

# $^{13}\text{C}$ MAS NMR mechanistic study of benzene alkylation with propane over Ga-modified H-ZSM-5 catalyst

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## Abstract

$^{13}\text{C}$  MAS NMR has been performed in situ to investigate the mechanism of benzene alkylation with propane over Ga/H-ZSM-5 catalyst. Propane 2- $^{13}\text{C}$  was used as a labelled reactant. In order to clarify the main reaction pathways, conversions of the individual starting materials and some of the reaction intermediates such as cumene and n-propylbenzene were also studied under similar conditions.

Benzene alkylation with propane begins at 573 K, toluene and ethylbenzene being the major primary products. The reaction is preceded by the induction period caused by stronger adsorption of benzene that prevents propane activation. The main reaction pathway includes bifunctional propane activation on Brønsted and Ga sites which leads to protonated pseudocyclopropane (PPCP) intermediate, which in turn decomposes preferentially to  $\text{CH}_4$  and  $\text{C}_2\text{H}_5^+$ , or  $\text{C}_2\text{H}_6$  and  $\text{CH}_3^+$ . The reaction of  $\text{C}_2\text{H}_5^+$  or  $\text{CH}_3^+$  carbenium ions with benzene leads to toluene or ethylbenzene, respectively. The less favourable reaction routes give propenium and cyclopropenium ions upon PPCP decomposition, and result in observation of the traces of cumene and n-propylbenzene. These routes are reversible, the equilibrium being shifted towards reactants at 573 K.

*Keywords:* Zeolite; H-ZSM-5; Gallium; MAS NMR; Mechanism; Alkylation; Benzene; Propane; Toluene

## 1. Introduction

The possibility of the catalytic synthesis of alkylaromatics from alkanes and benzene was disclosed by Schmerling and Vesely [1] for the Friedel–Crafts catalyst systems and then studied

in detail by Olah et al. in superacidic media [2]. Benzene alkylation with propane was found to occur over anhydrous fluoroantimonic acid even at 298 K. The major reaction product was cumene, although small amounts of n-propylbenzene and ethylbenzene were also formed. Two competitive mechanisms were suggested to account for cumene formation from benzene and propane [2]. The first one includes protolysis of the secondary C–H bond of propane leading to the formation of a two-electron, three-center bonded propenium ion transition

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state. Formation of the proponium ion is followed by cleavage of the three-center bond giving isopropenium ion and hydrogen molecule. Isopropenium ion in its turn reacts with benzene to yield cumene. The alternative mechanism includes benzene protonation which leads to benzenium ion, which in turn reacts with propane via an alkylation–cleavage mechanism to give cumene and hydrogen molecule.

These mechanisms however cannot readily be extended to benzene alkylation with alkanes over zeolite catalysts, since reaction products were found to be different in presence of zeolites [3–5]. Thus, in the case of benzene alkylation with propane over modified and non-modified H-ZSM-5 catalysts, the main reaction products were toluene, xylenes and condensed aromatics [5]. Cumene was not observed in the course of this reaction. It should be mentioned that alkylation with propane on zeolites requires much higher reaction temperatures (723–873 K) than in superacidic media and a set of side reactions such as conversion of individual propane [6–8] and benzene [9] and cumene fragmentation [10] can lead to the observed products under similar reaction conditions. The reaction pathway leading to alkylaromatics in presence of zeolites is therefore much more complicated and may include several parallel routes.

This paper aims to clarify the mechanism of benzene alkylation with propane over Ga-modified H-ZSM-5 catalyst. An *in situ*  $^{13}\text{C}$  MAS NMR technique is used to investigate the main reaction steps: adsorption, induction period, ac-

tivation, and primary and secondary reactions. Transformations of propane alone, benzene in presence of hydrogen, and cumene in presence of benzene are studied independently for better understanding the reaction mechanism.

## 2. Experimental

### 2.1. Materials

ZSM-5 zeolite (Si/Al = 35) was prepared as described elsewhere [11]. Gallium was introduced in the H-form of the catalyst by aqueous impregnation with  $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.9% from Alfa), followed by drying for 16 h at 393 K and calcination at 823 K for 4 h in air. The catalyst obtained contained 0.95 wt% of gallium.

The labelled reactants (propane-2- $^{13}\text{C}$  (99.9%-enriched), propene 2- $^{13}\text{C}$  (99%-enriched) and benzene (5%-enriched)) were obtained from ICON Services Inc. Cumene with  $^{13}\text{C}$  in  $\alpha$ -position of the alkyl chain was synthesized directly in the NMR cell over H-ZSM-5 by benzene alkylation with propene 2- $^{13}\text{C}$ . Details of this synthesis are described elsewhere [12,13].

