of its preparation by isomerization to more thermodynamically stable 3-*tert*-butyltoluene and by dealkylation to toluene and isobutylene. Ce-modification of basic mordenite is efficient way to suppress these secondary reactions at tert-butylation of toluene.

ABBREVIATIONS

TO – toluene, TBTO – *tert*-butyltoluene, X_{TO} – conversion of toluene, $S_{4\text{-TBTO}}$ – selectivity as a ratio of 4-TBTO/Σ TBTO, $X_{4\text{-TBTO}}$ – conversion of 4-TBTO.

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