

# The role of butylbenzene carbenium ions in the acid catalyzed cracking of polystyrene. Transformation of *n*-butylbenzene, *sec*-butylbenzene, *iso*-butylbenzene, *tert*-butylbenzene, 4-phenyl-1-butene, *n*-propylbenzene and *n*-hexylbenzene over silicaalumina and alumina acid catalysts

Marek Marczewski<sup>1</sup>  · Magdalena Kominiak<sup>1</sup> ·  
Magdalena Dul<sup>1</sup> · Hanna Marczevska<sup>1</sup>

Received: 24 May 2016 / Accepted: 27 June 2016 / Published online: 21 July 2016  
© The Author(s) 2016. This article is published with open access at Springerlink.com

**Abstract** The obtained results show that styrene dimers, which are the primary transition products of PS cracking undergo consecutive reactions over acid centers of high acid strength ( $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %);  $-10.8 < H_O \leq -7.9$ ) as well as centers of low acid strength ( $\gamma\text{-Al}_2\text{O}_3$ ;  $H_O > -3.3$ ) at sufficiently high reaction temperatures (723–773 K). It is proposed that phenylbutenyl carbenium ion obtained due to dealkylation reaction converts into coke by the successive elimination of  $\text{H}^+$  and  $\text{H}^-$  ions, which in turn take part in hydrogen transfer reactions resulting in the hydrogenation of styrene dimers to diphenylbutane. The dealkylation of this compound leads to active  $\gamma$ -butylbenzene carbenium ion which is a key intermediate for the formation of indane and naphthalene derivatives.

**Keywords** Polystyrene decomposition · Butylbenzenes reactions · Acid strength · Silicaalumina · Alumina

## Introduction

The catalytic processing of polymer wastes is a solution for their uncontrolled accumulation in numerous landfills. The choice of suitable catalysts makes it possible for the conversion of wastes to monomers, valuable raw materials for chemical syntheses or fuel components. Polystyrene (PS) is, one of the most important polymers, among polyolefins. Thus, PS waste recycling is an important challenge for modern technology.

---

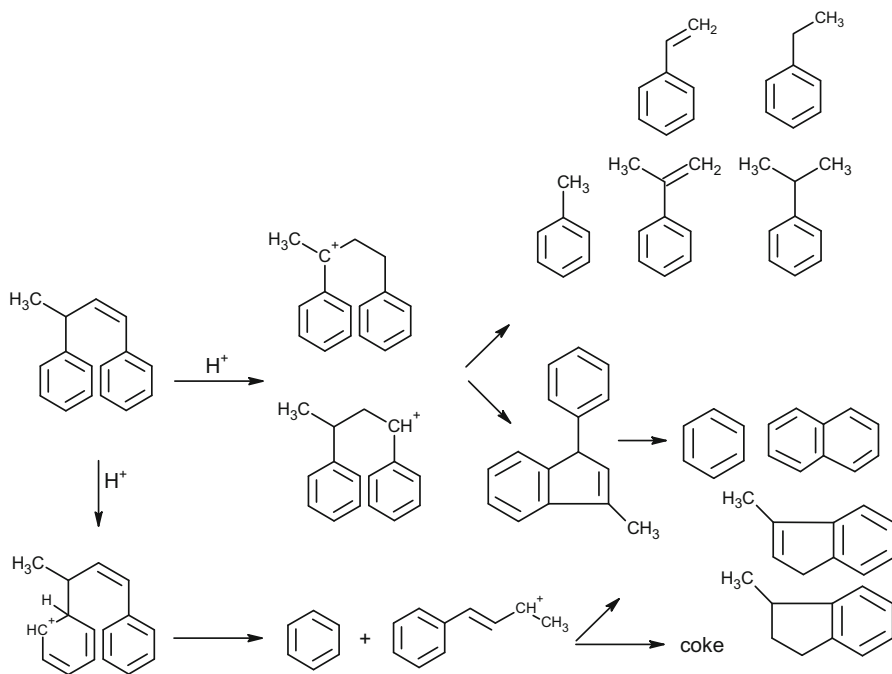
✉ Marek Marczewski  
marekm@ch.pw.edu.pl

<sup>1</sup> Chemistry Department, Warsaw University of Technology, Noakowskiego 3, 00-662 Warsaw, Poland

The activity of acidic, basic and redox catalysts in the transformation of PS has been the subject of numerous works. It was found that the first step of the transformation is a thermal degradation of PS to volatile oligomers (dimers, trimers) [1]. Such compounds undergo either further thermal cracking mostly to a monomer i.e. styrene [2–4] or in the presence of a catalyst, the transformation to the other final reaction products. The composition of the latter depends on the nature of catalyst active centers and definitely differs from the product composition of the thermal reaction. Benzene, toluene, ethylbenzene and cumene were obtained as the main cracking reaction products via  $\beta$ -scission over an acid catalyst. The other products such as the derivatives of indane and naphthalene resulted from internal alkylation followed by consecutive hydrogen transfer steps, both transformations are also catalyzed by acid sites [5–7]. By contrast, the action of basic active centers limits cracking and internal alkylation reactions but enhances the selectivity in depolymerization [8, 9].

The detailed mechanism of acid catalyzed styrene dimers transformation has already been proposed [10–12]. The main reaction pathways of thermally formed styrene dimers are presented below (Scheme 1).