### 2.2. Controlled atmosphere $^{13}\text{C}$ MAS NMR measurements
























The powdered catalysts samples ( $0.09 \pm 0.01$  g) were packed into the NMR tubes (Wilmad, 5.6 mm o.d. with constrictions), evacuated to a

Table 1  
Sample preparation

Experiment	Catalyst	Loaded reactants (molecules/u.c.)			
		Propane 2- $^{13}\text{C}$	Benzene	$\text{H}_2$	Cumene $\alpha$ - $^{13}\text{C}$
A	Ga/H-ZSM-5	–	9	3	–
B	Ga/H-ZSM-5	3	–	–	–
C	Ga/H-ZSM-5	3	9	–	–
D	Ga/H-ZSM-5	1	9	–	–
E	H-ZSM-5	–	6	–	3

Table 2

Assignments of the resonances in experiments A, B, C and D

Assignment <sup>a</sup>	Experimental $\delta$ (ppm) <sup>b</sup>		
	A	B	C; D
<b>Reactants:</b>			
 (13.7s)	-	16.9	17; 17
 (128.5s)	127.8	-	128.8; 128.6
<b>Products:</b>			
<b>Cycloalkenes:</b>			
 (124.1s)	-	-	124.4; -
 (124.8s)	-	-	-
<b>Alkylaromatics:</b>			
 (21.3s)	21	21	20.9; 21.3
 (137.8s)	138	-	137.6; 138
 (29.7s)	-	-	28.8; 29.2
 (24.1s)	-	-	23.5; 23.8 (  ,  )
 (34.4s)	-	-	34; 34
 (13.9s)	-	-	14; 14 (  )
 (25s)	-	-	24.9; 25 (  )
 (19.6 - 21.3s)	19.5 - 21	19 - 21	19.7 - 21; 19.8 - 21.3
 (137.6s)	138	-	137.6; 138
 (125.5 - 130s)	125 - 132	126 - 130	126 - 130; 126 - 130
<b>Alkanes:</b>			
 (13.2s)	-	13.4	-; -
 (24.9s)	-	26.0	-; -
 (24.6s)	-	24.1	-; -
 (23.3s)	-	-	-; -
 (16.1s; 15.4g)	-	15.8	overlaps; 15.8
CH <sub>3</sub> -CH <sub>3</sub> (6.5s; 3.2g)	6.2	6.1	6.5; 7.2
CH <sub>4</sub> (-2.3s; -11g)	-7.4, -11	-7.4, -11	-6, -11; -5.8, -10.9

<sup>a</sup> Chemical shifts reported in literature are given in brackets: (s) solution data [19], (g) gas phase data [21].<sup>b</sup> Less probable assignments of the corresponding lines are given in brackets.● Indicates <sup>13</sup>C labelled carbon atoms.

final pressure of  $6 \times 10^{-6}$  Torr after heating for 8 h at 573 K, and cooled down to 298 K before adsorption. In different experiments, the catalysts samples were loaded with propane 2- $^{13}\text{C}$ , mixtures of benzene and hydrogen or benzene and propane 2- $^{13}\text{C}$  or cumene  $\alpha$ - $^{13}\text{C}$  and benzene. Gaseous reactants were dosed volumetrically, while liquids were dosed gravimetrically. After reactants loading, 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 prepared is reported in Table 1.

Controlled-atmosphere  $^{13}\text{C}$  MAS NMR measurements were carried out using an MSL-400 Bruker spectrometer operating at 100.6 MHz for  $^{13}\text{C}$ . Quantitative conditions were achieved using high-power gated proton-decoupling with suppressed NOE effect ( $90^\circ$  pulse, recycling delay = 4 s). The experiments with cross-polarization were performed to distinguish between species of different mobilities. Spinning rates were within 3–3.8 kHz.

In typical NMR experiments, sealed NMR cells were rapidly heated to a selected temperature and maintained at this temperature for 5 min. MAS NMR spectra were recorded at 293 K after quenching of sample cells. After collection of the NMR data, NMR cells were returned to reaction conditions and heated for progressively longer periods of time. The following  $^{13}\text{C}$  spectra were recorded over the time course of the reaction always after quenching of sample cells. In the other set of experiments the temperature was increased stepwise and spectra were recorded as a function of temperature.

The conversion of propane ( $X_t$ ) at a time  $t$  was calculated as follows:

$$X_t = (1 - I_t/I_0) \times 100 (\%)$$

where  $I_t$  corresponds to the integrated intensity of the resonance lines of propane after heating the NMR cell for  $t$  min;  $I_0$  corresponds to the integrated intensity of the resonance lines of propane at initial time.

### 3. Results and discussion

#### 3.1. Adsorption

Fig. 1 shows in situ  $^{13}\text{C}$  MAS NMR spectra observed immediately after adsorption of benzene in the presence of hydrogen (sample A), propane 2- $^{13}\text{C}$  (sample B), and benzene–propane 2- $^{13}\text{C}$  mixtures (samples B and C) over Ga/H-ZSM-5 catalyst. The resonance line corresponding to benzene adsorbed on Ga/H-ZSM-5 is shifted significantly to higher field with respect to solution data (Table 2, Sample A) pointing to the high benzene distortion upon adsorption. This is in good agreement with IR results [14,15], indicating that OH groups of protonic zeolites interact with the  $\pi$  electrons of benzene through H-bonding, causing significant disturbance of the molecule.

