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An in situ ^{13}C MAS NMR study of benzene isopropylation over H-ZSM-11: cumene formation and side-reactions

Irina I. Ivanova^a, Daniel Brunel^b, Janos B. Nagy^a, Eric G. Derouane^{a,*}

^a *Facultés Universitaires N.-D. de la Paix, Laboratoire de Catalyse, 61, Rue de Bruxelles, B-5000 Namur, Belgium*

^b *Ecole Nationale Supérieure de Chimie, Laboratoire de Chimie Organique Physique, 8, Rue Ecole Normale, F-34053 Montpellier, France*

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Abstract

^{13}C -MAS NMR in the adsorbed phase was performed in situ to investigate the mechanism of the main and side-reaction pathways of benzene isopropylation over H-ZSM-11. Propene 1- ^{13}C , propene 2- ^{13}C and benzene (1–6)- ^{13}C were used as labelled reactants in different runs. Cumenes selectively labelled with ^{13}C -isotopes either on α - or on β -positions of the alkyl chain or in the aromatic ring were synthesized in situ at room temperature with 100% yield when the excess of benzene was used. In contrast, when the molar ratio of the reacting propene and benzene was equal to 1, alkylation was accompanied by propene oligomerization, followed by isomerization and cracking of oligomers and sec-butylbenzene formation. The results on tracing the fate of 1- ^{13}C and 2- ^{13}C carbon atoms of propene in course of benzene isopropylation are in line with classical carbenium ion alkylation mechanism. Desorption and/or diffusion of cumene is supposed to be a rate limiting step. The side-reactions become significant at 473 K due to cumene conversion. The main product of cumene conversion is n-propylbenzene, formed via intermolecular reaction of cumene and benzene. At long reaction times, the formation of n-propylbenzene is accompanied by complete scrambling of the alkyl chain carbon atoms of both cumene and n-propylbenzene. Formation of cracking products, i.e., toluene, ethylbenzene and butylbenzenes is also observed. The rate of isomerization is higher than the rates of scrambling and fragmentation. External surface passivation by silica deposition was performed to differentiate processes taking place at the external surface or inside the channels. All reaction pathways were found to proceed on both external and internal zeolite surface.

Keywords: Alkylation; Benzene; Cumene; H-ZSM-11; Isomerization; MAS NMR; Mechanism; Propene; Zeolite

1. Introduction

Alkylation of benzene with propylene leads to cumene – an important current intermediate in the production of phenol, acetone, and α -methylstyrene. The industrial processes are based on the use of Friedel–Crafts [1] or phosphoric acid on silica catalysts [2]. The environmental and corrosion drawbacks of these processes can be overcome by using solid acid catalysts, e.g., zeolites. In view of

this, extensive studies of benzene alkylation with propene on HY [3], rare-earth-modified Y [4,5], mordenite [5], ZSM-5 [6,7], ZSM-11 [8,9], ZSM-12 [5,10], EU-1 [11] zeolites, etc ... have been carried out.

Intermediate pore size zeolites, ZSM-5 and ZSM-11, were shown to be the preferred catalysts for aromatic reactions due to high coke resistance and stability [12–14]. However, the formation of cumene (isopropylbenzene, IPB) on these catalysts is accompanied by a variety of side-reac-

* Corresponding author.

tions: diisopropylation towards diisopropylbenzenes (DIPB), isomerization to *n*-propylbenzene (NPB), fragmentation towards toluene (T) and ethylbenzene (EB) and butylbenzene (BB) formation [6–9]. It is therefore of interest to search for possibilities to suppress these side-reactions. For this purpose, understanding the mechanism of this process could provide some directing clues. However, no direct information on this mechanism is available as yet.

The objective of our work was to understand the pathways leading to by-products, especially, NPB the most undesired one with respect to further processing of cumene to phenol and acetone. In situ ^{13}C MAS NMR of ^{13}C -labelled molecules in the adsorbed phase was used for this purpose. It permits one to observe different kinds of adsorbed entities, to distinguish unequivocally between mobile and adsorbed species, to monitor their fate during the course of the reaction, and to determine approximate reaction rates [15–20]. As a result, reaction mechanisms or pathways can be proposed.

2. Experimental

2.1. Catalysts

Zeolite H-ZSM-11 (Si/Al = 25) was prepared by ammonium exchange of Na-ZSM-11 and calcination at 823 K in air [8].

External surface sites passivation was accomplished by deposition of polymethylsiloxane (PMS) followed by calcination. The resulting catalyst was characterized by SEM and XPS. The total acidity was controlled by NH_3 TPD, the acidity of the external surface was characterized by ESR of adsorbed 2,2,6,6-tetramethyl-piperidine-1-oxyl. The catalytic activity was tested in model reactions: the conversion of mesitylene and the *p*-ethyltoluene synthesis. The combination of these methods and tests provided complementary proves for selective silica deposition on the external surface. The internal structure remains practically unaffected with this treatment. These

results are described and discussed elsewhere [21].

2.2. Labelled compounds

Propene 1- ^{13}C (99.9% ^{13}C), isopropanol 2- ^{13}C (99.9% ^{13}C), and benzene (5% ^{13}C) were obtained from MSD isotopes. Propene 2- ^{13}C (99.9% ^{13}C) was prepared at 623 K by dehydration of isopropanol 2- ^{13}C (99.9% ^{13}C) on zeolite NaY with 100% conversion and selectivity.

Cumene with ^{13}C in β -position of the alkyl chain and in the aromatic ring was synthesized directly in the NMR cell over H-ZSM-11 by benzene (5% ^{13}C) alkylation with propene 1- ^{13}C (99% ^{13}C), at room temperature with 100% yield and selectivity. High selectivity and yield of cumene formation is a unique feature of the reaction conditions (298 K, adsorbed phase).

2.3. In situ ^{13}C MAS NMR measurements

The powdered catalyst samples (0.07 ± 0.01 g) were evacuated in the NMR cells (Wilmad, 5 mm o.d. or 5.6 mm o.d. with constrictions) to a final pressure of $6 \cdot 10^{-6}$ Torr after heating for 8 h at 573 K, and cooled down to 298 K before adsorption. To avoid propene oligomerization and polymerization, and DIPB formation, benzene was always adsorbed first and the benzene/propene molar ratio was never less than 1. Benzene and cumene were dosed gravimetrically, while propene was dosed volumetrically. After loading reactants, the NMR cells, maintained at 77 K to ensure a quantitative adsorption were carefully sealed to achieve proper rotor balance and high spinning rates in the MAS NMR probe. The list of samples is reported in Table 1.