The reaction commences with the addition of the proton to a carbon–carbon double bond in the aliphatic chain of the styrene dimer which results in the formation of a carbenium ion. The latter undergoes either cracking to toluene, ethylbenzene, styrene, cumene and  $\alpha$ -methylstyrene or internal alkylation to



**Scheme 1** Acid catalyzed styrene dimer transformation

phenylindane derivatives, which upon dealkylation heads to indane and naphthalene derivatives. In our work [12] based on the reaction of 2-phenyl-1-indene, it was observed that in the presence of a silicaalumina  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %) at 753 K, the reaction pathway of indane and naphthalene derivatives formation discussed above is possible though it is characterized by low conversion. On the other hand, we also pointed out that a more probable transformation is the reaction taking place with the formation of a saturated butylbenzene carbenium ion transition state [12].

The presented work has been done in order to determine which of different phenylbutyl carbenium ions can be the transition state in the formation of indane and naphthalene derivatives. The reactions of *n*-butylbenzene, *sec*-butylbenzene, *iso*-butylbenzene and *tert*-butylbenzene being the different phenylbutyl carbenium ions precursors over solid acid as  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %) at broad range of temperature 423–753 K were studied. The transformation of 4-phenyl-1-butene, which easily forms the respective carbenium ion, as well as *n*-propylbenzene and *n*-hexylbenzene were additionally examined. The two latter compounds were chosen to examine the reactivity of alkyl aromatics with other than four-carbon aliphatic chains. Some of the reactions were performed over  $\gamma\text{-Al}_2\text{O}_3$ , which is a weaker acid than silicaalumina acid. The acidity of both catalysts applied in the reactions has been already established by means of test reaction method and was found to be:  $-0.8 < \text{H}_0 \leq -7.9$  for  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %) and  $\text{H}_0 > -3.3$  respectively [13].

## Experimental

### Catalysts

The following solids were used as catalysts:  $\gamma\text{-Al}_2\text{O}_3$  (ABCR Karlsruhe,  $S_{\text{BET}}$  206  $\text{m}^2 \text{g}^{-1}$ ), silicaalumina:  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %) with 45 % of  $\text{Al}_2\text{O}_3$  (Ventron GmbH,  $S_{\text{BET}}$  114  $\text{m}^2 \text{g}^{-1}$ ). 1.02–1.20 mm grain fraction was used for catalytic measurements.

### Catalytic reactions

The reactions were performed in a flow reactor. 2  $\text{cm}^3$  of the catalyst was placed in a reactor and heated for 24 h at 753 K in a stream of dry air. After catalyst activation, the reactor was cooled to the desired temperature (from 473 to 753 K) and the reactant fed to it with an infusion pump at 3.6  $\text{cm}^3/\text{h}$  for 60 min.

FTIR investigation of pyridine adsorption. IR spectra were recorded on a Nicolet-FTIR-800 spectrometer with an accuracy of  $2 \text{ cm}^{-1}$ . A self-supported wafer was placed in a cell and activated for 3 h at 773 K in a stream of dry air. After cooling to room temperature (298 K), the spectrum was registered and pyridine was adsorbed (the pressure was equal to the saturated vapor pressure at this temperature). The spectra were recorded at room temperature after an earlier evacuation at 298 K.

## Materials

All the reactants: *n*-butylbenzene, *sec*-butylbenzene, *tert*-butylbenzene, *iso*-butylbenzene, *n*-propylbenzene and *n*-hexylbenzene were supplied by Aldrich.

## Analysis

The reaction products were analyzed in a GC (Agilent 6890 N with FID detector) equipped with a 30 m HP5 capillary column (I.D. 0.32 mm,  $d_f$  0.25  $\mu\text{m}$ , temperature 343 K (5 min), to 543 K at 3 K/min).

## Results

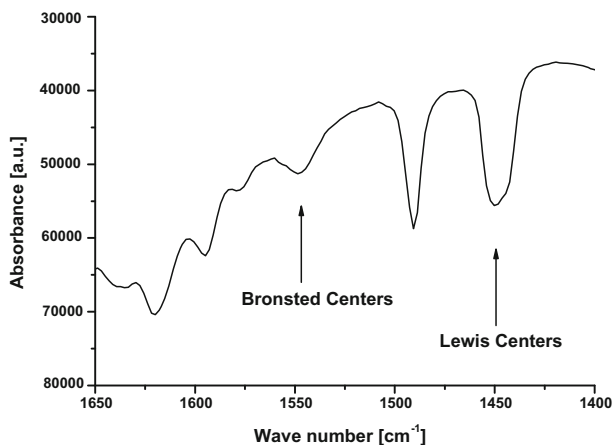
### Catalysts

Amorphous silicaalumina containing of 45 %  $\text{Al}_2\text{O}_3$  was used as an acid catalyst. FTIR measurements of pyridine adsorption at ambient temperature (Fig. 1) enable the evaluation of the nature of acid centers.

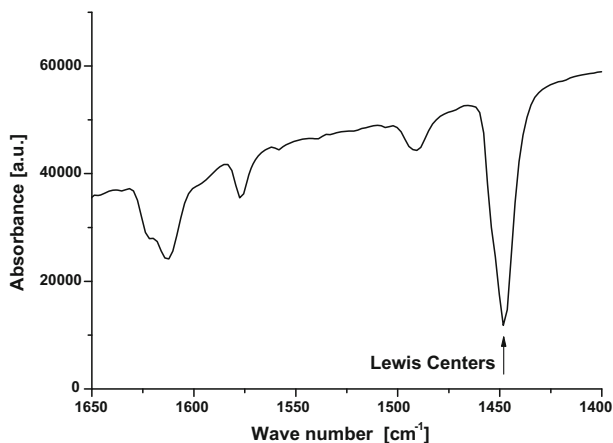
The bands at 1550 and 1450  $\text{cm}^{-1}$  indicate the existence of acid sites of both Brønsted and Lewis nature [14]. For comparison purposes, the other solid acid with weaker protic centers [13, 15] was also used. It was  $\gamma\text{-Al}_2\text{O}_3$ . The band at 1450  $\text{cm}^{-1}$  (Fig. 2) is ascribed to pyridine bonded to a Lewis acid center. This vibration confirms the essentially strong aprotic nature of alumina.

