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Pentane Transformation over Silicaalumina/BCl_3 Solid Superacid*

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Pentane transformation over SiO_2(87%) – Al_2O_3/BCl_3 superacid was studied. It was found that Brönsted superacid centres formed in the reaction between the carrier and BCl_3 vapours are active in n-pentane low temperature transformation. Pentane is converted over them into carbenium ion (through intermediate carbonium ion), which either undergoes isomerization to form 2-methylbutane or reacts with a second molecule of the reactant forming 2-methylpropane and a longer surface carbenium ion. The latter acts as a secondary active centre for 2-methylpropane formation and also undergoes further transformation leading finally to coke.

Key words: superacids, silicaalumina, boron trichloride, pentane isomerization, pentane decomposition

The mechanism of low temperature alkane transformation catalysed by solid superacids is still a matter of controversy. It has been proposed that, depending on superacid nature, strong Brönsted acid centres [1–7], Lewis acid sites [8–11] or even redox ones [12–14] could ionise a neutral alkane molecule transforming it into a reactive carbenium ion. The latter can either undergo isomerization, forming a branched alkane isomer in a monomolecular transformation [15,16], form an alkene and then a dimer, which decomposes to branched isomers of the parent alkane and other decomposition products [14,17–19], or act as a surface initiator of an isomerization chain reaction [19]. It was also postulated that the alkane isomerization proceeds through a cation radical transition state [17,20].

In our previous work [4] we showed that SiO_2(87%) – Al_2O_3 carrier undergoes a reaction with BCl_3 vapours to become a superacid of Brönsted nature. This catalyst was used as a model protic alkane activating system in our study of reaction pathways of low temperature n-pentane transformations.

EXPERIMENTAL

Detailed procedure of superacid preparation has been described elsewhere [4]. Catalyst synthesis were performed in a batch reactor (60 ccm) in three steps: (a) carrier (SiO_2(87%) – Al_2O_3, 370 m^2 g^{-1}, 1.02–1.2 mm grain fraction, Aldrich) calcination (1 g, 753 K, 1.3×10^{-2} Pa, 3 hrs) followed by cooling of

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*Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

the system to 333 K, (b) reaction with BCl_3 (Aldrich) at saturated vapour pressure in 273 K (63.595 kPa) for 10 minutes and (c) evacuation (5 sec.). After the synthesis, 0.4 ccm of n-pentane, n-hexane or n-heptane (all supplied by Aldrich) was injected into the reactor. Poisoning experiments of acid centres were carried out by feeding mixtures of n-pentane with n-butylamine (Aldrich) as reactants. The amine had earlier been purified by distillation and stored over KOH. The analysis of reaction products was performed using gas chromatograph fitted with 30 m squalane capillary column.

RESULTS AND DISCUSSION

Transformations of n-pentane. 2-Methylbutane and 2-methylpropane were the main products of n-pentane transformation over Brönsted superacid centres of SiO_2(87%) – Al_2O_3/BCl_3 system (Fig. 1A).