In situ ^{13}C NMR measurements were carried out on CXP-200 and MSL-400 Bruker spectrometers operating at 50.3 and 100.6 MHz, respectively. Quantitative conditions were achieved using high-power gated proton decoupling with suppressed NOE effect (90° pulse, recycling delay 4 s). The highly symmetrical 5.6 mm o.d. sealed capsules were used in a standard Bruker MAS

Table 1
Sample preparation

Experiment	NMR cell type	Catalyst	Loaded reagents (molecules/u.c.)					
			C ₆ H ₆	C ₆ H ₆ (1-6)- ¹³ C	C ₃ H ₆ 1- ¹³ C	C ₃ H ₆ 2- ¹³ C	IPB (1-6),β- ¹³ C	IPB
A	1	H-ZSM-11	9	–	–	1	–	–
B	1	H-ZSM-11	9	–	1	–	–	–
B'	2	H-ZSM-11	9	–	1	–	–	–
C	1	H-ZSM-11	9	–	9	–	–	–
D	1	H-ZSM-11	8	–	–	–	4	–
E	1	H-ZSM-11	–	8	–	–	–	4
F	1	Silylated H-ZSM-11	9	–	3	–	–	–

Note: NMR cell No. 1 is obtained from 5.6 mm o.d. tube with constriction (Wilmad). NMR cell height 10 mm; NMR cell volume: 0.24 cm³. NMR cell No. 2 is obtained from 5.0 mm o.d. tube without constriction (Wilmad). NMR cell height 30 mm; NMR cell volume: 0.59 cm³.

probe, while the 5.0 mm o.d. sealed capsules were used directly in a home-made probe [22,23]. The spinning rates were up to 4 kHz for the former and 2.5 kHz for the latter.

In a typical in situ experiment, the sealed NMR cell is rapidly heated to a selected temperature between 298 and 473 K and maintained at this temperature for various lengths of time. MAS NMR spectrum is recorded at ambient temperature after rapid cooling of the sample cell. After collection of the NMR data, the NMR cell is returned to reaction conditions, and heated for progressively longer periods of time.

2.4. Definitions

Quantification of the results requires a number of definitions which are listed below:

- (i) Conversion of the reactant *r* at a time *t*:
 $X_{r,t} = (1 - I_{r,t}/I_{r,0}) \cdot 100$ (%), where:
 $I_{r,t}$ – integrated intensity of the resonance line, corresponding to reactant *r* after heating the NMR cell for *t* min;
 $I_{r,0}$ – integrated intensity of the resonance line, corresponding to reactant *r* at initial time.
- (ii) Yield of product *p* at a time *t*: $Y_{p,t} = I_{p,t}/I_{r,0} \cdot 100$ (%), where:
 $I_{p,t}$ – integrated intensity of the resonance line, corresponding to product *p* after *t* min of reaction.

- (iii) Concentration of product *p* at a time *t*:

$$C_{p,t} = Y_{p,t} \cdot C_{r,0} \text{ (molecules/u.c.)}, \text{ where:}$$

$C_{r,0}$ – initial concentration of the reactant *r*.

3. Results and discussion

3.1. Cumene formation

Fig. 1 shows the in situ ¹³C MAS NMR spectra observed immediately after adsorption of propene 2-¹³C (a) or propene 1-¹³C (b) with the excess of benzene (Samples A and B, respectively). Both spectra show two NMR lines at 34 and 128 ppm, and at 24 and 128 ppm, respectively. Table 2 lists the chemical shifts of the carbon atoms of reactants and products which could be formed in the course of benzene isopropylation. Assignments are straightforward (Table 3). NMR lines observed in the aliphatic regions correspond to cumene α-¹³C in case A and cumene β-¹³C in case B. The weak resonance at 128 ppm observed in both cases is assigned to ¹³C in benzene (natural abundance).

No resonance line from reactant propene is observed, indicating rapid and complete conversion of propene in cumene at 298 K upon contacting with benzene. This is consistent with recent reports by Haw et al [17,19] showing that propene is very mobile and reactive on zeolite catalysts even at temperatures below 273 K.

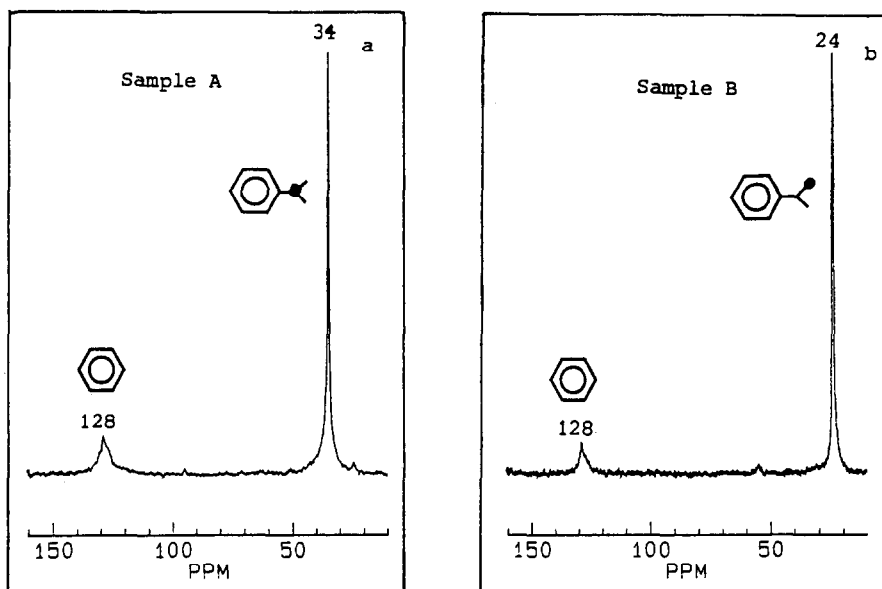








Fig. 1. ^{13}C MAS NMR spectra observed immediately after adsorption of propene 2- ^{13}C (a) or propene 1- ^{13}C (b) and benzene at 298 K. Benzene/propene = 9.

Table 2
Expected chemical shifts (δ_c in ppm) for reactants and main products [24]

Compound	C-1	C-2	C-3	C-4	C- α	C- β	C- γ
benzene	128.5						
isopropylbenzene (IPB)	148.8	126.6	128.6	126.1	34.4	24.1	
<i>n</i> -propylbenzene (NPB)	142.5	128.6	128.3	125.8	38.3	25.0	13.9
toluene (T)	137.8	129.2	128.4	125.5	21.3		
ethylbenzene (EB)	144.3	128.1	128.6	125.9	29.7	15.8	
sec-butylbenzene (BB)	148.4	127.9	129.3	126.8	42.3	31.7	12.2
<i>p</i> -diisopropylbenzene (DIPB)	145.7	126.3			33.9	24.1	
propylene (P)	115.9	133.4	19.4				

Table 3
 ^{13}C label positions and corresponding chemical shifts (δ_c in ppm) in NMR spectra during benzene isopropylation at 298 K

Experiment	Reagents		Products
	Benzene	Propene	
A	 128	 133	 34
B	 128	 119	 24

Note (*) indicates the position of ^{13}C label.

The expanded aliphatic regions of the spectra are presented in Fig. 2. Interestingly, cumene α - ^{13}C has only one signal, whereas the NMR line corresponding to cumene β - ^{13}C is split into two lines at 24.2 and 23.7 ppm, respectively. These lines have a different linewidth and approximately the same integrated intensities estimated from the decomposed spectrum B (Fig. 2b). Splitting of the resonance, corresponding to cumene β - ^{13}C is probably due to different mobility of the two methyl groups in the adsorbed cumene. The broader line at 23.7 ppm corresponds to a less mobile methyl group. Thus, one of the isopropyl methyl groups interacts more favourably with the H-ZSM-11 channel walls.