Co-adsorption of propane results in a shift of benzene resonance to the lower field (Fig. 1 and Table 2, Samples C and D). The presence of benzene, in turn, affects the resonance corresponding to the labelled methylene group of propane (Fig. 1, Sample C and D), leading to two resonance lines, a narrow and a broad one, both centered at ca. 17 ppm. The narrow line, observed also in the case of neat propane adsorption (sample B), is attributed to mobile species, while the broad component corresponds to more rigid species as evidenced by experiments with cross polarization. The restricted

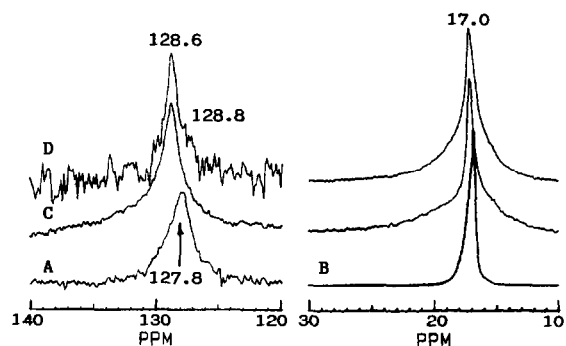


Fig. 1.  $^{13}\text{C}$  MAS NMR spectra observed over samples A, B, C and D immediately after adsorption of reactants at 298 K. Samples A, B, C and D are characterized in Table 1.

propane mobility in the presence of benzene could be either due to the less space available within zeolite channels after benzene adsorption or most likely due to the chemical interaction of propane methylene group with adsorbed benzene.

Our NMR results may be further discussed using the following model. Benzene which is obviously stronger adsorbed than propane occupies zeolite active sites upon adsorption. Note that 9 molecules of benzene per unit cell loaded in our experiments (Table 1) is sufficient to engage both protonic and Ga sites of the catalyst. Upon adsorption, benzene is supposed to be H-bonded to the surface acidic OH groups and/or electron bonded to Ga sites. As a result, positive charge can be partially transferred to benzene molecule leading in fact to formation of a weak acid. This weak acid can in its turn interact with propane, which is considered to be a weak base, and cause significant disturbance of propane methylene group.

### 3.2. Induction period

Reaction of propane with benzene begins at 573 K similarly as observed for neat propane on Ga/H-ZSM-5 catalyst [16,17]. However, the initial kinetics of propane consumption is different (Fig. 2). The major difference is a long induction period (40–160 min) observed in presence of benzene. The duration of induction periods is determined by benzene/propane molar ratio. The higher propane concentration in the reactants, the shorter is the induction period.

The aliphatic regions of the  $^{13}\text{C}$  MAS NMR spectra, observed for sample C during the induction period, are shown in Fig. 3. Upon heating the sample at 573 K for the first 5–30 min, the broad resonance line at ca. 17 ppm, corresponding to a rigid propane species, shifts to lower field and becomes more pronounced. Further heating for 40 min leads to the formation of the first reaction products and simultaneous disappearance of the broad resonance corresponding to the rigid propane species, which suggests

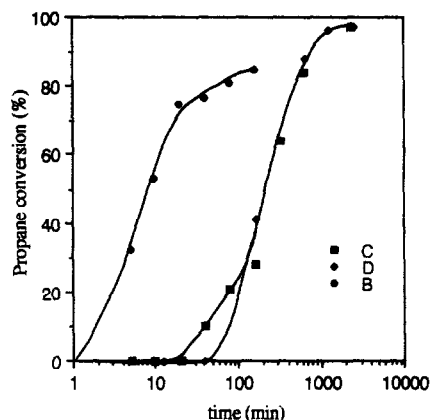


Fig. 2. Variation of propane conversion as a function of reaction time in experiments B, C and D at 573 K.

that these species may be responsible for the induction period.

These observations allow for the conclusion that the stronger adsorption of benzene with respect to propane over Ga/H-ZSM-5 zeolite and/or strong interaction between adsorbed benzene and propane methylene group prevent direct contact of propane molecules with the active sites of the zeolite and induce the induction period preceding propane activation.

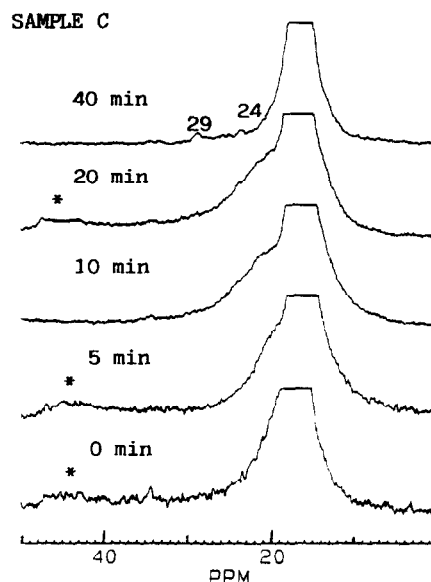


Fig. 3. Aliphatic regions of the  $^{13}\text{C}$  MAS NMR spectra observed before and after heating the sample C at 573 K during the induction period. (\*) indicates spinning side bands.