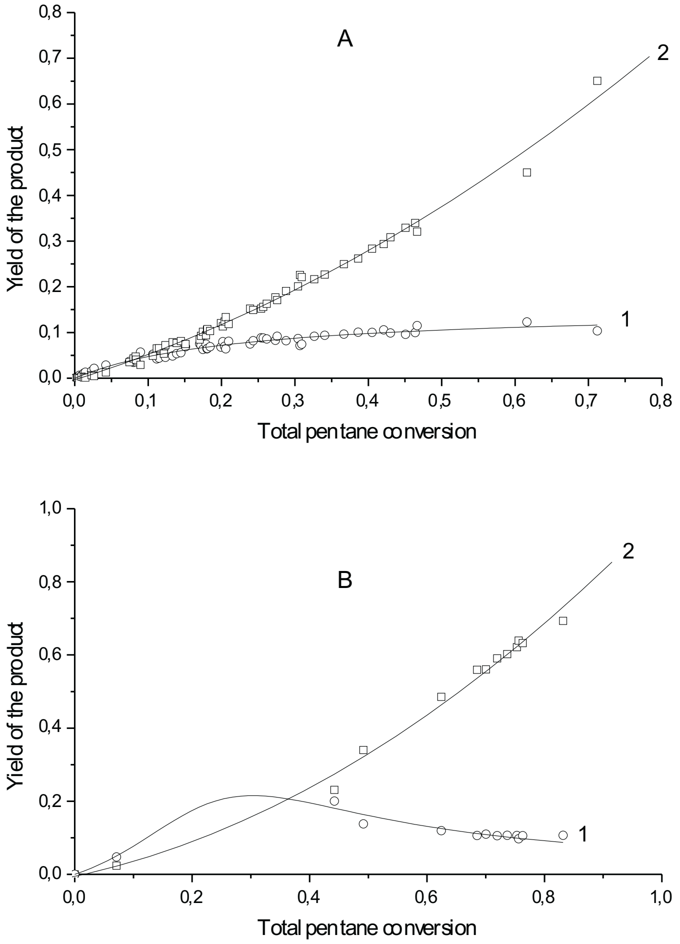


Figure 1. Pentane transformations at 333 K in the presence of (A) SiO_2(87%) – Al_2O_3/BCl_3 superacid and (B) SiO_2(87%) – Al_2O_3/SbF_5 superacid into (1) 2-methylbutane and (2) 2-methylpropane.

The morphology of *product yield/total reactant conversion* curves reflects the network of complex reactions [21]. Non zero value of initial product yield indicates that the product is formed in the primary reaction, while initial conversion equal to zero classifies the reactant as a secondary product. The presence of a maximum on the curve indicates that the product becomes a substrate for consecutive reactions. In the discussed case it is evident that both products are formed in the primary parallel reactions. For comparison purposes, the results of n-pentane reaction catalysed by a very active superacid, also of Brönsted nature, *i.e.*, $SiO_2(87\%) – Al_2O_3/SbF_5$ [3] are presented in Fig. 1B. In this case, the obtained curves are typical for a different reaction pathway: 2-methylpropane is a secondary product resulting from 2-methylbutane consecutive transformation. Such change in the reaction scheme, from parallel to consecutive, has been attributed by us [21] to an increase in the acid strength of superacid active centres. The lower acidity of the $SiO_2(87\%) – Al_2O_3/BCl_3$ system in comparison with superacid containing SbF_5 influences not only the reaction network, but also the reaction rate. In the presence of the former system, an n-pentane conversion of 44% is observed after 240 minutes of the reaction, while for the latter catalyst this level of conversion is reached within 7 minutes.

Poisoning experiments of acid centres. In order to study whether two main products of n-pentane transformations, *i.e.*, 2-methylpropane and 2-methylbutane are formed with the participation of acid centres, reactions with pentane/n-butylamine mixtures of different ratios were performed. It was found that amine adsorbs on active sites resulting in the inhibition of the reactions leading to both isomerization and decomposition products (Fig. 2).

Transformations of n-hexane and n-heptane. Longer alkanes *i.e.*, n-hexane and n-heptane also react in the presence of $SiO_2(87\%) – Al_2O_3/BCl_3$ system. Hexane isomerizes to 2- and 3-methylpentanes, 2,3- and 2,2-dimethylbutanes and decomposes to form 2-methylpropane and 2-methylbutane. Heptane transformations lead analogously to methylhexanes as well as to propane, 2-methylpropane and 2-methylbutane. With an increase in the carbon chain length of the reacting alkane, the value of the ratio of conversions into decomposition and isomerization products also increases. The results of decomposition reactions of n-pentane, n-hexane and n-heptane are presented in Fig. 3 and 4. The straight lines in the *product yield/total reactant conversion* plot depict the conversion of all substrates into 2-methylpropane as well as hexane and heptane into 2-methylbutane.