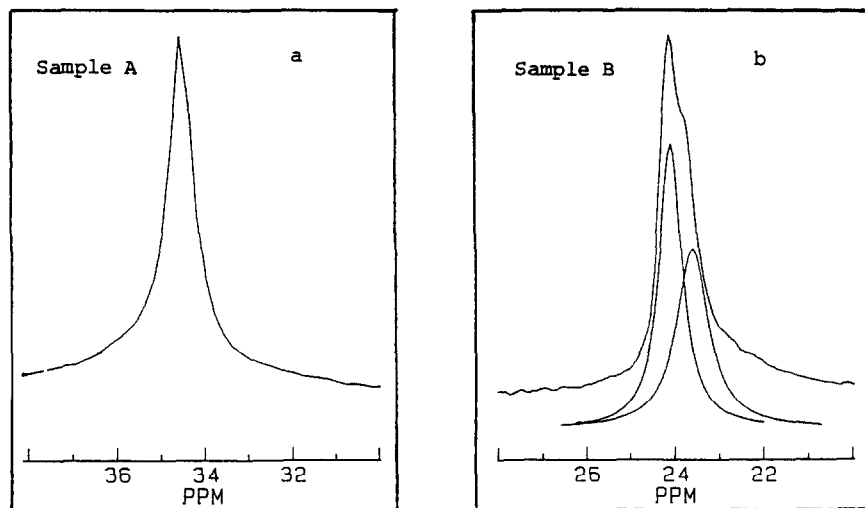


Fig. 2. Aliphatic regions of the ^{13}C MAS NMR spectra observed immediately after adsorption of benzene and propene 2- ^{13}C (a) or propene 1- ^{13}C (b) at 298 K. Benzene/propene = 9.

It is noteworthy that no broad lines in the range of 20–40 ppm corresponding to oligomerization products were detected when the excess of benzene was used. It provides an indication for suppression of the competitive oligomerization of

propene in the presence of excess benzene. Benzene acts as a trap for the active species obtained from propene.

In contrast, when the molar ratio of the reacting propene 1- ^{13}C and benzene was equal to 1 (Sample C) two additional broad resonances at ca. 30 and 14 were detected (Fig. 3). These NMR lines were assigned to propene oligomers [17,19]. Interestingly, after heating of the sample to 413 K a new broad resonance line at ca. 40 ppm appeared, suggesting isomerization and ^{13}C scrambling in oligomers. Further heating led to oligomers cracking and benzene alkylation with the fragments formed. As a result weak resonances corresponding to cumene α - ^{13}C and sec-butylbenzene were observed (Fig. 3).

These experimental observations can be accounted for by the mechanism presented in Fig. 4.

According to classical concepts [25], applied later to zeolites [26], alkylation occurs via olefin protonation, formation of carbenium ion intermediate, and subsequent electrophilic attack on the aromatic π -system to form a benzenium cation which can re-aromatize by proton loss. The formation of carbenium ion is believed to be the rate-limiting step.

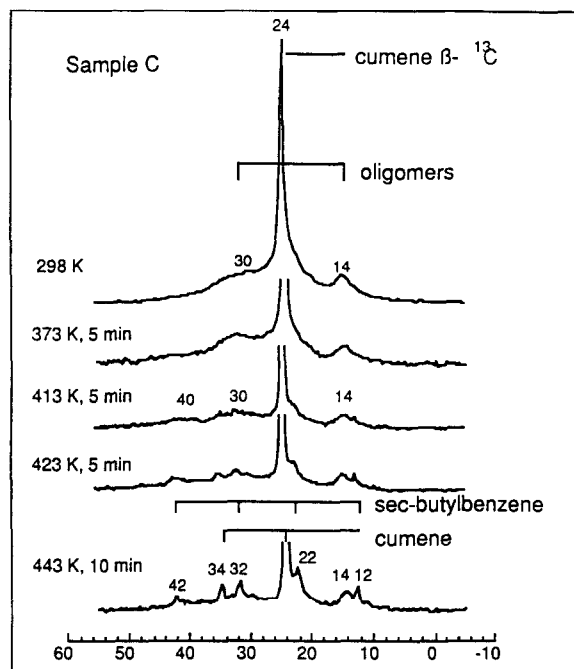


Fig. 3. Aliphatic regions of the ^{13}C MAS NMR spectra observed after reaction of benzene and propene 1- ^{13}C at progressively increasing temperatures. Benzene/propene = 1.

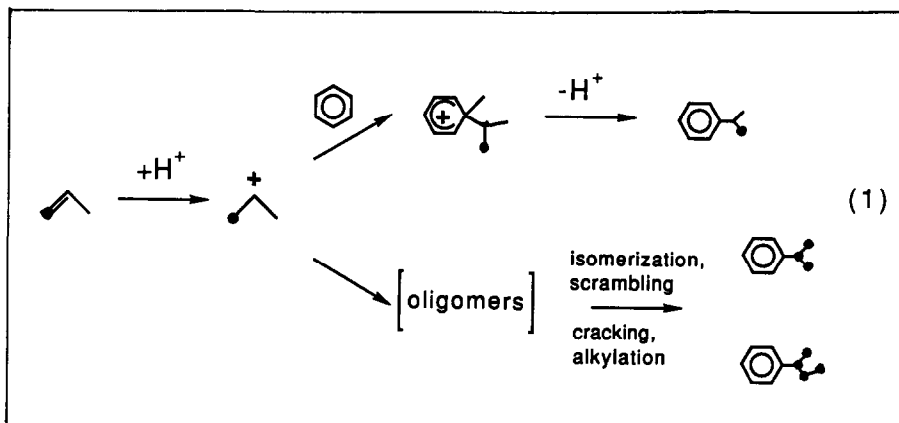


Fig. 4. ^{13}C label tracing in course of cumene formation. (*) indicates ^{13}C labelled carbon atom.

Our results on tracing the fate of 1- ^{13}C and 2- ^{13}C carbon atoms of propene in course of alkylation are fully in line with the classical carbenium ion reaction mechanism as shown in Fig. 4. However, the nature of the rate-limiting step could be questioned. Indeed, extremely rapid alkylation at 298 K in the adsorbed phase is in conflict with the significantly higher temperatures (≈ 473 K) required when the reaction is conducted in the liquid phase [7], suggesting that desorption and diffusion of product might be a rate-limiting step at temperatures below 473 K. Rapid catalyst deactivation at 473 K [7] confirms this.

The second pathway of propene conversion (Fig. 4) suggested by our in situ experiment (Fig. 3) explains high concentrations of sec-butylbenzene observed during benzene alkylation with propene in flow conditions at comparatively low temperatures [7,8].

The classical alkylation and oligomerization mechanisms are based on carbenium ion intermediates. However, recent investigations [17,18,27] question the existence of free carbenium ion at least in the case of non-branched, light olefins. Alkoxy-like species formed from protonated alkenes and zeolite framework oxygen anions adjacent to aluminium sites were suggested to be important intermediates in oligomerization and bond shift reactions. A concerted mechanism including subsequent formation and decomposition of surface alkoxy groups was proposed

[17,28]. Since the transition state in this mechanism has a cationic character it obeys all rules of the carbenium ion formalism.

Accepting that propene activations in oligomerization and alkylation are similar, the above considerations on oligomerization via alkoxy-like species may be applied to alkylation. Experiments are in progress in our laboratory.