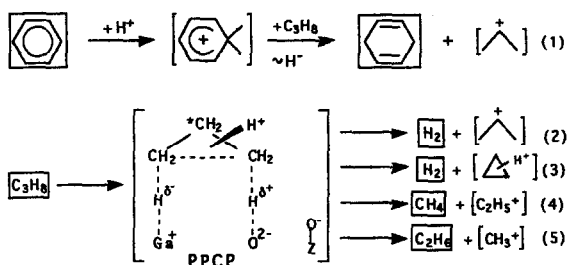


Fig. 4. Possible mechanisms of propane activation in the presence of benzene over Ga-containing H-ZSM-5 catalyst.

### 3.3. Activation step

Benzene alkylation with propane can be initiated in two different ways, requiring preliminary activation of either propane or benzene [2]:

(1) Benzene activation on H-ZSM-5 was reported to occur by benzene protonation on strong acid sites, and the formation of benzenium ion [18]. Benzenium ion can initiate reaction with the nearest propane molecule by hydride abstraction, which leads to isopropenium ion, as shown in Fig. 4 (1). The latter can further alkylate benzene to give cumene which can be converted to toluene and ethylbenzene via secondary reactions [10,12].

(2) Propane activation over Ga/H-ZSM-5 occurs by a bifunctional mechanism involving pseudo-protonated cyclopropane (PPCP) intermediate [16,17]. The PPCP intermediate can decompose in various ways resulting in the formation of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2$  and methyl, ethyl and propyl carbenium ions (Fig. 4 (2–5)). These carbenium ions can lead to the corresponding alkylbenzenes: toluene, ethylbenzene, cumene and n-propylbenzene, if the reaction is carried out in presence of benzene.

Our NMR results indicate that both activation pathways may operate under our reaction conditions:

- The appearance of the small but distinct NMR line at ca 124,4 ppm at the very beginning of the reaction (Fig. 5) and its disappearance at longer reaction times indicates intermediate formation of cyclohexadienes since the chemical shift of this resonance line is close to those reported for CH

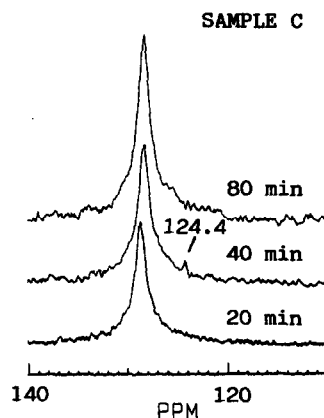


Fig. 5. Aromatic regions of the  $^{13}\text{C}$  MAS NMR spectra observed on sample C, suggesting intermediate formation of cyclohexadienes in the course of benzene alkylation with propane over Ga/H-ZSM-5 catalyst at 573 K.

groups of 1,4-cyclohexadiene (124.1 ppm) or 1,3-cyclohexadiene (126.1 and 124.8 ppm) in solution [19]. Moreover, weak resonances at ca. 23.5 and 34 ppm observed in the early stages of the reaction point to the formation of small amounts of cumene labelled in the  $\beta$  and  $\alpha$  positions of the alkyl chain, respectively [12,13]. These observations favour the activation pathway (1).

- The monotonous shift of the resonance line at 17 ppm, corresponding to initially labelled methylene group of propane, to the higher field in course of reaction (Fig. 6) indicates that the resonance corresponding to propane

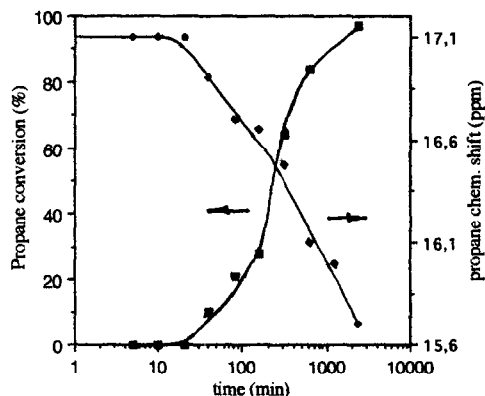


Fig. 6. Variation of propane conversion and the chemical shift of the NMR line corresponding to propane as a function of reaction time over the sample C at 573 K.

methyl group may appear at ca. 16 ppm and contribute to the resonance line as reported for the reaction of neat propane over the same catalyst [16,17]. The resonances of methyl and methylene groups of propane are not resolved in the presence of benzene because of significant line broadening. Scrambling of the  $^{13}\text{C}$  label in propane in the early stages of propane conversion suggests a PPCP-type intermediate, and points to the second activation route.

Although evidence for both activation pathways was obtained, the induction period preceding reaction on Ga/H-ZSM-5 (Section 3.2) suggests that preliminary activation of propane is the major activation pathway.