In our work [4] we showed that Brönsted centres of the superacid transform pentane into reactive carbenium ions. The latter undergo isomerization and desorb as branched reaction product. We found [4] that the first step of the reaction controls the rate of isomerization. Based on the above finding and using the Time On Stream theory of catalysts decay [22] we derived the kinetic equation, which also includes the terms describing the observed catalyst decay, solved it and calculated the value of n-pentane to 2-methylbutane conversion (x):

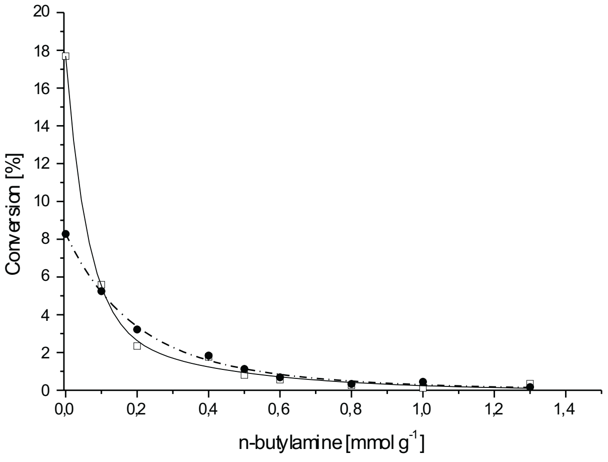


Figure 2. The influence of n-butylamine on the pentane isomerization (F) and decomposition (•) in the presence of SiO_2(87%) – Al_2O_3/BCl_3 superacid. Reaction temperature 333 K, reaction time 50

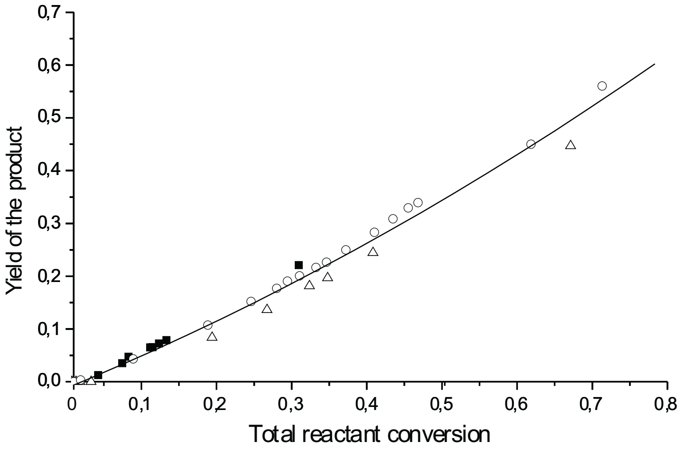


Figure 3. 2-Methylpropane formation from n-pentane (o), n-hexane (Δ) and n-heptane (■) in the presence of SiO_2(87%) – Al_2O_3/BCl_3 superacid at 333 K.

$$x = 1 - \exp\left(\frac{r_O t}{1 + Gt}\right)$$

where r_O is the initial reaction rate, G denotes the rate constant of catalyst decay and t is reaction time in batch reactor experiments. The obtained data were a good approximation of experimental results and supported the proposed scheme of pentane monomolecular isomerization [4].

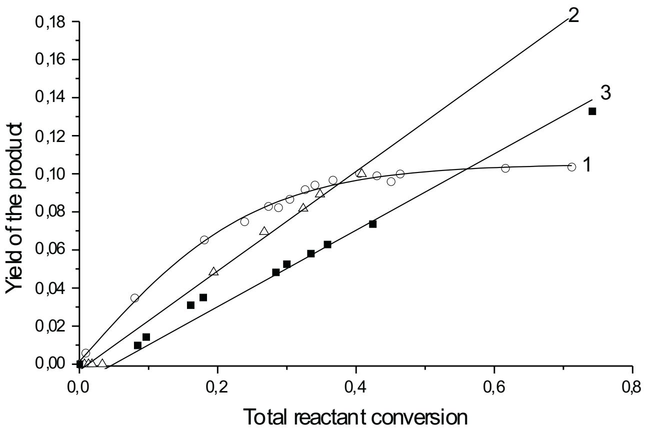


Figure 4. 2-Methylbutane formation from n-pentane (1), n-hexane (2) and n-heptane (3) in the presence of SiO_2(87%) – Al_2O_3/BCl_3 superacid at 333 K.

