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Regioselective H/D isotope exchange and skeletal rearrangement reactions of propane over strong solid acids

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Abstract

The regioselectivity of the hydrogen/deuterium exchange reaction of propane over D_2O-exchanged ZSM-5 zeolite, unpromoted (SZ), and Al_2O_3-promoted sulfated zirconia (SZA) using a batch recirculation reactor was studied by means of ^1H and ^2H liquid state NMR spectroscopy. Low-temperature H/D exchange, below 100 °C, between acidic deuterium of the solid surface and propane was observed only on sulfated zirconia-based catalysts involving specifically the methyl protons. Detection of deuterium in the methylene position however occurred at higher temperatures as a consequence of skeletal rearrangement of the intermediate carbenium ion, evidenced by the ^{13}C scrambling in propane 1-^{13}C as well as by the ^2H scrambling in 1,1,1,3,3,3 propane-d_6 and 2,2-propane-d_2. The regioselectivity of the initial H/D exchange and the label redistribution observed at higher temperatures support the assumption that the exchange between propane and catalyst acidic surfaces proceeds via carbenium-ion-type intermediates and exclude possible pentavalent carbonium ion intermediates under these conditions.

Keywords: Alkane activation; H/D exchange; Acidic zeolite; Sulfated zirconia; Al_2O_3-promoted SZ; Carbenium ion mechanism

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1. Introduction

Activation of C–H bonds of alkanes can be achieved on the surface of solid acid catalysts at high temperatures, leading to various parallel reactions including cracking, isomerization, dehydrogenation, oligomerization, and disproportionation [1]. The hydron exchange between hydrocarbons and acidic protons of the solid acid occurring in the early stages of these reactions [2] can be monitored by isotopic labeling to provide useful information concerning the reaction mechanisms. Regiospecific exchange, like that observed for isobutane [3–5], is in agreement with a general mechanism based on intermediate carbenium ions, whereas an exchange that proceeds via a simple proton transfer between the solid surface and the alkane in a concerted step like that observed in methane [6,7] or ethane [7] involves generally a mechanism based on a pentacoordinated carbon (carbonium-ion-type) intermediate. In comparison with the well-established H/D exchange mechanism in liquid superacids [8,9], the mechanistic aspects on strong solid acids are still nowadays a subject of debate. The σ-basicity concept of alkanes was found to be extremely useful for explaining the formation of the pentavalent carbonium ions [10] observed in liquid superacid media. This situation is not obvious with solid acids because the superacidic character in solid acid catalysts is still not fully demonstrated [11–14]. However, recent studies of hydrogen exchange of propane adsorbed on acidic zeolites have concluded, based on apparent activation energies, that the exchange could be considered as proceeding via a concerted mechanism through the covalent transition state with pentacoordinated geometry [15,16]. Both methyl and methylene groups of propane were reported to be equally involved in the H/D exchange on zeolite H–ZSM-5 within the temperature range 457–543 K [15]. Moreover, in a study using ^{13}C-labeled propane, Derouane and co-workers demonstrated the occurrence of ^{13}C scrambling in propane upon interaction of propane with H–ZSM-5 [17]. To explain their results, the authors suggested that protonation of propane occurs on strong Brønsted acid sites of the zeolite, leading to the formation of carbonium-ion-type transition states (methylethonium ion). Nevertheless, our previous reports showed regiospecific H/D exchange in a one-pass mode reaction of propane on a series of catalysts, namely,

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H–USY, H–Beta, and H–ZSM-5 zeolites and sulfated zirconia; e.g., only methyl hydrons were involved in the H/D exchange [18,19]. This regiospecificity of hydron exchange implies alkene formation during the activation process followed by reprotonation and supports a mechanism based on formation of intermediate carbenium ions present on the surface as adsorbed alkoxy species [20].

In this paper we present a complementary regiospecific H/D exchange study of propane on zeolite H–ZSM-5 and sulfated zirconia-based catalysts using recirculation reactor mode, to achieve an extended degree of exchange, and selectively labeled starting materials. We show that the loss of regioselectivity at elevated temperature can be rationalized by the existence of parallel routes favoring skeletal rearrangement via formation of protonated cyclopropane ion intermediate as well as intramolecular hydride shifts.