3.2. Cumene conversion

The major side-reactions of cumene production by vapour-phase alkylation conducted in flow reactors over pentasil type catalysts are cumene isomerization and fragmentation [6–9]. To gain a deeper insight in the mechanism of these pathways, the cumene conversion was investigated in situ in the presence of excess benzene.

3.2.1. Reaction network

Cumene conversion was studied by heating the NMR cells at progressively higher temperatures. ^{13}C MAS NMR spectra were recorded after each 30° heating step. No changes were observed until the temperature reached 473 K. The aliphatic ^{13}C MAS NMR regions taken from samples A and B before and after treatment at 473 K for various lengths of time are shown in Fig. 5. Heating of the samples for 15 min leads to conversion of cumene α - ^{13}C (34 ppm) to NPB β - ^{13}C (25 ppm) and cumene β - ^{13}C (24 ppm) to NPB α - ^{13}C (38 ppm)

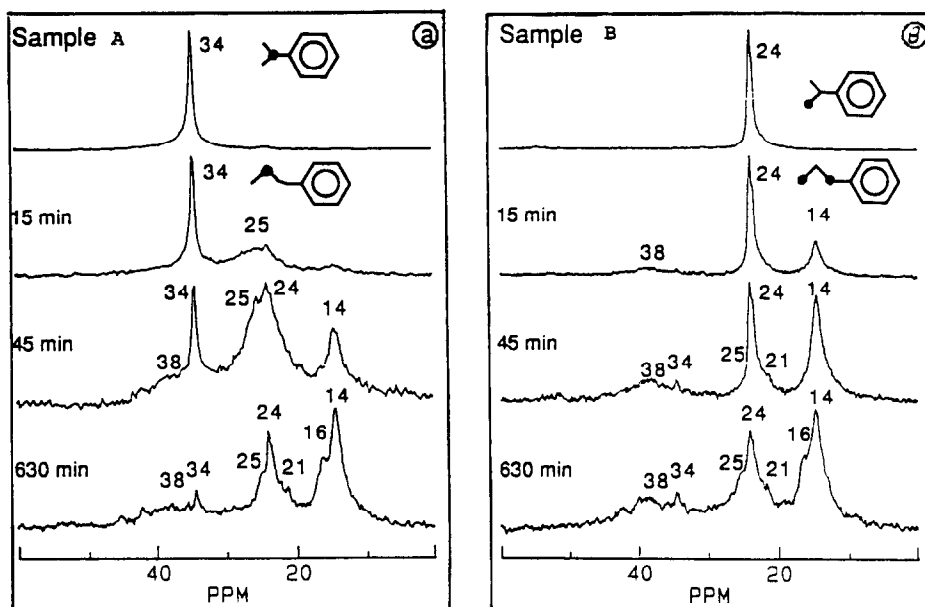


Fig. 5. ^{13}C MAS NMR spectra of samples (a) A and (b) B observed before and after treatment at 473 K for various lengths of time.

and NPB γ - ^{13}C (14 ppm), the latter two species being obtained in equal amounts.

The lines corresponding to NPB are broader than those of cumene. It indicates a lower mobility of the n-propyl group and thus a stronger interaction of the n-propyl group relative to the isopropyl chain with the zeolite. This could be due to a better accommodation of the straight alkyl chain of NPB along the wall of the zeolite channel. The narrowing of the lines corresponding to the alkyl chain of NPB from α - to γ -carbon atoms also indicate an increasing sequential mobility in that order.

Further heating of the samples for another 30 min results in the appearance of all lines corresponding to cumene (24 and 34 ppm) and NPB (14, 25 and 38 ppm) alkyl chains on each sample (Fig. 5). This observation can result from three different pathways:

- (i) ^{13}C scrambling in the alkyl chain of cumene, followed by isomerization, the rate of scrambling being lower than the isomerization rate;
- (ii) ^{13}C scrambling in the alkyl chain of NPB, followed by reverse reaction to cumene–NPB isomerization;

- (iii) Parallel ^{13}C scrambling in both cumene and NPB.

To find out which pathway was operating, the kinetic curves for differently labelled NPB and cumene formed in course of the reaction were analyzed (Fig. 6a and 6b). The kinetic curves of the primarily formed NPB (sample A: β 25 ppm; sample B: α 38 ppm and γ 14 ppm) exhibit an initial increase followed by a decrease in yield, meanwhile the secondary resonances of NPB appear (sample A: α 38 ppm and γ 14 ppm; sample B: β 25 ppm). Thus, NPB undergoes a secondary rearrangement, i.e., ^{13}C scrambling in the alkyl chain. Scrambling in cumene is not significant (Fig. 6).

After heating the samples for 630 min, lines at 21 and 16 ppm, corresponding to the α -carbon atom of toluene and the β -carbon atom of ethylbenzene, appear together with lines at 42, 22 and 12 ppm, which can be assigned to different atoms of sec-butylbenzene (Fig. 5 and Table 2), indicating the fragmentation of NPB or cumene, which accompanies the isomerization of cumene on H-ZSM-11.

The final spectra can be decomposed into 11 lines as shown in Fig. 7: lines 2, 5, and 10 being ascribed to NPB alkyl chain atoms, 3 and 6 to IPB,

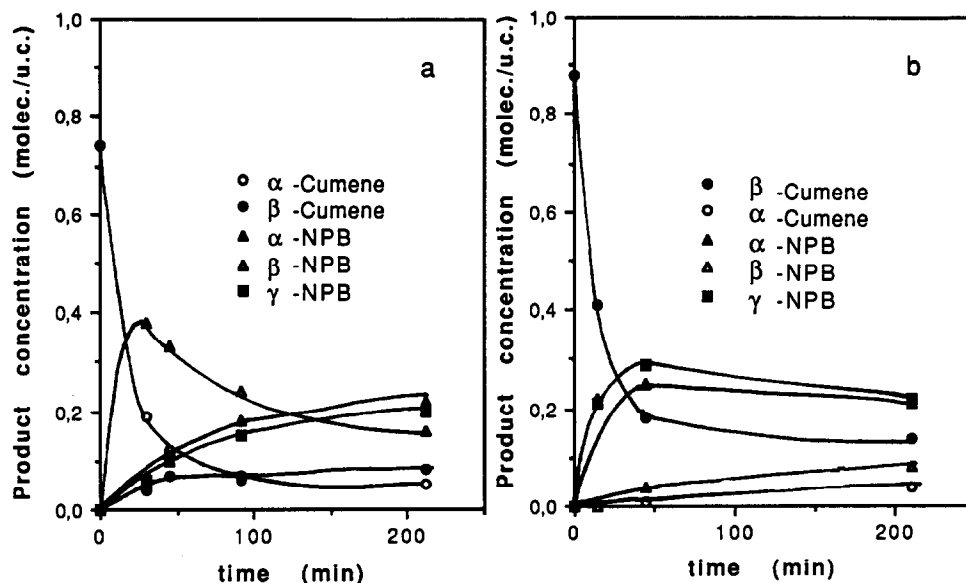


Fig. 6. Kinetic curves of cumene and NPB specifically labelled in alkyl chain during benzene isopropylation at 473 K on the samples (a) A and (b) B.