The formation of the second reaction product, *i.e.*, 2-methylpropane is more complex. The lack of an equivalent amount of six-carbon hydrocarbons among the reaction products excludes a simple bimolecular reaction suggested by Gates [5].

$$2C_5H_{12} \longrightarrow i\text{-}C_6H_{14} + i\text{-}C_4H_{10}$$

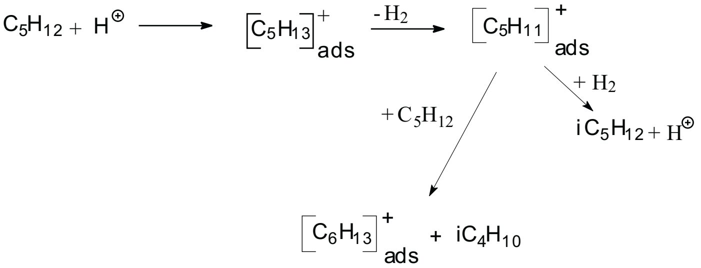
Thus, to fulfil the carbon balance of the reaction, for every molecule of 2-methylpropane formed one CH_2 group should be retained by the surface. Such groups, in the form of a coke could either block superacid centres causing the observed decay in isomerizing activity or after further transformation into surface carbenium ions could act as the secondary active sites. We have already suggested [16,23], that in the presence of previously examined Lewis-type superacids: $Al_2O_3/AlCl_3$ and $Al_2O_2/ZrCl_4$ 2-methylpropane is obtained in the reaction of surface carbenium ions bonded to the carrier and the substrate, *i.e.*, n-pentane. In the recent works dealing with the mechanism of catalytic cracking of alkanes, Wojciechowski [24,25] proposed a similar reaction scheme for alkane decomposition. He showed that an adsorbed carbenium ion formed as a result of the action of Brönsted centre (H^+B^-) can react with an alkane giving a transformation product, *i.e.*, new alkane as well as a modified surface carbenium ion, which is ready for the next reaction:

$$C_5H_{12} + H^{\oplus}B^{\ominus} \longrightarrow [C_5H_{13}]^{\oplus}B^{\ominus} \longrightarrow [C_5H_{11}]^{\oplus}B^{\ominus} + H_2$$

$$[C_5H_{11}]^{\oplus}B^{\ominus} + C_5H_{12} \longrightarrow C_4H_{10} + [C_6H_{13}]^{\oplus}B^{\ominus}$$

Not only surface stabilized carbenium ions take part in alkanes decomposition. Fărcaşiu [26] studied n-hexane reaction in liquid phase catalysed by trifluoromethanesulphonic acid and found that alkenyl cations formed during the reaction were responsible for the substrate decomposition into 2-methylpropane and 2-methylbutane. All these findings indicate that both acid centres and surface carbenium ions formed as a result of their activity can be active in alkanes transformations.

Based on the obtained *product yield/total pentane conversion* relations (Fig. 1) and the above discussion, a reaction scheme of n-pentane over SiO_2(87%) – Al_2O_3/BCl_3 superacid can be proposed:



where the Brönsted superacid centre transforms n-pentane into carbenium ion. The latter can either isomerize to 2-methylbutane or remain on the surface as bonded, positively charged species able to transform the alkane substrate into decomposition products. The transition state of the latter reaction is still controversial. It could be a decane carbenium ion resulting from the protonation of either a pentane dimer or a decene molecule. The first possibility is strongly supported by thermodynamic calculation [12]. Depending on the acid strength of the superacid present in the reacting system n-pentane forms:

- a carbonium ion, which, after transformation into a carbenium ion undergoes isomerization ($H_O < -27.3$),
- an unstable dimer which immediately reacts with a proton ($H_O > -24.5$).