### Catalytic reactions

The results of the reactions performed over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  at 732 K are gathered in the Table 1.



**Fig. 1** FTIR spectrum of pyridine adsorbed at 298 K on  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst



**Fig. 2** FTIR spectrum of pyridine adsorbed at 298 K on  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst

**Table 1** The results of alkyaromatics reaction at 723 K in the presence of  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ (45 %) catalyst (flow reactor,  $2 \text{ cm}^3$  of the catalyst, reactant space velocity  $3.6 \text{ cm}^3 \text{ h}^{-1}$ , time on stream 60 min.)

Reactant	Products					
	Benzene	Toluene	Ethylbenzene	Phenylbutenes	Indenes <sup>a</sup>	Naphtalenes <sup>b</sup>
Conversion (%)						
<i>n</i> -Hexylbenzene	39.5	12.8	9.8	0.0	0.0	11.1
<i>n</i> -Propylbenzene	17.6	2.2	2.0	0.0	0.0	0.0
<i>iso</i> -Butylbenzene	29.7	1.3	0.8	0.5	1.0	0.9
<i>n</i> -Butylbenzene	41.5	10.1	5.7	1.7	4.6	2.5
<i>sec</i> -Butylbenzene	73.3	0.9	0.9		0.9	0.4
<i>tert</i> -Butylbenzene	88.1	0.0	0.0		0.0	0.0
4-Phenyl-1-butene	6.9	6.9	2.0	23.3	20.5	5.8

<sup>a</sup> Indane, indene and their methyl derivatives

<sup>b</sup> Naphthalene and methylnaphthalenes

The alkyaromatic reactants such as *n*-propylbenzene, *iso*-butylbenzene, *n*-butylbenzene, *sec*-butylbenzene and *tert*-butylbenzene undergo mainly dealkylation to benzene with conversions varying from 18 % (*n*-propylbenzene) to 88 % (*tert*-butylbenzene). The selectivities of these transformations were 80.2, 84.3, 62.9, 93.7 and 100 % for *n*-propylbenzene, *iso*-butylbenzene, *n*-butylbenzene, *sec*-butylbenzene and *tert*-butylbenzene respectively. For *n*-hexylbenzene, the dealkylation product benzene appeared with a selectivity of 49.1 % while only 10.3 % was achieved for 4-phenyl-1-butene. For these two catalysts,  $\beta$ -scission in side chain leading to toluene and ethylbenzene as well as an internal alkylation resulting in the formation of indane and naphthalene derivatives were the main transformation

routes. In the case of 4-phenyl-1-butene, double bond isomerization was also observed as an additional reaction. Indane, naphthalene and their derivatives were formed if *n*-hexylbenzene, *n*-butylbenzene, *iso*-butylbenzene, *sec*-butylbenzene and 4-phenyl-1-butene were fed as reactants. These products were not observed for the reactions with *n*-propylbenzene and *tert*-butylbenzene.

The results of the chosen reactions performed over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 732 K are gathered in the Table 2.

Only *tert*-butylbenzene was observed to undergo distinct dealkylation (conversion 21 %, selectivity 100 %) in the presence of this weaker solid acid. Benzene was obtained in the dealkylation of *sec*-butylbenzene and 4-phenyl-1-butene with much less conversion ( $\sim$ 1 %). The selectivity of *sec*-butylbenzene dealkylation was 100 % while for 4-phenyl-1-butene it was only 1.6 %. Double bond isomerization (selectivity 67.9 %), cracking in the side chain (selectivity 15.8 %) and internal alkylation (selectivity 14.7 %), were observed to be the main reactions.

The transformation of the chosen reactants over SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>(45 %) catalyst at different temperatures was also examined. Benzene formation depended strongly on temperature and the structure of the reactant (Fig. 3).

*Tert*-butylbenzene underwent reaction from the lowest point in the temperature range (423 K). Apart from benzene, di-*tert*-butylbenzenes were also identified in the reaction products indicating that disproportionation of *tert*-butylbenzene took place. This is better illustrated when benzene to di-*tert*-butylbenzene ratio against reaction temperature is presented (Fig. 4).

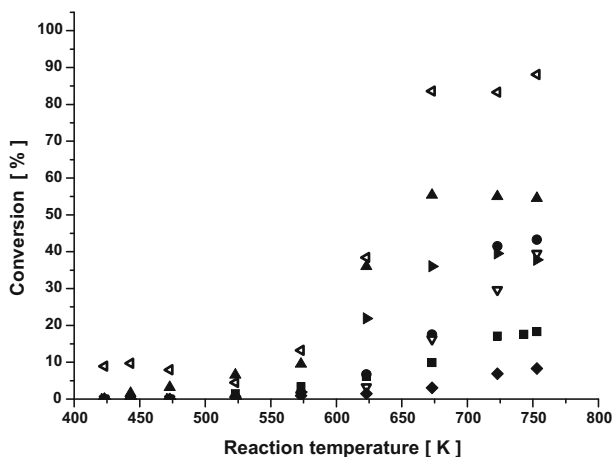
In the temperature range from 423 to 532 K, the ratio is close to unity ( $\sim$ 1.3). In this case benzene is formed due to *tert*-butylbenzene disproportionation. The dealkylation of *tert*-butylbenzene became the prevailing reaction and the value of the benzene: di-*tert*-butylbenzene ratio began to increase exponentially when the temperature exceeded 523 K. Disproportionation reaction was not observed in the case of other reactants and benzene was formed solely in the dealkylation reaction. *Sec*-butylbenzene began reacting to react at 443 K while for the remaining reactants i.e. *n*-propylbenzene, *n*-butylbenzene, *iso*-butylbenzene, *n*-hexylbenzene and

**Table 2** The results of alkylaromatics reaction at 723 K in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (flow reactor, 2 cm<sup>3</sup> of the catalyst, reactant space velocity 3.6 cm<sup>3</sup> h<sup>-1</sup>, time on stream 60 min.)

