

tert-Butylation of toluene with isobutylene over zeolite catalysts: Influence of water

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Received 20 September 2006; received in revised form 14 February 2007; accepted 14 February 2007

Available online 20 February 2007

Abstract

tert-Butylation of toluene with isobutylene in the liquid phase was studied over large pore zeolite catalysts (H-MOR CBV 21A with Si/Al = 10.5 and H-BEA CP 814E with Si/Al = 12.5) and over cerium modified parent zeolite H-MOR with 2 wt.% of cerium. The influence of catalyst and different amount of added water on *tert*-butylation of toluene with isobutylene as alkylating agent on catalytic activity and *para*-selectivity was studied. H-MOR was slightly more active than H-BEA when *tert*-butylation of toluene with isobutylene in the liquid phase was carried on in the absence of water (45% and 40% conversion of toluene, respectively) at 180 °C after 8 h with *para*-selectivity for both catalysts near 68%. When different amount of water was added to the reaction mixture (0–200 mmol) the maximum conversion increased significantly in the case of both catalysts H-MOR and H-BEA and it was obtained at 120 mmol of water/40 mmol of toluene. At optimum amount of added water (120 mmol/40 mmol of toluene) the conversion over H-MOR and H-BEA of toluene reached 60% and 66% respectively which is maximum at given reaction conditions. Maximum constant *para*-selectivity for both catalysts was near 90% (93% for H-MOR and 90% for H-BEA respectively for maximum amount of added water (200 mmol/40 mmol of toluene)). The positive influence of optimal amount of added water on catalytic activity and *para*-selectivity in *tert*-butylation of toluene with isobutylene in the liquid phase over H-MOR and H-BEA is shown in this paper. *para*-Selectivity increased monotonically within studied range of added water. The influence of water on coke deposits on catalysts was demonstrated by TGA analyses which clearly demonstrated that added water has inhibition effect on carbon deposition. *tert*-Butylation of toluene with isobutylene over shape-selective zeolite catalysts H-MOR and H-BEA can be an ecofriendly process for industrial preparation of 4-*tert*-butyltoluene which is important intermediate product for fine chemicals.

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Keywords: Alkylation; *tert*-Butylation; Zeolites; Isobutylene; 4-*tert*-Butyltoluene; *para*-Selectivity; Water; TGA

1. Introduction

The acid catalyzed reactions as alkylation, acylation, isomerisation, etc., are important processes in hydrocarbon technology, petrochemistry as well as in fine chemicals syntheses [1,2]. 4-*tert*-Butyltoluene (4-TBTO) has commercial importance as intermediate product for 4-*tert*-butylbenzoic acid and 4-*tert*-butylbenzaldehyde which find applications as modifiers in alkylated resins, in production

of fragrances, pharmaceuticals and polymerization regulators for polyesters [2,3]. 4-TBTO is industrially produced by alkylation of toluene with isobutylene using Friedel–Crafts alkylation catalysts [4].

Typical homogeneous acid catalysts such as AlCl₃, BF₃, H₂SO₄, HF, H₃PO₄, etc., are still commonly employed in industrial processes but these catalysts are not environmentally friendly. Therefore considerable attention is devoted in the last years to the development of solid acid catalysts in petrochemistry and organic syntheses which are environmentally more acceptable. 4-*tert*-Butyltoluene can be produced by alkylation of toluene with different alkylation agents as isobutylene, diisobutylene, MTBE and *tert*-butanol in the liquid phase and in the presence of activated clay or silica-alumina catalysts at 150–200 °C [5].

Abbreviations: TO, toluene; TBA, *tert*-butanol; IB, isobutylene; TBTO, *tert*-butyltoluene; X_{TO}, conversion of TO; S_{4-TBTO}, selectivity = (4-TBTO/ΣTBTO) × 100

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Joffe et al. [6] studied different catalytic systems as AlCl_3 , $\text{AlCl}_3\text{-CH}_3\text{NO}_2$, sulphonic acid and polyphosphoric acid as catalysts in the liquid phase alkylation of toluene by C_4 -alcohols. By *tert*-butylation of toluene with *tert*-butanol and AlCl_3 as catalyst at 25 °C after 30 min they obtained mixture of *tert*-butyltoluenes with distribution of isomers near to the equilibrium composition (64% *meta*- and 36% *para*-isomer) and with the yield 64% of *tert*-butyltoluenes. *Ortho*-isomer (2-TBTO) was not present in the reaction products [6].

tert-Butylation of toluene with *tert*-butylchloride catalyzed by calcinated iron sulphate treated by hydrogen chloride carried out at room temperature leads to a 86% conversion of toluene with products distribution of 5% *meta*- and 95% *para*-isomer [7].

Up to now, the use of zeolites as catalysts in *tert*-butylation of toluene has not been widely studied. The use of Ni–Y zeolite has been published, but catalytic activity and *para*-selectivity to desired 4-TBTO was very low [8].