Since the acid strength (H_O) of all known solid superacids does not exceed the value of –16 [13,27], the existence of such a transition state is very probable. The second possibility is based on the assumption that the carbenium ion undergoes deprotonation with alkene formation [14,17–19]:

$$C_5H_{11}^+ \rightleftarrows C_5H_{10} + H^+$$

Pentene undergoes further alkylation forming a surface decane carbenium ion:

$$C_5H_{11}^+ + C_5H_{10} \rightleftarrows C_{10}H_{21}^+$$

The most controversial step in this mechanism is the release of a proton from the surface pentane carbenium ion. Such reaction has already been postulated for the alumina-butene reacting system [28]. However, for the catalyst of Brönsted superacid properties, the equilibrium of the reaction should be completely shifted toward the carbenium ion. It is worth noting that irrespective of the formation mechanism of a dimer transition state its structure remains the same: $C_{10}H_{21}^+$ surface species.

The formation of both reaction products, *i.e.*, 2-methylpropane and 2-methylbutane, should depend on the concentration of the same Brönsted superacid centres since both products result from different reactions of the same precursor, *i.e.*, pentane carbenium ion. To confirm this we performed experiments where mixtures of n-pentane with different amounts of n-butylamine were used as reactants (Fig. 2). Indeed, the applied amine equally poisoned the formation of both discussed reaction products.

According to the proposed reaction scheme initially formed surface carbenium ions became responsible for 2-methylpropane formation. A comparison of the results of n-pentane, n-hexane and n-heptane transformations confirms the proposed reaction scheme (Fig. 3 and 4). In the *product yield/total reactant conversion* plot, the conversion of all substrates into 2-methylpropane lies on one straight line. This finding suggests that irrespective of reacting alkane chain length, 2-methylpropane is formed according to the same reaction pathway. In all cases, the proper reaction substrate could be the surface carbenium ion of a chain length varying from 5 to 7 carbon atoms. The other transformations leading to 2-methylbutane are depicted by curves of various shapes. It can be seen that this product is formed, depending on substrate, as a result of two different reactions. The first is isomerization, which takes place when n-pentane is used as the reactant. In this reaction a limited conversion caused by deactivation of the superacid centres is observed. The second one is characteristic for the remaining two longer alkanes when 2-methylbutane is formed after an induction period, and its yield increases proportionally with total conversion as observed in the case of 2-methylpropane. It can be explained assuming that 2-methylbutane forms from n-hexane and n-heptane similarly as 2-methylpropane, *i.e.*, through the formation and further reactions of surface bonded carbon chains.

The activity of surface carbon chains was confirmed in the following experiments. After 1200 min of n-pentane or 2-methylbutane reaction at 333 K, the reactants were evacuated and n-pentane or 2-methylbutane was introduced into the reactor. A substantial increase in the initial rate of 2-methylpropane formation observed for the second, consecutive reactions confirm catalytic activity of surface bonded carbenium ions in alkanes decomposition (Table 1).

Table 1. Results of consecutive experiments. After 1200 minutes of the first reaction with substrate 1 the reactor was evacuated and substrate 2 was introduced. Catalyst: SiO_2(87%) – Al_2O_3/BCl_3, 1 g. Reactor: batch type. Reaction temperature: 333 K. Reaction time: 1200 min.

Substrate 1	Products[a] [%]			Substrate 2	Products[a] [%]			$\frac{r_{02}}{r_{01}}$[b]
	2-MP	2-MB	n-P		2-MP	2-MB	n-P	
n-pentane	37.1	12.6	–	n-pentane	6.9	3.1	–	1.8
2-methylbutane	68.8	–	1.8	2-methylbutane	19.0	–	0.0	5.0

a) 2-MP, 2-MB and n-P denote 2-methylpropane, 2-methylbutane and n-pentane respectively.

b) r_{01} and r_{02} denote the rates of 2-methylpropane formation (for 2 min of the reaction) for the first and the second reaction respectively.