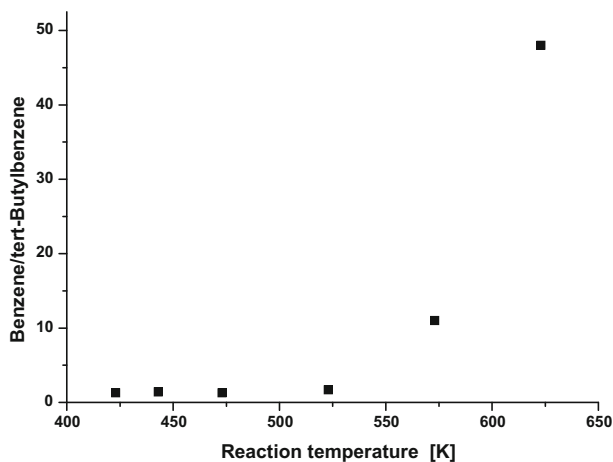
Reactant	Products					
	Benzene	Toluene	Ethylbenzene	Phenylbutenes	Indenes <sup>a</sup>	Naphtalenes <sup>b</sup>
Conversion (%)						
<i>n</i> -Butylbenzene	0.0	0.0	0.0	0.0	0.0	0.0
<i>sec</i> -Butylbenzene	0.8	0.0	0.0	0.0	0.0	0.0
<i>tert</i> -Butylbenzene	20.7	0.0	0.0	0.0	0.0	0.0
4-Phenyl-1-butene	1.0	6.9	2.8	41.7	6.9	2.1

<sup>a</sup> Indane, indene and their methyl derivatives

<sup>b</sup> Naphthalene and methylnaphthalenes



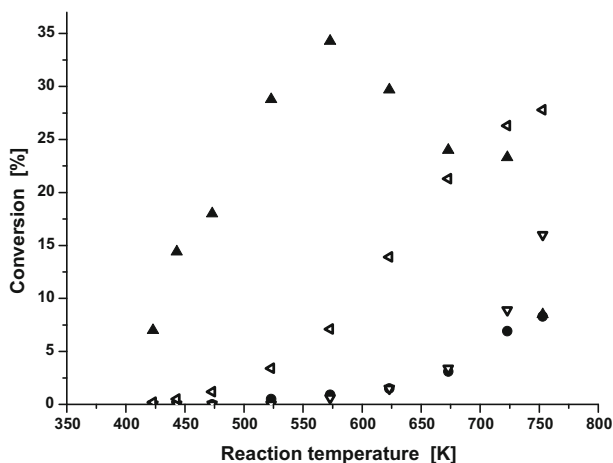
**Fig. 3** Benzene formation from: (left triangle arrow) *tert*-butylbenzene, (filled triangle) *sec*-butylbenzene, (filled inverted triangle) *iso*-butylbenzene, (circle) *n*-butylbenzene, (right filled triangle arrow) *n*-hexylbenzene, (filled square) *n*-propylbenzene, (filled diamond) 4-phenyl-1-benzene over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst for different reaction temperatures. Tubular flow reactor, catalyst volume:  $2\text{ cm}^3$ , reactant flow rate  $3.6\text{ cm}^3\text{ h}^{-1}$ , time on stream 60 min



**Fig. 4** The dependence of benzene/*tert*-butylbenzene ratio on reaction temperature over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst for *tert*-butylbenzene reaction. Tubular flow reactor, catalyst volume:  $2\text{ cm}^3$ , reactant flow rate  $3.6\text{ cm}^3\text{ h}^{-1}$ , time on stream 60 min

4-phenyl-1-butene, this took place at the at 523–573 K temperature range. Such a sequence of benzene appearance in the reaction products is in agreement with the stability of carbenium ions formed in the transformation: tertiary for *tert*-butylbenzene, secondary for *sec*-butylbenzene and primary for other reactants.

4-Phenyl-1-butene is an unusual reactant because a proton can be attached both to its aromatic ring as well as to the carbon–carbon double bond in the side chain.



**Fig. 5** 4-Phenyl-1-butene transformation over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst for different reaction temperatures. (filled circle) dealkylation reaction, (inverted triangle) cracking reaction, (filled triangle) isomerization reaction, (left triangle arrow) internal alkylation reaction. Tubular flow reactor, catalyst volume:  $2\text{ cm}^3$ , reactant flow rate  $3.6\text{ cm}^3\text{ h}^{-1}$ , time on stream 60 min

The transformation sequence for this reactant over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst at different temperatures is presented in Fig. 5 as follows: isomerization and internal alkylation (above 423 K), dealkylation (above 523 K) and side chain cracking (573 K and above).