### 3.4. Reaction

#### 3.4.1. Reaction products

The  $^{13}\text{C}$  MAS NMR spectra observed after the induction period over the samples C and D

are presented in Fig. 7. The reaction products identified and the corresponding chemical shifts are listed in Table 2 together with those observed in reactions of individual reactants (samples A and B).

In the initial stages of the reaction major resonances corresponding to toluene (21 ppm), ethylbenzene (29 ppm), ethane (7 ppm) and methane (–6 and –11 ppm) are observed along with weak resonances assigned to cyclohexadienes (124.4 ppm), cumene (23.5 and 34 ppm) and n-propylbenzene (14 and 25 ppm). After heating for 300 min the lines corresponding to cyclohexadiene and cumene disappear and the xylene lines at ca. 19–21 ppm appear. Toluene and methane become the major reaction products. Further increase of the reaction time causes ethylbenzene and n-propylbenzene to disappear and a continuous increase of the lines corresponding to toluene, xylenes, ethane and methane. Finally, toluene and xylenes are converted into condensed aromatics, evidenced by

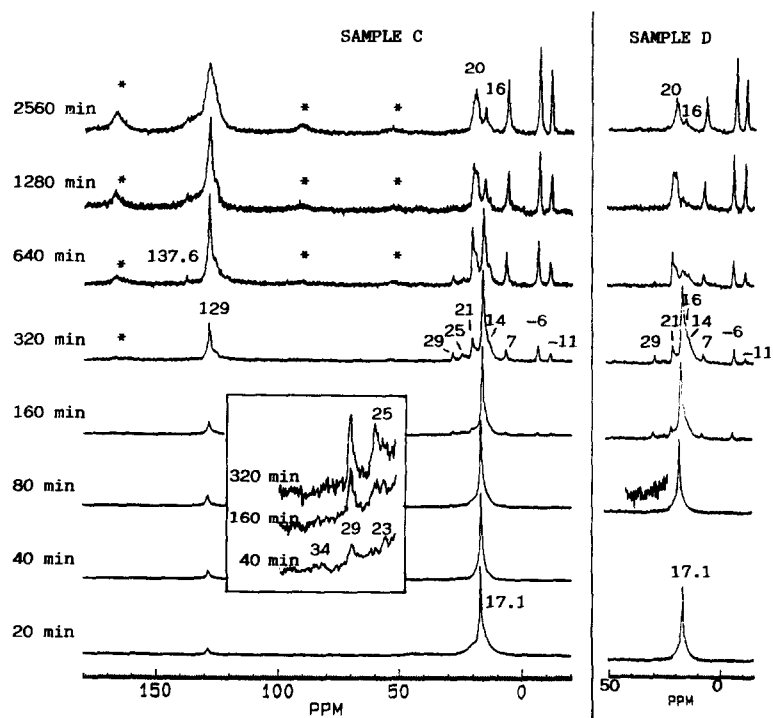


Fig. 7.  $^{13}\text{C}$  MAS NMR spectra observed in course of benzene alkylation with propane over sample C and D at 573 K. The inset shows enlarged spectra of sample C in the region of 40–22 ppm. (\*) indicates spinning side bands.

the observation of the spinning sidebands in the aromatic part of the spectra, the enhancement of cracking towards ethane and methane and the decrease of the total integrated intensity of the resonance lines.

Special attention was paid to the identification of the weak NMR lines in the 23–26 ppm and 13–14 ppm regions of the spectra, since their assignments are not straightforward because they can arise from various reaction products. The first NMR line which shows up in these regions at 23.5–23.8 ppm was attributed to cumene  $\beta$ - $^{13}\text{C}$  (24.1 ppm in solution) because it appears and disappears simultaneously with the line at 34 ppm corresponding to cumene  $\alpha$ - $^{13}\text{C}$  [12,13]. Note, however that the same line might be assigned to isobutane 2- $^{13}\text{C}$  (23.3 ppm in solution) or methylene group of 1,3-cyclohexadiene (22.6 ppm in solution) (Table 2). The latter assignments are less probable for the following reasons: (1) The line corresponding to isobutane on Ga/H-ZSM-5 is usually observed at a higher chemical shift (Table 2) [16,17]. Moreover, in the course of conversion of neat propane over this catalyst, *i*-butane lines appear simultaneously with those corresponding

to *n*-butane (13.4 and 26 ppm), which are not observed in our case. (2) The line at 124.4 ppm which is assigned to CH groups of cyclohexadienes disappears earlier than the one at 23.5 ppm as follows from the comparison of Fig. 5 and inset of Fig. 7.