The surface species formed in the first stage of the experiment did not desorb during the evacuation and could readily react with n-pentane or 2-methylbutane giving 2-methylpropane.

The basic assumption of the proposed mechanism for 2-methylpropane formation is that surface carbenium chains act as active centres. Their number should be proportional to the number of decayed sites active in pentane isomerization.

$[C_5H_{11}]^+B^-$ $\longrightarrow$ isomerization and superacid
centre restoration
$\downarrow$
superacid centre transformation
into the secondary active site

In our work [4], based on Time on Stream theory of catalyst decay [22], we calculated the value of centre fraction Θ_{iC5} active in pentane isomerization as a function of reaction time (t).

$$\Theta_{iC5} = (1 + 0.06532\ t)^{-2}$$

The fraction of the sites responsible for 2-methylpropane formation is then given by the following formula:

$$\Theta_{iC4} = (1 - \Theta_{iC5})(1 + Gt)^{-N}$$

where G and N are decay constants while t denotes reaction time.

The second term in the above equation, according to the Time on Stream theory, depicts the active sites decay caused by the surface chain transformation into coke. Based on the assumption that the reaction of carbon chain with n-pentane is the rate determining step of the reaction we derived [16] the kinetic equation of 2-methylpropane formation:

$$r_{iC4} = A(1 - x)(1 - (1 + 0.06532\ t)^{-2})(1 + Gt)^{-N}$$

where: A is the product of the rate constant, the initial superacid centres concentration and initial pentane pressure, while x denotes pentane into 2-methylpropane conversion.

The experimental data, *i.e.*, r_{iC4}, x and t were fitted to the above equation and all parameters were determined (Table 2).

Table 2. Kinetic constants of n-pentane to 2-methylpropane reaction rate equation: $r_{iC4} = A(1 - x)(1 - (1 + 0.06532\ t)^{-2})(1 + Gt)^{-N}$

Catalyst	Calculated parameters
$SiO_2(87\%) - Al_2O_3/BCl_3$	A = 0.36075 G = 13.2148 N = 0.7877

Wojciechowski [22] proposed the use of the parameter N for the classification of catalyst stability. If N is low ($N < 1$) the catalysts active centres are stable and their decay is slow. Higher values of N ($N > 1$) are characteristic for rapidly decaying systems. The value of N equal to 0.7877 obtained for pentane to 2-methylpropane decomposition is much lower than the value calculated [4] for pentane isomerization ($N = 2$). This confirms that these two reactions are catalysed by different active sites of different stability. The calculated changes of their concentration with reaction time are presented in Fig. 5.

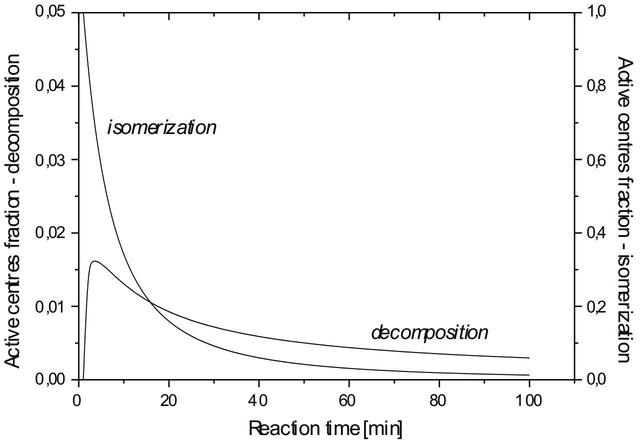


Figure 5. Evolution of superacid centres fraction of $SiO_2(87\%) - Al_2O_3/BCl_3$ superacid for pentane transformations at 333 K with reaction time.

The superacid sites responsible for pentane isomerization undergo rapid deactivation, while the fraction of active centres responsible for 2-methylpropane formation initially rises, reaches a maximum and finally decreases to a value close to 0.003. Using the data from Table 2 it was possible to compare the model and experimental results of pentane decomposition. A good agreement of experimental and calculated data supports the proposed mechanism of 2-methylpropane formation (Fig. 6).