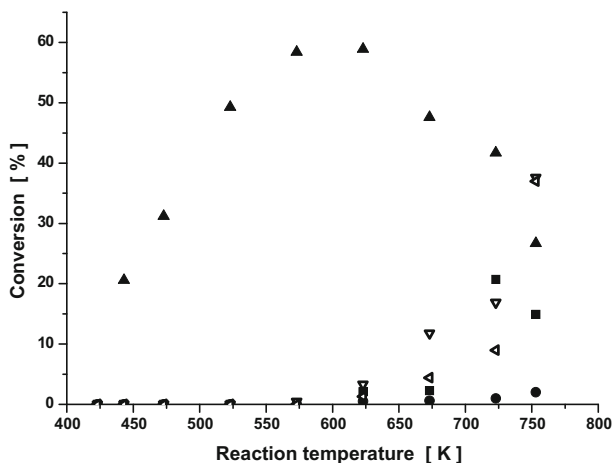
The transformation of chosen reactants over  $\gamma\text{-Al}_2\text{O}_3$  catalyst at different temperatures was also examined. The results showed that only *tert*-butylbenzene and 4-phenyl-1-butene underwent distinct reactions (Table 2; Fig. 6).

The other reactants underwent only dealkylation but with very low conversion values (*n*-butylbenzene: 1.2 % at 753 K, *sec*-butylbenzene 0.8 % at 732 K). Only 4-phenyl-1-butene reacted at low temperatures (from 443 to 573 K). The only products observed were phenylbutenes with the double bond in the side chain appearing at different positions. The yield of the obtained isomers increased with temperature up to 60 %. Benzene (dealkylation), toluene and ethylbenzene (side chain cracking) and indane derivatives (internal alkylation) were observed among transformation products at 623 K. Simultaneously, a gradual decrease in conversion to 4-phenyl-1-butene isomers was observed. *Tert*-butylbenzene underwent only dealkylation reaction over  $\gamma\text{-Al}_2\text{O}_3$  at temperatures above 623 K.

## Discussion

Amorphous silicaalumina and alumina are frequently used as catalysts for acid initiated reactions. It is believed that Brønsted acid centers (bridged type groups  $\text{Al-OH-Si}$ ) [16] are responsible for the activity of silicaaluminas, while Lewis sites ( $\text{Al}^{3+}$  cations) and OH groups activated by adjacent Lewis centers [17] are considered as the source of  $\gamma\text{-Al}_2\text{O}_3$  catalytic activity. The acid strength of the protic





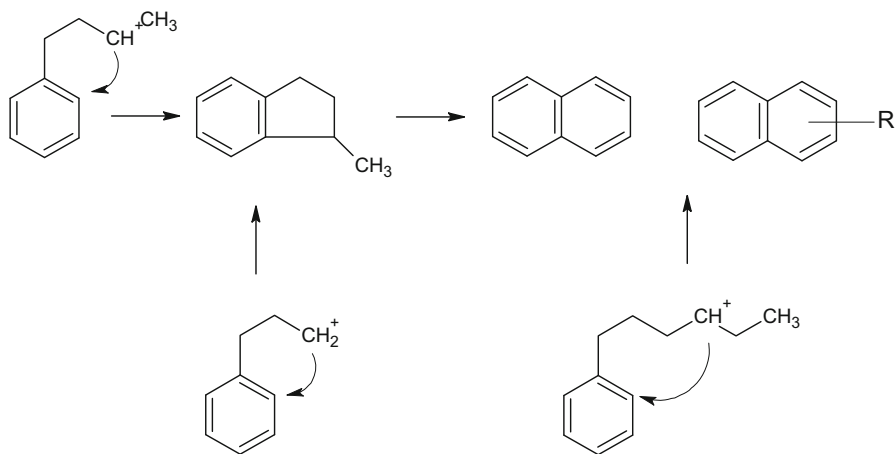
**Fig. 6** *Tert*-butylbenzene and 4-phenyl-1-butene reactions over  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst at different reaction temperatures. (filled square) *tert*-butylbenzene dealkylation reaction, (filled circle) 4-phenyl-1-butene dealkylation reaction, (filled triangle) 4-phenyl-1-butene isomerization reaction, (inverted triangle) 4-phenyl-1-butene cracking reaction, (left triangle arrow) 4-phenyl-1-butene internal alkylation reaction. Tubular flow reactor, catalyst volume: 2  $\text{cm}^3$ , reactant flow rate 3.6  $\text{cm}^3 \text{h}^{-1}$ , time on stream 60 min

sites of alumina is much lower than those of silicaalumina and zeolites but higher than for  $\text{SiO}_2$  [16, 17]. The results of pyridine adsorption followed by FTIR measurements (Fig. 1) confirmed the presence of Brønsted acid centers on the surface of  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ (45 %) catalyst. Test reactions (at 303 K) of  $\alpha$ -methylstyrene, styrene, 2,4-diphenyl-4-methyl-1-pentene, cyclohexene and 4-phenyl-1-butene which can be performed over silicaalumina and the lack of *tert*-butylbenzene transformations over it head to the evaluation of its acid strength to be in the  $-10.8 < \text{H}_\text{O} \leq -7.9$  range [13]. FTIR measurements of pyridine adsorption on  $\gamma$ - $\text{Al}_2\text{O}_3$  (Fig. 2) and the lack of  $\alpha$ -methylstyrene reaction at ambient temperature indicate that the acid strength of Brønsted sites of alumina is weak ( $\text{H}_\text{O} > -3.3$ ) [13]. The transformation of different butylbenzenes such as *tert*-butylbenzene, *sec*-butylbenzene, *n*-butylbenzene, iso-butylbenzene as well as 4-phenyl-1-butene were studied (Figs. 3 and 6). Benzene formation can be considered as an additional test for acid properties due to dealkylation and disproportionation reactions. The results confirmed a difference in acidity between  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ (45 %) and  $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts. Silicaalumina, a strong solid acid, initiated dealkylation of all butyl- and butylene aromatics at the 423–573 K temperature range while the protonation of the aromatic rings only of the most reactive compounds such as *tert*-butylbenzene and *sec*-butylbenzene started over alumina at considerably higher temperatures (723–753 K). These two different solid acids were used to study reactions of possible transition states (carbenium ions) in PS cracking.