Mravec et al. [9] studied recently catalytic activity and selectivity of three large-pore commercial zeolites H-MOR, H-BEA and H-Y in the liquid phase *tert*-butylation of toluene with *tert*-butanol. Zeolite H-MOR (CBV 30A with Si/Al = 17.5) showed the best catalytic activity (59% conversion) and *para*-selectivity (near 90%) after 8 h. *tert*-Butylation was carried out at 180 °C and at autogenous pressure. An excess of *tert*-butanol in the reaction mixture had a positive effect to suppress secondary dealkylation reaction.

Sebastian et al. [10] investigated the influence of acidity on regio-selective *tert*-butylation of toluene over high silica mordenite catalysts with varying silica–alumina ratio in the vapour phase and in the temperature range 140–160 °C. They obtained the best results over commercial H-MOR zeolite with Si/Al = 90 with conversion of toluene 18% and selectivity to 4-TBTO 67% at 160 °C and at the molar ratio TBA/toluene equal 1:8 and at WHSV = 3.

Kostrab et al. [11] studied *tert*-butylation of toluene with *tert*-butanol in the liquid phase over large-pore mordenite zeolite catalyst (H-MOR CBV 21A with Si/Al = 10.5) and over cerium modified parent zeolite with 1–6 wt.% of cerium at 180 °C and at autogeneous pressure. Non-modified H-MOR was catalytic active with 66% conversion of toluene and *para*-selectivity near 84% at 180 °C after 8 h. Cerium modification of parent mordenite by impregnation decreased catalytic activity but enhanced and retained constant high *para*-selectivity. The maximal selectivity (near 91%) was obtained over catalysts with small amount of cerium/ceria (1–2 wt.%). The positive influence of cerium/ceria on *para*-selectivity can be explained by partial deactivation of outer surface of zeolite with inhibition effect on undesired secondary reactions (isomerisation, dealkylation, etc.).

Water strongly influences the catalytic behaviour of zeolites, modifying their catalytic performances and lifetime [12]. Investigation of the adsorption of water is therefore of great importance with respect to practical applications. Treatments of zeolites with water vapour may influence the Al distribution even at mild conditions, with or without changes of its overall content in the zeolite [13–17]. Attention to the re-hydration of

zeolite Beta has been paid in order to both verify the possible recovering of the Brønsted acidity lost during thermal treatments or to avoid the harmful effects of the Lewis acid sites during reaction [15–18].

Flego et al. [19] studied the influence of water adsorption on zeolite H-BEA (with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the range 20–33). They concluded that water adsorbed on zeolite H-BEA gives rise to different effects as a function of the location of the Al atoms in the zeolite and the amount of water introduced. At low water coverage, water decreases the density of the Lewis acid sites and favours the formation of new weak Brønsted acid sites. At high water coverage, the total density of acid Al(Td)-OH sites is suppressed due to the formation of highly hydrated OH species.

Schmitz and Song [12] studied combined use of partially dealuminated mordenites and added water in isopropylation of naphthalene with propylene and isopropyl alcohol over two dealuminated H-Mordenites having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 38 and 74. They have found considerably different activity patterns in response to added water. For H-MOR(38) they concluded that by water adsorption Brønsted acid sites are being passivated probably involving interactions between water and acidic hydroxyl groups since catalyst activity decreased monotonically with increased amount of added water. Further, they concluded that adsorption of water on the external acid sites of this catalyst has little effect on alkylated isomer selectivity. For H-MOR(74), the initial decrease in activity, which was accompanied by a decrease in α -alkylation, is attributed to passivation of external surface Brønsted acid sites. From increased conversion in the range of 20–45 mmol water/g they concluded that water addition generated new active sites that are located inside the shape-selective H-MOR channels. Beyond this range they observed conversion to decrease due to deactivation of Brønsted acid sites within the pores by adsorbed water.

The key quantitative insight into the structural properties of zeolites is based on TG–DTA experiments (thermal analysis). Crucial thermogravimetric (TG) mass losses are related to the phase changes represented by differential thermal analysis (DTA) effects of individual minerals occurring in temperature region 20–800 °C. Based on these, the tests employing TG mass losses and related DTA curves answer the question if the mineral is present in individual temperature regions and what is its quantitative state at individual temperature levels [29,30].

In our previous works [9,11] we have studied *tert*-butylation of toluene with *tert*-butanol in the liquid phase over large-pore zeolites H-MOR, H-BEA and H-Y. Since alkylation of toluene with *tert*-butanol in the first step involves dehydration of *tert*-butanol to isobutylene and water and since water is present in the reaction mixture for whole duration of experiment we have decided to study *tert*-butylation of toluene with isobutylene as alkylating agent in the liquid phase over large-pore zeolites H-MOR and H-BEA and to observe how different portions of added water influence the catalytic activity and *para*-selectivity of these catalysts. In addition we have performed experiments in which we have tried to understand whether there is any synergic effect when modification of external surface by ceria

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