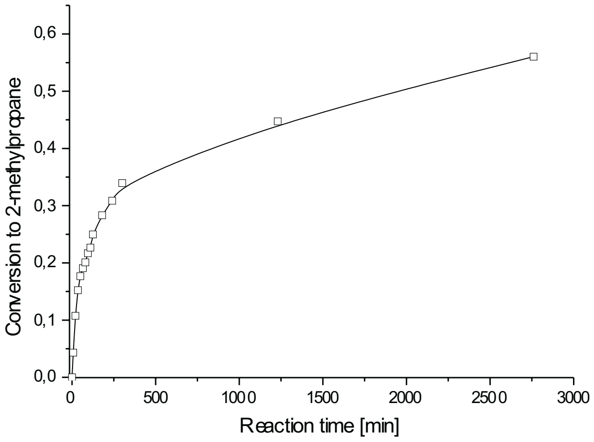
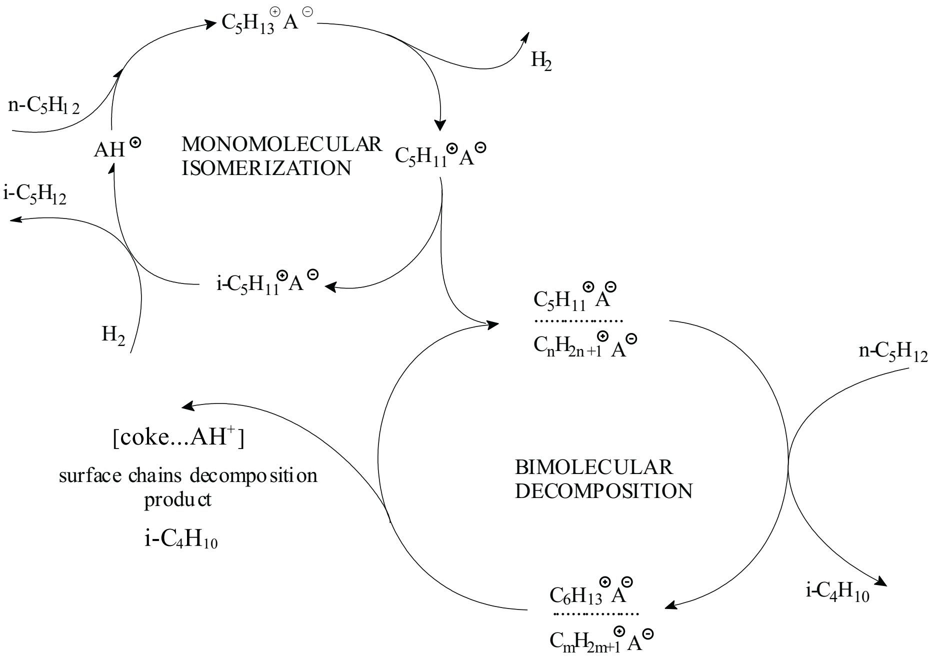


Figure 6. Comparison of experimental data of n-pentane to 2-methylpropane conversion (F) with the results of model calculation (line).

Based on the above discussion, a reaction scheme for n-pentane transformation can be proposed:



where AH$^+$ denotes active, superacid Brönsted centres.

It is comprised of two catalytic cycles: one depicting n-pentane isomerization over Brönsted superacid centres while the other describes 2-methylpropane formation. The latter reaction is catalysed by secondary active sites, *i.e.*, surface carbenium ions.

In conclusion to the presented results we propose that:

- superacid centres transform n-pentane into carbenium ion, which either isomerizes and desorbs as 2-methylbutane or become a secondary active site responsible for 2-methylpropane formation;
- the formation of secondary active centres from superacid sites and n-pentane is accompanied by superacid centres decay;
- consecutive reactions of surface carbenium ions result in coke formation and secondary active centres decay.

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