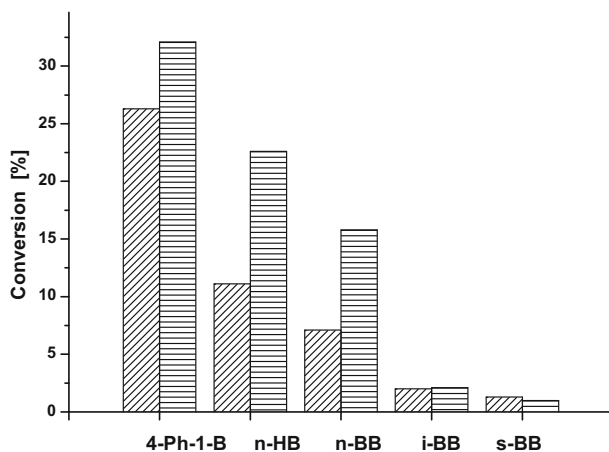
The catalytic degradation of PS is a complex process. The first step is of thermal nature and involves the decomposition of PS to volatile oligomers, mainly dimers (diphenylbutenes), whose protonation heads to carbenium ions which undergo further transformation. The dealkylation of diphenylbutenes heads to the formation

of benzene as well as an aromatic carbenium ion where the positive charge is located on an unsaturated four-carbon side chain (Scheme 1). This carbocation can undergo two types of transformation: the first heading to coke, also a less effective second type, to indane and naphthalene derivatives [12, 18]. We assumed that  $H^+$  and  $H^-$  ions evolved during coke formation [19] could hydrogenate styrene dimers to dibutylbenzene, whose dealkylation heads to saturated butylbenzene carbenium ion, which can be considered a transition state in the reactions which take place in the catalytic degradation of PS. It is assumed that one of the possible reactions i.e. internal alkylation (Scheme 2) leads to of indane and naphthalene derivatives, which were actually observed in the reaction products. It was therefore necessary to determine which of the butyl- and butenylbenzene carbenium ions would most likely be considered precursors for condensed aromatics. To achieve this, the different isomers of mono butylbenzenes as well as 4-phenyl-1-butene were selected as reactants. The reactions of other alkylaromatics such as *n*-propylbenzene and *n*-hexylbenzene were also examined. *n*-Propylbenzene may undergo reaction through a primary carbenium ion to obtain indene while stable naphthalene derivatives are obtained from *n*-hexylbenzene through the secondary carbenium ion reaction pathway. The results obtained for  $SiO_2-Al_2O_3(45\%)$  catalyst (Table 1; Fig. 5) indicate that the acid strength of the catalyst is sufficient for the formation of butylbenzene carbenium ions. The cracking to simple alkylaromatics such as toluene and ethylbenzene, and also internal alkylation reaction products which were observed are an indirect indication of the presence of such carbocations. The following reactions were observed at 723 K (Fig. 7).

The compounds with straight side chains such as: *n*-hexylbenzene, *n*-butylbenzene and 4-phenyl-1-butene were more reactive (dealkylation, internal alkylation) than their counterparts with branched side chain (*iso*-butylbenzene) and with phenyl substituent localized inside of aliphatic chain (*sec*-butylbenzene). Both *n*-propylbenzene and *tert*-butylbenzene did not undergo any internal alkylation reaction.



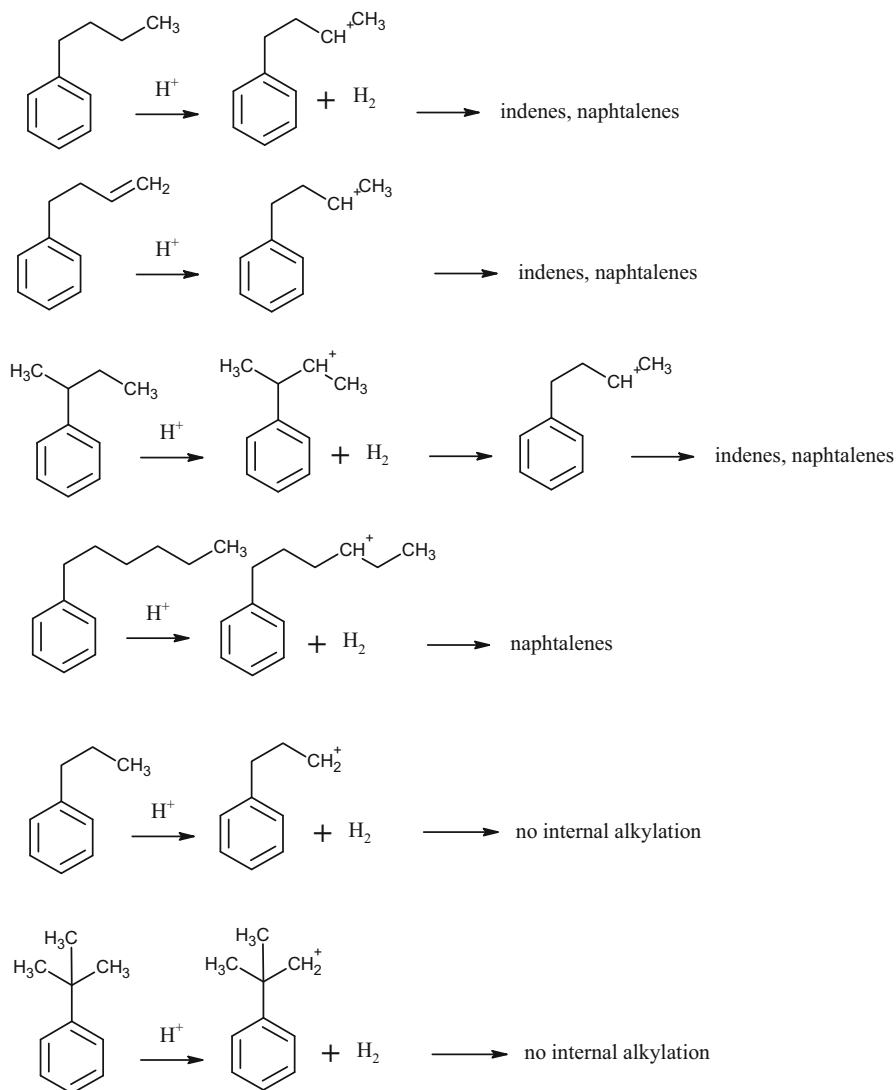
**Scheme 2** Phenylbutyl carbenium ion internal alkylation