8 to T, 4 and 9 to EB, and 1, 4, 7 and 11 to BB. A similar distribution of line intensities is observed for samples A and B. The conversion of cumene into NPB, T, EB and BB estimated from the final spectrum is about 90%. The selectivity towards isomerization is $\approx 60\%$.

The complexity of the final spectra do not allow a precise kinetic analysis and to conclude whether

T, EB and BB are formed from cumene or from NPB. However, the appearance of these products after formation of significant amounts of NPB indicates that they may be formed from NPB.

The resulting reaction network is schematized in Fig. 8 using as example sample A.

3.2.2. Proposed mechanism for cumene–NPB isomerization

Appearance of NPB as the only product at the initial stage of reaction at 473 K in the presence of excess benzene allows one to consider cumene–NPB isomerization separately from the other side-reactions and, thus, to get a deeper insight in the mechanism of this pathway. The experiments with cumene and benzene labelled at different positions: aromatic ring or alkyl chain are the basis for understanding this mechanism [29].

3.2.2.1. Evidence for intermolecular mechanism

The mechanisms proposed for cumene–NPB isomerization over acidic catalysts [30–35] suggest that both inter- and intramolecular pathways for different types of catalysts and reaction conditions may occur.

Neitzescu et al [30,31] reported intramolecular mechanism for cumene–NPB isomerization over

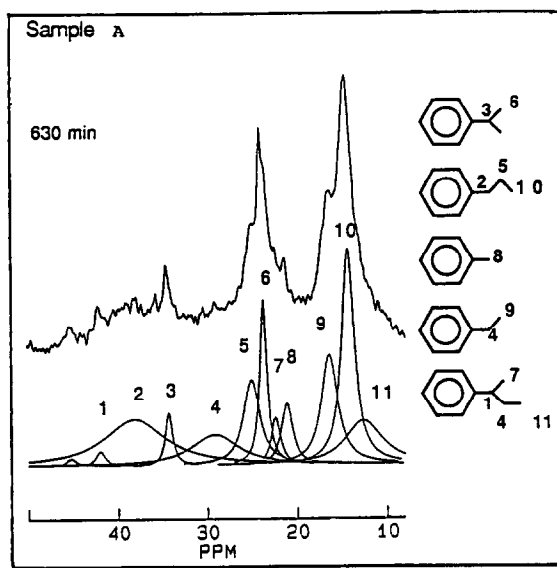


Fig. 7. Decomposed ^{13}C MAS NMR spectrum of sample A treated at 473 K for 630 min.

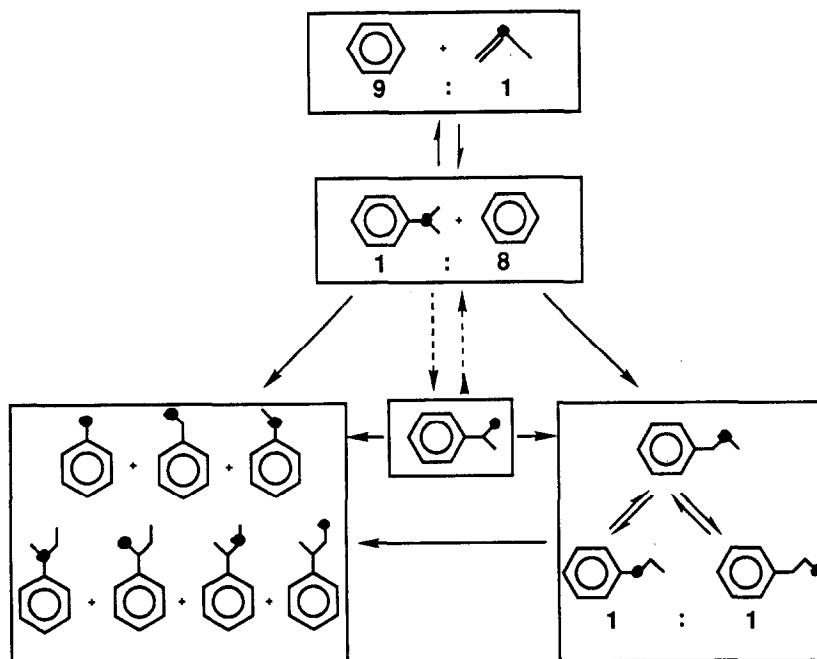


Fig. 8. Reaction network. (*) indicates ^{13}C labelled carbon atom.

AlCl_3 at 373 K. In their opinion, the isomerization of the side chain occurs via hydride abstraction resulting in the formation of benzylic ion, which then rearranges into primary cation, the latter undergoes rearrangement into n-propylbenzene secondary cation by methyl shift. A similar mechanism was proposed by Douglas and Roberts [32] for the same type of catalyst and reaction conditions. In this proposal, however, phenonium ion intermediate was postulated.

The latter mechanism was suggested to be preferred for NPB formation in course of cumene conversion at 635–775 K over different types of zeolite catalysts [33,35]. The remarkable tenfold increase in NPB selectivity over H-ZSM-5, compared to HY, LaY and amorphous Si/Al, was reported by Fukase and Wojciechowski [35]. The authors explained this by the relative enhancement of monomolecular isomerization versus other bimolecular reaction pathways constrained by steric effects in small pore diameter H-ZSM-5.













Monomolecular isomerization is, however, in conflict with the results of Beyer and Bordely [34] for cumene-NPB isomerization over H-ZSM-5 catalysts at comparatively low tempera-

tures (500–600 K). No conversion was detected with pure cumene as a feed, while addition of benzene or toluene provided considerable amounts of n-propylbenzene and propyltoluene, respectively. Hence, the conclusion was that the side chain isomerization over H-ZSM-5 proceeds via intermolecular alkyl transfer, but no detailed mechanism was offered.

The question whether isomerization occurs inter- or intramolecularly, or through both pathways, is best answered by in situ tracing of either cumene or benzene labelled in the aromatic ring as shown in Table 4. Indeed, starting, for example, with labelled cumene and unlabelled benzene, one should end up with labelled benzene if the reaction is intermolecular and with labelled NPB if the reaction is intramolecular or with both species if the two reaction pathways do occur in parallel. The ability of ^{13}C MAS NMR to distinguish unambiguously between ^{13}C -1 carbon of IPB and NPB and all the other aromatic carbons (Table 2) allows discrimination between the first and the last two possibilities, as shown in Table 5. An additional experiment with labelled benzene can dis-

Table 4

Effect of the isomerization mechanism and of the initial ^{13}C label position in the aromatic rings of cumene and benzene, on the ^{13}C label distribution in resulting NPB and benzene

Reagent	 + 	 + 
Mechanism	(D)	(E)
INTRA	 + 	 + 
INTER	 + 	 + 

Note: (*) indicates the position of ^{13}C label.