Upon disappearance of the lines at 23.5 and 34 ppm, the resonances at ca. 24.9 ppm and 14 ppm appear (Fig. 7); the latter is overlapping with the broad resonance corresponding to propane. These NMR lines can arise from both *n*-butane methylene and methyl groups (24.9 and 13.2 ppm in solution) or *n*-propylbenzene  $\beta$ - and  $\gamma$ -carbons (25 and 13.9 ppm in solution), respectively (Table 2). Note that the line corresponding to *n*-propylbenzene  $\alpha$ - $^{13}\text{C}$  may not be observed because of its significant broadening upon adsorption of propylbenzene on pentasil type zeolites [12,13]. By their chemical shifts, the lines are closer to those reported for *n*-propylbenzene adsorbed on zeolites (25 and 14 ppm) [12,13] than to those of *n*-butane on Ga/H-ZSM-5 (26 and 13.4 ppm) [16,17]. The formation of butanes in the course of benzene alkylation with propane is thus rather improbable.

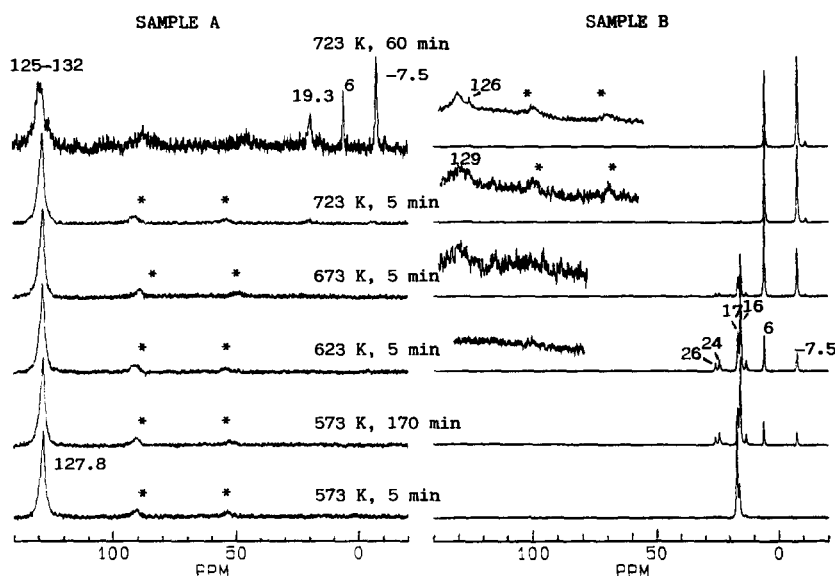


Fig. 8.  $^{13}\text{C}$  MAS NMR spectra observed in course of benzene (sample A) and propane (sample B) reactions over Ga/H-ZSM-5 catalyst as a function of reaction time and temperature. (\*) indicates spinning side bands.



The spectra observed on samples C and D with different starting ratios of propane and benzene (Table 1) do not show significant differences except that the induction period is longer on sample D.

In conclusion the major reaction products observed in course of benzene alkylation with propane are toluene, ethylbenzene, xylenes, ethane and methane. Small amounts of cumene, n-propylbenzene and cyclohexadiene possessing intermediate behavior are also identified. These observations support the activation model presented in Fig. 4 and suggest that the five different alkylation routes may operate simultaneously.

Note that the direct formation of alkylaromatics from individual reactants cannot be completely excluded at this step.

### 3.4.2. Comparison with reactions of individual reactants

Since each starting material is known to undergo reactions over H-ZSM-5 the individual reactants were tested independently over Ga/H-ZSM-5. Benzene was loaded on the catalyst together with H<sub>2</sub> (sample A, Table 1) in order to make reaction conditions closer to those of alkylation with propane.

At 573 K benzene is inert as indicated by <sup>13</sup>C MAS NMR spectra presented in Fig. 8 (sample A). The reaction begins only after heating at 723 K. The major products are toluene, xylenes, methane and ethane (Table 2). Although the main products are similar to those observed in course of alkylation, conversion of individual benzene cannot account for them at 573 K.

By contrast neat propane is very reactive at 573 K (Fig. 8, sample B). The main products are propane 1-<sup>13</sup>C, ethane, methane and butanes (Table 2, sample B). Observation of significant amounts of butanes when starting with neat propane and their absence when reaction is performed in the presence of benzene indicates that benzene acts as a trap for the active species leading to butane. These active species are most probably CH<sub>3</sub><sup>+</sup> carbenium ions which may alkylate

late propane or benzene to give butanes or toluene, respectively. As  $\pi$ -aromatic substrates undergo alkylation much more readily than  $\sigma$  donor alkanes, the latter reaction is obviously more favorable. These results support a previous hypothesis on the mechanism of the formation of butanes at high propane partial pressures over Ga/H-ZSM-5 [16,17].

The formation of alkylaromatics from neat propane is not observed at 573 K (Fig. 8). Small amounts of benzene, toluene and xylenes appear only at 673 K, evidenced by a set of weak resonances in the 126–130 ppm range of the spectra. The lines belonging to alkyl chains of alkylaromatics could also be identified in the range of 19–21 ppm (Table 2, sample B).