**Fig. 7** Reaction observed: (slanting line square) internal alkylation, (horizontal line square) cracking reaction for different reactants: (*n*-Ph-1-B) 4-phenyl-1-benzene, (*n*-HB) *n*-hexylbenzene, (*n*-BB) *n*-butylbenzene, (*i*-BB) *iso*-butylbenzene and (*s*-BB) *sec*-butylbenzene over  $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)$  catalyst at 723 K. Tubular flow reactor, catalyst volume:  $2\text{ cm}^3$ , reactant flow rate  $3.6\text{ cm}^3\text{ h}^{-1}$ , time on stream 60 min

These results indicate that a secondary carbenium ion with a positive charge localized in the side chain in  $\gamma$  position is formed in the reaction of internal alkylation of butylbenzenes (Scheme 3). The unique product of such a reaction is methyl indane, which undergoes further isomerization to obtain naphthalene [18]. The latter can also be formed as a product of the cyclization of primary  $\delta$ -butylbenzene carbenium ion. However, the absence of cyclization products in *n*-propylbenzene and *tert*-butylbenzene indicates that primary carbocations are not formed in their reactions. Such reaction pathway explains also the low conversion in cyclization observed for *iso*-butylbenzene and *sec*-butylbenzene. This type of reaction is only possible when active  $\gamma$ -butylbenzene carbenium ions are formed through skeletal isomerization. This reaction is slow; therefore, the naphthalene yield is low. The  $\gamma$ -butylbenzene carbenium ion can be formed most easily by the attachment of a proton to the double bond in 4-phenyl-1-butene, therefore indane and naphthalene derivatives are obtained from this compound with the highest yields. In the case of *n*-hexylbenzene, a secondary  $\delta$ -butylbenzene carbenium ion which is probably formed, directly undergoes internal alkylation to obtain naphthalene derivatives.

$\gamma\text{-Al}_2\text{O}_3$  is a weaker protic acid than the silicaalumina. Brønsted acid centers of alumina were able to protonate the aromatic ring only in the case of *tert*-butylbenzene and *sec*-butylbenzene exclusively at high temperatures (732–753 K). These centers were not able to convert *n*-butylbenzene into an active  $\gamma$ -butylbenzene carbenium ion (Table 2; Fig. 6). When 4-phenyl-1-butene was used as the reaction substrate, such carbocation was formed at temperatures as low as 443 K. It underwent only isomerization resulting different phenylbutenes formation. An increase in the reaction temperature up to 623 K led to the appearance of toluene