Table 5

Experimental and predicted ^{13}C aromatic region chemical shifts (δ_c in ppm) for different pathways of cumene isomerization in the presence of benzene excess (benzene: cumene ratio = 2)

Experiment	Labelled reagent	Labelled product			Experimental
		Predicted			
		inter	intra	inter + intra	
D (labelled cumene)	126–128; 149	128	126–128; 143	126–128; 143	128
E (labelled benzene)	128	126–128; 143	128	126–128; 143	126–128; 143

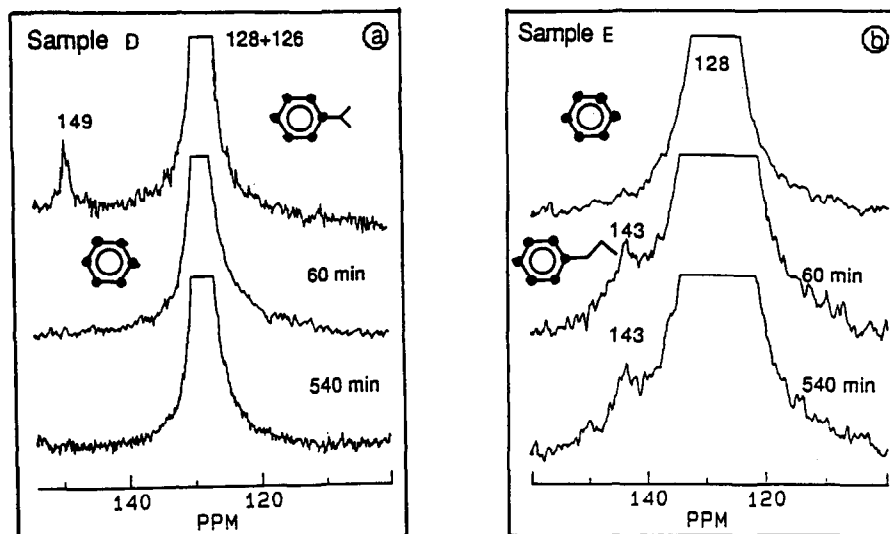


Fig. 9. ^{13}C MAS NMR spectra of samples (a) D and (b) E observed before and after treatment at 473 K for various lengths of time.

criminate unambiguously between all of three variants (Table 5).

In experiment D, cumene labelled in the ring as well as in the alkyl chain was used to follow the

fate of the aromatic ring atoms and to simultaneously follow the cumene conversion to NPB and other products. Aromatic regions of the ^{13}C MAS NMR spectra taken from sample D before and

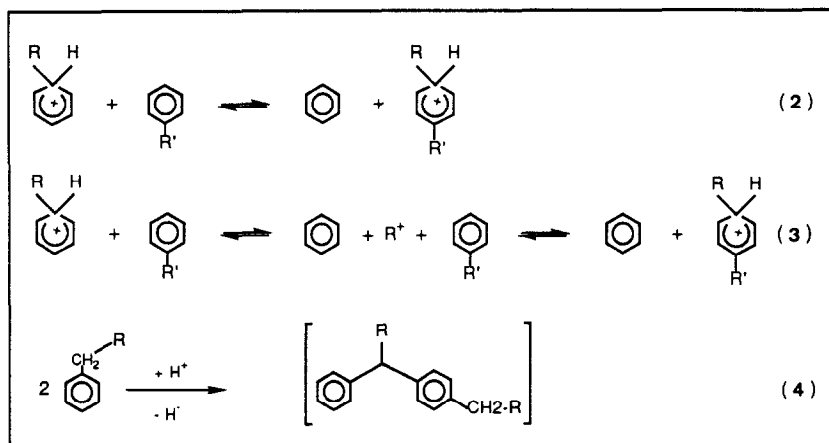


Fig. 10. Transalkylation mechanisms suggested in the literature.

after treatments at 473 K for 60 and 540 min are shown on Fig. 9a. The spectrum of initial unheated sample contains 3 lines: at 149 ppm, corresponding to ^{13}C -1 in cumene, at 128.5 ppm, ascribed to ^{13}C -3,5 in cumene, and natural abundance ^{13}C in benzene, and at 126.5 ppm – to ^{13}C -2,4,6 in cumene. After heating for 60 min, the conversion of cumene to NPB, estimated from the aliphatic part of the spectrum, was more than 60%. The concentration of the other by-products was comparatively low. The line at 149 ppm, corresponding to ^{13}C -1 in cumene disappeared and the line at 142.5 ppm corresponding to ^{13}C -1 in NPB was not observed.

The disappearance of the ^{13}C -1 resonance of cumene and the absence of NPB labelled in the aromatic ring (Table 5) demonstrate the intermolecular character of the isomerization mechanism. It is confirmed by the appearance of the resonance at 143 ppm (Fig. 9b) when using labelled benzene and unlabelled cumene as reactants (sample E).

Consequently, transalkylation mechanisms should be considered for the cumene–NPB isomerization in presence of benzene.

3.2.2.2. Transalkylation mechanisms

Three mechanisms have been proposed previously for transalkylation of alkylaromatics on zeolites [36,37]. The schemes are presented in Fig. 10:

- (i) The first assumes that the alkyl group of a benzenium ion undergoes nucleophilic attack by another aromatic molecule. It does not appear as a free alkyl carbocation. This mechanism occurs mostly for methyl substituted aromatics [36].
- (ii) In the second, alkyl carbenium ions appear because of a dealkylation step. Dealkylation–alkylation $\text{S}_{\text{N}1}$ mechanism is more probable when the carbenium ion is more stable (R^+ = secondary or tertiary ion) [38,42].
- (iii) The third is a $\text{S}_{\text{N}2}$ mechanism involving bimolecular intermediates in which aromatic rings are bridged by a C atom of the alkyl group. Two substrate activation routes over zeolite type catalysts were suggested in literature for this mechanism: hydride abstraction resulting in formation of benzylic carbocations [36–41] and protonation of the aromatic ring with subsequent rearrangement of the benzenium ion towards a primary carbocation [36,42].

Applying these general concepts to cumene isomerization, one should first exclude the first mechanism. It is unlikely for large alkyl groups [36] and it cannot account for alkyl chain isomerization. It will only result in a simple isopropyl transfer to another benzene molecule, leading again to cumene formation [43].

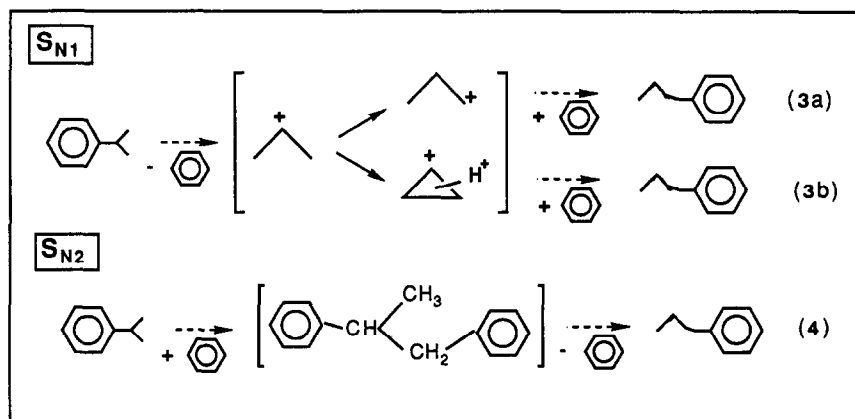


Fig. 11. Intermolecular transalkylation pathways for cumene isomerization.

The S_{N1} (3) mechanism implies isopropyl group cleavage, followed by the formation of a 2-propenium ion. To form NPB by this mechanism, 2-propenium ions must further rearrange either to unstable 1-propenium cations or to the cyclopropenium ions with intermediate stability [44,45]. Both of them, in principle, may give NPB by alkylation of benzene as shown in Fig. 11.