In conclusion, whereas alkylation of benzene with propane to give alkylaromatics already occurs at 573 K, formation of alkylaromatics from individual benzene and propane requires much higher temperatures. Consequently, alkylation is

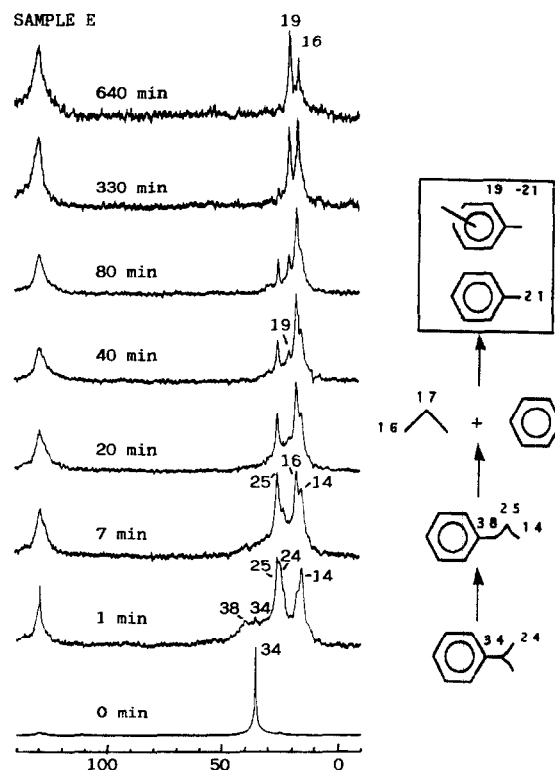


Fig. 9. <sup>13</sup>C MAS NMR spectra observed before and after treatment of the sample E at 573 K for various lengths of time.

the only pathway leading to alkylaromatics at 573 K.

### 3.4.3. Reaction pathways leading to toluene and ethylbenzene

The formation of large amounts of toluene and ethylbenzene with respect to n-propylbenzene and cumene in the very early stages of alkylation (Fig. 7) suggests that the reaction pathway involves mainly routes (4) and (5)

(Fig. 4). However it should be noted that cumene and n-propylbenzene may easily be converted to toluene and ethylbenzene by fragmentation over acidic zeolite [10,12,13]. In order to check whether toluene and ethylbenzene are a result of a direct alkylation or are a consequence of cumene and/or n-propylbenzene transformations, cumene conversion was carried out in the presence of benzene under the similar reaction conditions (Table 1, sample E).

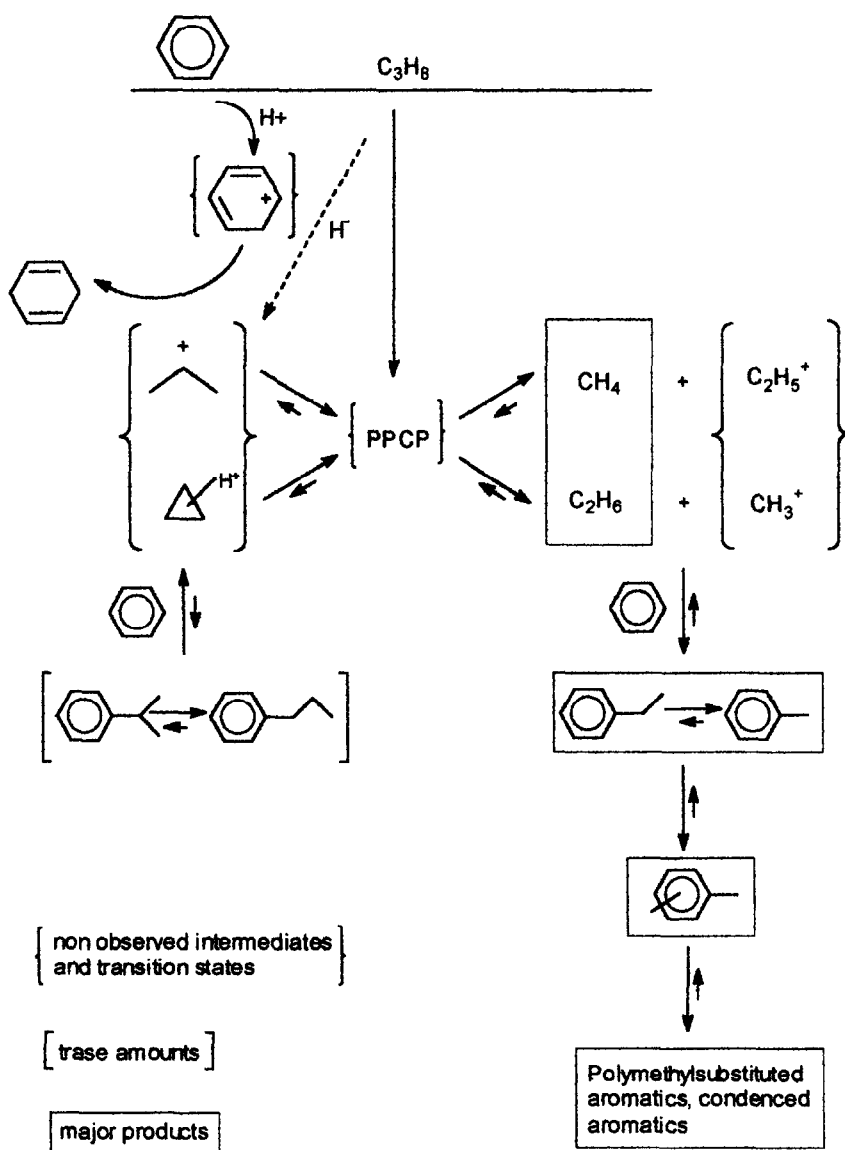


Fig. 10. Proposed mechanism for benzene alkylation with propane over Ga/H-ZSM-5 catalyst.