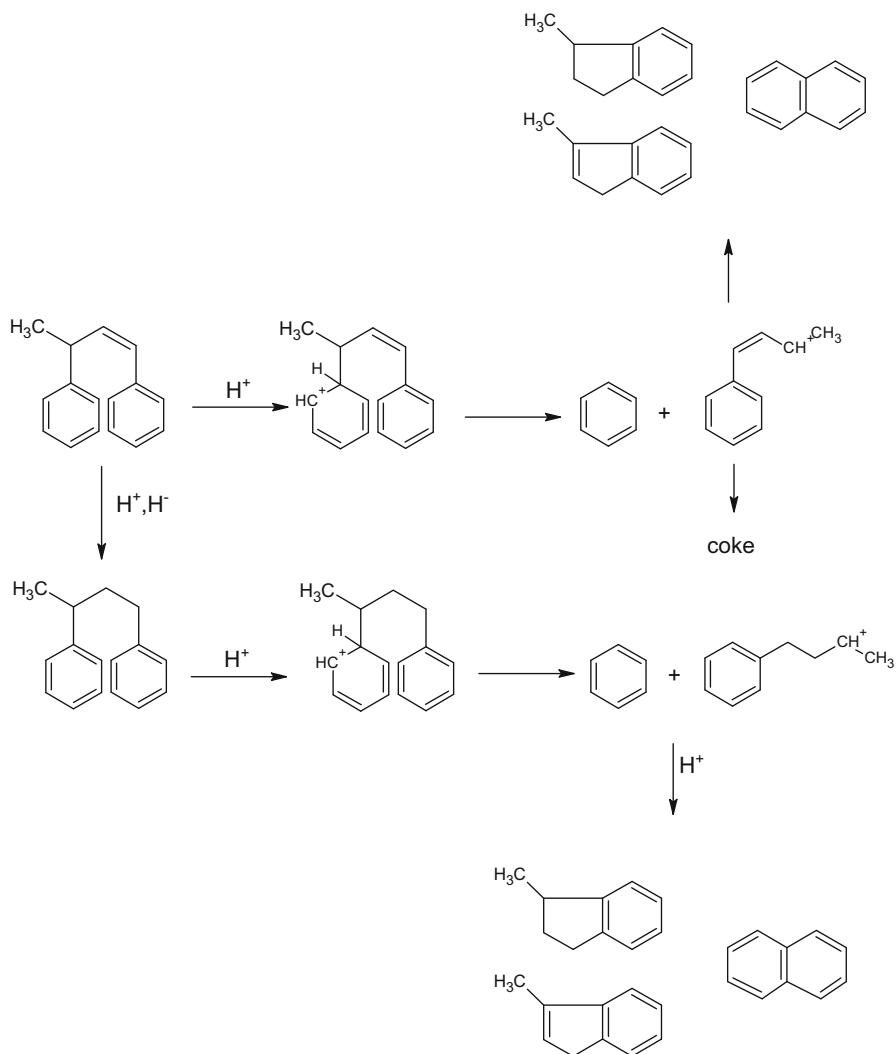


**Scheme 3** Acid initiated alkyl—and alkenyl aromatics reactants transformations occurring at side chain

and ethylbenzene (cracking) and indane and naphthalene derivatives (internal alkylation) in the reaction products.

The obtained results are the basis for the proposal of a more detailed scheme for polystyrene dimer transformation (Scheme 4).

The styrene dimer, a product of the decomposition of PS undergoes dealkylation in the presence of acid centers. Benzene and phenylbutenyl carbenium ion are obtained as a result of dealkylation. Due to the presence of a conjugated system of bonds, the latter can preferably successively detach  $H^+$  and  $H^-$  ions to form coke



**Scheme 4** Acid catalyzed indane and naphthalene derivatives formation during PS cracking

deposit [11, 19]. The protons and hydride ions formed can participate in hydrogen transfer reactions heading to the hydrogenation of styrene dimer to diphenylbutane. After the dealkylation step, the latter is transformed to benzene and  $\gamma$ -butylbenzene carbenium ion which undergo cyclization according to the internal alkylation mechanism. Such transformation can proceed, at typical PS cracking temperatures (723–773 K), not only over strong Brønsted acids ( $SiO_2-Al_2O_3$ (45 %);  $-10.8 < H_O \leq -7.9$ ) but also with much less acidic catalysts ( $\gamma-Al_2O_3$ ;  $H_O > -3.3$ ).

## Conclusion

The obtained results show that styrene dimers, which are the primary transition products of PS cracking undergo consecutive reactions over acid centers of high acid strength  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (45 %);  $-10.8 < \text{H}_\text{O} \leq -7.9$ ) as well as centers of low acid strength ( $\gamma\text{-Al}_2\text{O}_3$ ;  $\text{H}_\text{O} > -3.3$  at sufficiently high reaction temperatures (723–773 K). It is proposed that phenylbutenyl carbenium ion obtained due to dealkylation reaction converts into coke by the successive elimination of  $\text{H}^+$  and  $\text{H}^-$  ions which in turn take part in hydrogen transfer reactions resulting in the hydrogenation of styrene dimers to diphenylbutane. The dealkylation of this compound leads to active  $\gamma$ -butylbenzene carbenium ion, which is a key intermediate for the formation of indane and naphthalene derivatives.

**Acknowledgments** This work was sponsored by Faculty of Chemistry, Warsaw University of Technology.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

1. Woo OS, Ayala N, Broadbelt J (2000) *Catal Today* 55:161–171
2. Chauhan RS, Gopindath S, Razdam P, Delattre C, Nirmala GS, Natarajan R (2008) *Waste Manag* 28:2140–2145
3. Ide S, Ogawa T, Kuroki T, Ikemura T (1984) *J Appl Polym Sci* 29:2561–2571
4. Xie C, Liu F, Yu S, Xie F, Li L, Zhang S, Yang J (2998) *Catal Commun* 9:1132–1136
5. Lin R, White RL (1997) *J Appl Polym Sci* 66:1287–1298
6. Lee SY, Yoon JH, Kim JR, Park DW (2002) *J Anal Appl Pyrolysis* 64:71–83
7. Lee SY, Yoon JH, Kim JR, Park DW (2001) *Polym Degrad Stab* 74:297–305
8. Zhang Z, Hirose T, Nishio S, Morioka Y, Azuma N, Ueno A, Ohkita H, Okada M (1995) *Ind Eng Chem Res* 34:4514–4519
9. Ukei H, Hirose T, Horikawa S, Tahai M, Azuma N, Ueno A (2000) *Catal Today* 62:59–75
10. Marczewski M, Kamińska E, Marczewska H (2013) *Reac Kinet Mech Cat* 108:59–68
11. Marczewski M, Kamińska E, Marczewska H, Ciecierska K, Walczyk W (2014) *Reac Kinet Mech Cat* 111:549–567
12. Marczewski M, Kamińska E, Marczewska H, Godek M, Rokicki G, Sokołowski J (2013) *Appl Catal B: Env* 129:236–246
13. Marczewski M, Marczewska H, Popielarska D, Ciecierska K, Herman M, Kamińska A, Kamińska E, Wiedro R, Roguska A (2015) *Reac Kinet Mech Cat* 114:513–533
14. Jacobs P (1984) In: Dalannay F (ed) *Characterization of heterogeneous catalysts*. Marcel Dekker, Amsterdam, pp 367–401
15. Gabrienko AA, Arzumanov SS, Toktariev AT, Stepanov AG (2012) *J Phys Chem C* 116:21430–21438
16. Marcellly C (2006) *Acido-basic catalysis*. Edition Technip, Paris, pp 93–96
17. Trombetta M, Busca G, Rossini SA, Piccoli V, Cornero U (1997) *J Catal* 168:334–348
18. Xu T, Haw JF (1994) *J Am Chem Soc* 116:10188–10195
19. Gates BC, Katzer JR, Schuit GCA (1979) *Chemistry of catalytic processes*. McGraw-Hill Book Company, New York, pp 12–18