Formation of NPB by S_{N2} (4) mechanism will need a 1,2-diphenyl,1-methylethane intermediate instead of diphenylmethane (Fig. 10 and 11). 1,2-Diphenyl,1-methylethane formation also requires unstable primary cation as an intermediate. However, this route may be the lower energy process due to resonance stabilization of the carbocation intermediate.

Table 6
Effect of the isomerization mechanism and of the initial ^{13}C label position in the aliphatic chain of cumene on the ^{13}C label distribution in the resulting NPB

Reagent Mechanism	(A)	(B)
S_{N1} (3a)		:
S_{N1} (3b)		: :
S_{N2} (4)		:

Note: (*) indicates the position of ^{13}C label.

^{13}C MAS NMR experiments with ^{13}C label in the alkyl chain may help to discriminate between the (3b) and two other mechanisms as shown in Table 6, since only (3b) mechanism leads to complete scrambling of ^{13}C in the alkyl chain (Fig. 11). Mechanisms (3a) and (4) lead to similar label distributions in the alkyl chain. Results obtained in experiments A and B (Fig. 5) suggest that isomerization may proceed by any of these two mechanisms.

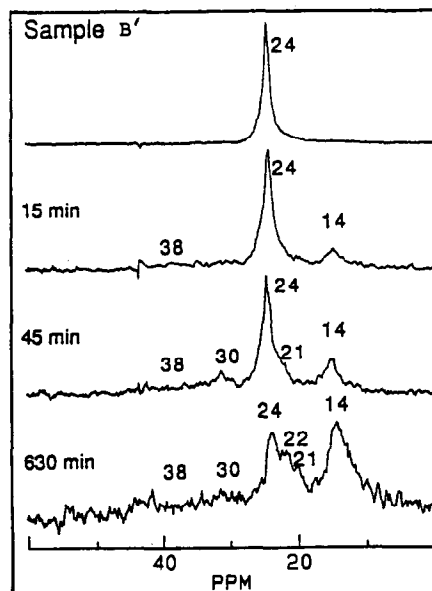


Fig. 12. ^{13}C MAS NMR spectra of sample B' observed before and after treatment at 473 K for various lengths of time.

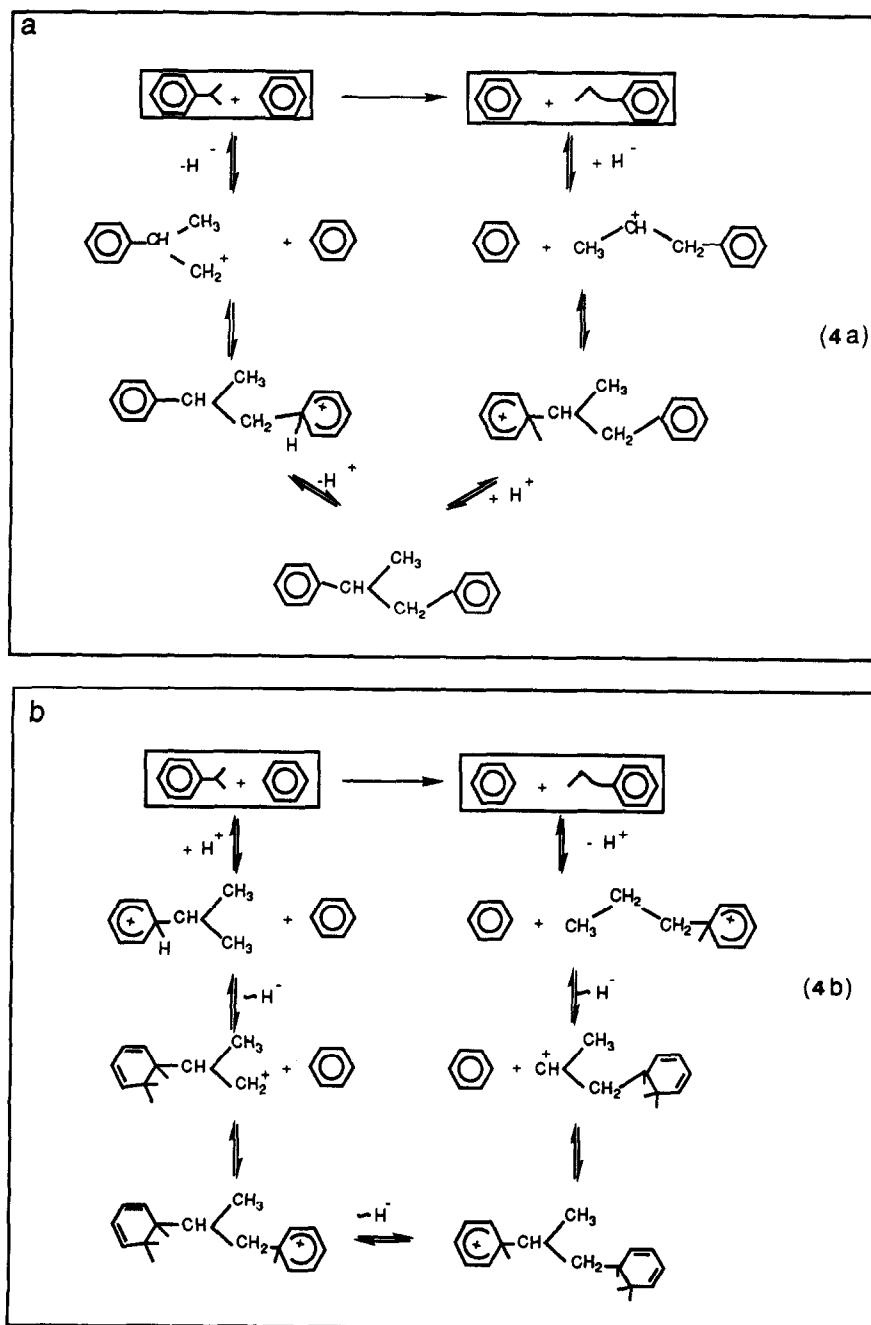


Fig. 13. Mechanism proposals for cumene-NPB isomerization in presence of benzene.

To discriminate further between bimolecular S_{N2} (4) and monomolecular S_{N1} (3b) mechanisms an effect of pressure on the reaction rate was studied. For this purpose an experiment B' (Table 1) was performed and compared with experiment B. The different pressure in experi-

ment B' was achieved by changing the volume of the NMR cell, the amounts of catalyst and reactants being as in B.