After 1 min at 573 K cumene is predominantly converted to n-propylbenzene as evidenced by the  $^{13}\text{C}$  MAS NMR spectra presented in Fig. 9. The main resonances at 14, 24.8, and 38 ppm are assigned to n-propylbenzene  $\gamma$ -,  $\beta$ - and  $\alpha$ - $^{13}\text{C}$ , respectively, and those at 23.8 and 34.5 ppm to cumene  $\beta$ - and  $\alpha$ - $^{13}\text{C}$ . Small amounts of toluene (21 ppm) and ethylbenzene (16 and 29 ppm) are also observed. A detailed description of the line assignments is given elsewhere [12,13].

Further heating at 573 K causes disappearance of the lines corresponding to cumene and n-propylbenzene, meanwhile the line at 16 ppm begins to grow. This resonance line may correspond as to ethylbenzene  $\beta$ - $^{13}\text{C}$  so as to propane methyl or methylene groups. The former assignment is however less probable as it is not evidenced by the growing resonance line at 29 ppm, corresponding to ethylbenzene  $\alpha$ - $^{13}\text{C}$ . In contrast, ethylbenzene  $\alpha$ - $^{13}\text{C}$  disappears rapidly with increasing reaction time. Consequently, the main reaction pathway observed for cumene and n-propylbenzene conversion at 573 K is dealkylation. Note that propylene is not observed due to its rapid self-hydrogenation or oligomerization in batch conditions [16,17,20]. Propane further reacts with benzene or other alkylaromatics to form various methyl-substituted aromatic compounds. This is evidenced by disappearance of the propane line and appearance of the resonance centered at 19.4 ppm also observed in the course of benzene alkylation with propane.

The above observations, schematized in the left-hand part of Fig. 9, indicate that the formation of methyl-substituted aromatics from cumene and n-propylbenzene requires propane as an intermediate; only a small portion of the toluene and ethylbenzene can be formed directly from cumene and n-propylbenzene. Consequently, toluene and ethylbenzene are obtained by direct alkylation.

In conclusion the reaction pathways (1–3) are less probable than pathways (4–5). The trace amounts of cumene and n-propylbenzene which are formed via pathways (1–3) are con-

verted back to benzene and propane at longer reaction times, as the reverse reaction is more favorable at 573 K.

### 3.5. Mechanism proposal

We have demonstrated that the main reaction pathway of benzene alkylation with propane include the following reaction steps (Fig. 10):

- Propane adsorption on a bifunctional active site including Brønsted acidic center and neighboring Ga site. This step is preceded by induction period because of concurrent stronger adsorption of benzene on the same type of centers, and strong interaction of adsorbed benzene with propane.
- Propane activation on a bifunctional active site leading to PPCP intermediate evidenced by scrambling of the  $^{13}\text{C}$  label in propane.
- Evolution of PPCP intermediate into  $\text{CH}_4$  and  $\text{C}_2\text{H}_5^+$  or  $\text{C}_2\text{H}_6$  and  $\text{CH}_3^+$  or  $\text{H}_2$  and  $\text{C}_3\text{H}_7^+$  species.
- Reaction of  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_7^+$  carbenium ions with benzene to give toluene, ethylbenzene, cumene and n-propylbenzene.
- Reverse reaction of unstable cumene and n-propylbenzene to propane and benzene followed by alkylation leading to more stable toluene and ethylbenzene.
- Conversion of toluene and ethylbenzene into xylenes and further into other methyl-substituted aromatics.
- Conversion of alkylaromatics to condensed aromatics.

Although the direct propane activation on bifunctional site seems to be more probable, participation of benzene in initial propane activation (route 1) cannot be completely excluded.

## 4. Conclusions

1. Co-adsorption of benzene and propane 2- $^{13}\text{C}$  on Ga/H-ZSM-5 leads to strongly adsorbed benzene species and two types of propane 2- $^{13}\text{C}$  species of different mobility.

2. Induction period observed in the course of alkylation is due to stronger benzene adsorption and interaction of adsorbed benzene with propane methylene groups, which prevent direct contact of propane molecules with active sites of zeolites.
3. The reaction mechanism includes formation of protonated cyclopropane intermediate, its evolution towards  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_7^+$  carbenium ions and their reaction with benzene to give toluene, ethylbenzene, cumene and n-propylbenzene, respectively. The major reaction pathways lead to toluene and ethylbenzene. Cumene and n-propylbenzene are not stable at 573 K and undergo the reverse reaction.

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