The aliphatic regions of the ^{13}C MAS NMR spectra from samples B and B' after treatment at 473 K can be compared in Fig. 5b and 12. After

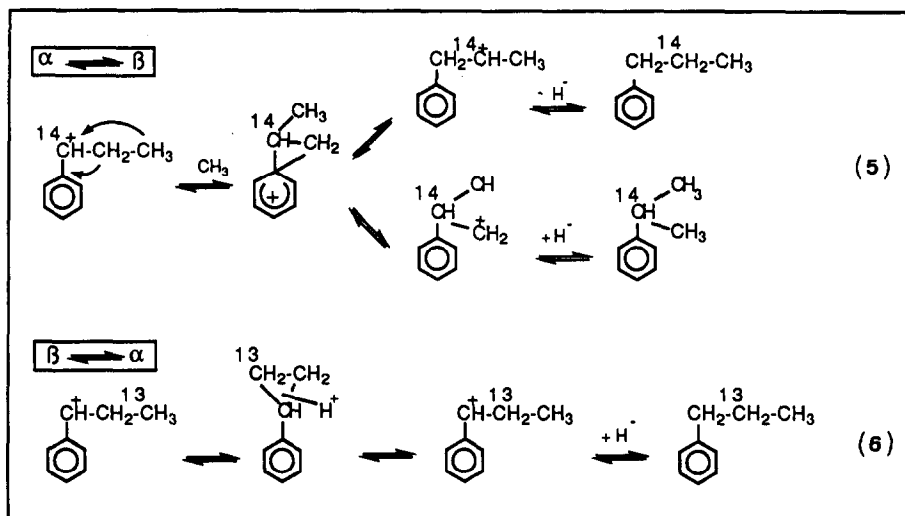


Fig. 14. Mechanisms of NPB alkyl chain rearrangement suggested in [47] (5) and this work (6).

heating the samples for 15 min, spectra are qualitatively similar. However, the initial rates of isomerization derived from the initial slopes of the kinetic curves for NPB were twice higher for sample B. Thus, the rate of isomerization increases with the pressure of reactants. It indicates that the

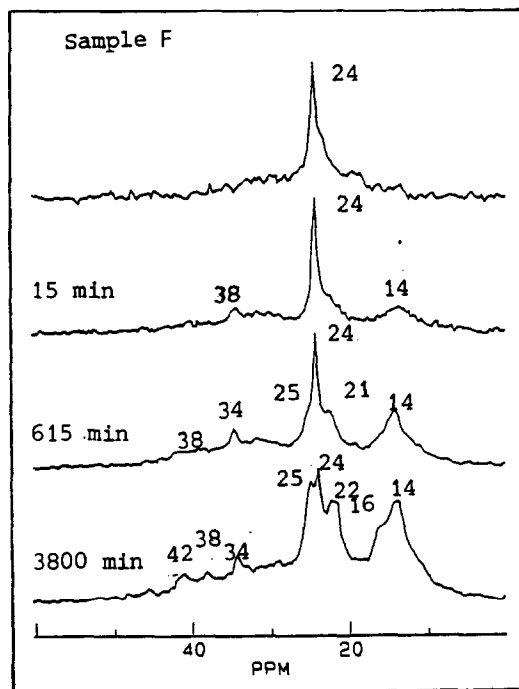


Fig. 15. ^{13}C MAS NMR spectra of sample F observed before and after treatment at 473 K for various lengths of time.

rate-limiting step of isomerization must be bimolecular. The $\text{S}_{\text{N}}1$ (3b) mechanism was, therefore, excluded by default. This conclusion agrees with the energetic considerations discussed above.

The $\text{S}_{\text{N}}2$ mechanism is further detailed in Fig. 13. In agreement with literature data two routes of cumene activation are considered:

- (4a) Hydride abstraction resulting in formation of 2-phenylpropenium-1.
- (4b) Protonation of the aromatic ring of cumene with subsequent rearrangement of the benzenium ion into 2-cyclohexadienylpropenium-1.

Mechanism (4a) is preferred due to its obvious simplicity.

Energetically unfavourable hydride abstraction from β position might result from a confinement (nest) effect [46] within the channels of H-ZSM-11. This can explain the tenfold increase in NPB selectivity compared to large pore zeolites.

3.2.3. Scrambling of C atoms in the alkyl chains of cumene and NPB

^{14}C scrambling in NPB has been reported, when NPB was treated with AlCl_3 at 373 K for 6.5 h [47]. The α - and β -carbon atoms interchanged, but the γ -carbon atom remained unchanged. Only a very small amount of NPB rearranged to IPB.

The proposed mechanism postulates the removal of the benzylic hydrogen, followed by methyl migration, leading to phenonium ion as shown in Fig. 14 (5). Phenonium ion rearranges preferentially towards NPB β - ^{14}C . The rearrangement towards IPB α - ^{14}C is relatively slow because it involves a primary carbocation.

This mechanism explains $\alpha \rightleftharpoons \beta$ scrambling in NPB and IPB. However, in the presence of H-ZSM-11 (Fig. 8), γ -NPB is also engaged in scrambling. We suggest an additional mechanism to explain this (Fig. 14 (6)). The first step would also lead to the benzylic carbocation, whereas the rearrangement could be towards protonated phenylcyclopropane. Preferential α - β cleavage of protonated phenylcyclopropane may account for $\gamma \rightleftharpoons \beta$ scrambling in NPB.

3.3. Benzene isopropylation over silylated H-ZSM-11

It is accepted in the literature [7,35] that benzene isopropylation is very strongly influenced by steric constraints due to the intermediate pore diameter of H-ZSM-5 and -11 catalysts. Fukase and Wojciechowski [35] reported that such constraints prevent the occurrence of bimolecular steps in cumene conversion over H-ZSM-5.

External surface passivation by silica deposition was achieved to differentiate between reactions taking place on the external surface and inside the zeolite channels, during alkylation over H-ZSM-11. Experiment F was performed over silylated H-ZSM-11, in conditions similar to those of experiment B. The aliphatic regions of the ^{13}C MAS NMR spectra taken from sample F before and after treatment at 473 K for various lengths of time are shown in Fig. 15. The observed NMR spectra were qualitatively similar to those obtained from sample B. Thus, all the reaction steps, including bimolecular isomerization, do proceed inside the zeolite channels. Despite the apparent bulkiness of the supposed intermediates (Fig. 13), their cross-sections are close to that of cumene. Thus, isomerization can take place in the channels of H-ZSM-11. This result is in good

agreement with recent reports [48–50] stating that the isomerization of *para*-cymene into *n*-propyltoluene occurs via a bimolecular mechanism inside the channels of MFI zeolites oppositely to Fraenkel and Levy's conclusions [51].

All reaction rates were lower for F relatively to B. This may result from a decrease in the total acid site concentration because of poisoning of the active sites on the external surface, and/or to partial blocking of some of the pore openings.

4. Conclusions

1. Benzene isopropylation proceeds in the adsorbed phase at 298 K over H-ZSM-11 yielding cumene with 100% conversion and selectivity, when the excess of benzene is used. The method could be applied for the small scale preparation of selectively labelled cumene.

2. When the molar ratio of the reacting propene and benzene is equal to 1, alkylation is accompanied by oligomerization of propene. Oligomers are further cracked and benzene is alkylated with the fragments formed. The major product of this pathway is *sec*-butylbenzene.

3. At 473 K, in the presence of excess of benzene, the primary product of cumene conversion is *n*-propylbenzene. At longer reaction times, the formation of *n*-propylbenzene is accompanied by complete scrambling of the carbon atoms in the alkyl chains of cumene and *n*-propylbenzene and the formation of toluene ethylbenzene and butylbenzene. The rate of isomerization is higher than the rate of scrambling and fragmentation.

4. *n*-Propylbenzene is formed by intermolecular transalkylation between cumene and benzene, via an $\text{S}_{\text{N}2}$ mechanism. The probable reaction intermediate is 1,2-phenyl,1-methylethane.

5. Direct and side-reactions proceed on both external and internal surface of HZSM-11.

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