2. Experimental

2.1. Catalyst preparation and materials

Zeolite ZSM-5 ($Si/Al = 39$) was obtained from P.Q. Corporation under the sample code CBV8020 [5,6]. Sulfated zirconia (SZ) and Al_2O_3-promoted sulfated zirconia (SZA) with an alumina content of 3 mol% ($Al_2O_3 + ZrO_2$) were prepared according to the procedure previously published [6]. Propane and propane 1-^{13}C were used as purchased without further purification, whereas propane 1,1,1,3,3,3-d_6 and propane 2,2-d_2 were synthesized. Propane 1,1,1,3,3,3-d_6 was prepared by reacting 2-bromopropane 1,1,1,3,3,3-d_6 with $NaBH_4$ in DMSO under a nitrogen atmosphere at 60 °C. After triple distillation of the raw product, propane 1,1,1,3,3,3-d_6 was obtained in a yield of 70%. ^{1}H and ^{2}H NMR analyses showed an isotopic purity of 97.3% D in the methyl position and no deuterium in the methylene position. 2-Bromopropane 1,1,1,3,3,3-d_6 was obtained after reduction of acetone-d_6 with $NaBH_4$ and subsequent bromination of the resulting isopropanol 1,1,1,3,3,3-d_6 with 47 wt% HBr aqueous solution. Propane 2,2-d_2 was synthesized from reaction of 2,2-dibromopropane with deuterated acetic acid at room temperature under nitrogen in the presence of granulated zinc. The yield of propane 2,2-d_2 was 61% after triple distillation. According to ^{1}H and ^{2}H NMR analyses, an isotopic purity of 93.2% D in the methylene position and no deuterium in the methyl group was found.

2.2. General experimental procedures

The catalytic reaction was run in a batch recirculation reactor at atmospheric pressure. About 1 g of catalyst in the case of SZ and SZA and 300 mg in the case of ZSM-5 was pretreated in situ with dry air (40 $ml\,min^{-1}$) at 450 °C (10 $°C\,min^{-1}$) for SZ and SZA and 500 °C (5 $°C\,min^{-1}$) for ZSM-5 for 2 h. Deuteration of the catalyst was carried out with 3 mol% D_2O in N_2 at 200 °C for 1 h, followed by a N_2 purge of 30 min. The reactor was then brought to reaction temperature and the alkane (ca. 5 ml) was introduced to the catalytic circuit. The amount of protons provided by the hydrocarbon were in large excess with respect to the acid protons/deuterons of the solid since surface concentrations of D_2O-exchanged acid sites at 200 °C as determined by a NMR method [21] were found to be 0.31, 0.66, and 0.96 $mmol\,g^{-1}$ for SZ, SZA, and ZSM-5 zeolite, respectively. On sulfated zirconia-based catalysts, the reaction temperature ranged from 50 to 100 °C and on ZSM-5 zeolite from 150 to 300 °C. The gas mixture (hydrocarbon and nitrogen) was circulated by a membrane pump at a speed of 5 $ml\,min^{-1}$. In all cases and within these temperature ranges, side products from oligomerization cracking were negligible and represents less than 1 mol% as determined by GC. After equilibrium was reached, which depends on experimental conditions, the reacted hydrocarbon was collected in a precooled (−117 °C) U-tube and then put in a $CF_2ClCFCl_2$ solution for NMR analysis.

^{1}H and ^{2}H NMR spectra were recorded at −30 °C on a Bruker AM400 spectrometer operating at a static magnetic field of 9.40 T. Free induction decays (FID) were recorded in a quantitative mode with 30° flip angle preparation pulses and ca. 4 and 3 s recycle delays for ^{1}H and ^{2}H NMR, respectively. A well-known amount of $CDCl_3$ and $CHCl_3$ were added to the NMR samples and used as an internal quantitative standard.

3. Results and discussion

3.1. H/D exchange between propane and D_2O-exchanged solid acid catalysts

The NMR technique was a tool of choice to study the H/D exchange of propane over solid acids regarding, first, the separation between methyl and methylene groups that IR and mass spectrometry could not provide and, secondly, the ease of quantification using an internal reference. An example of typical spectra obtained upon reaction with ZSM-5 at 300 °C is shown in Fig. 1. A summary of the NMR quantitative results of deuterium content in both methyl and methylene groups as well as in the overall molecule of propane after H/D reaction on deuterated ZSM-5, SZ, and SZA is given in Table 1. On ZSM-5 zeolite, hydrogen exchange reaction required temperatures in the range of 150–300 °C, whereas on sulfated zirconia-based catalysts, the exchange took place at much lower temperatures, i.e., 50–100 °C. No trace of deuterium was detected after 65 h of recirculation reaction on ZSM-5 at 100 °C. Sulfated zirconia catalysts seem to be more reactive since they required lower temperatures than the zeolite. Nevertheless, based on kinetic studies by mass spectrometry [5], the apparent activation energies were found on the same order of

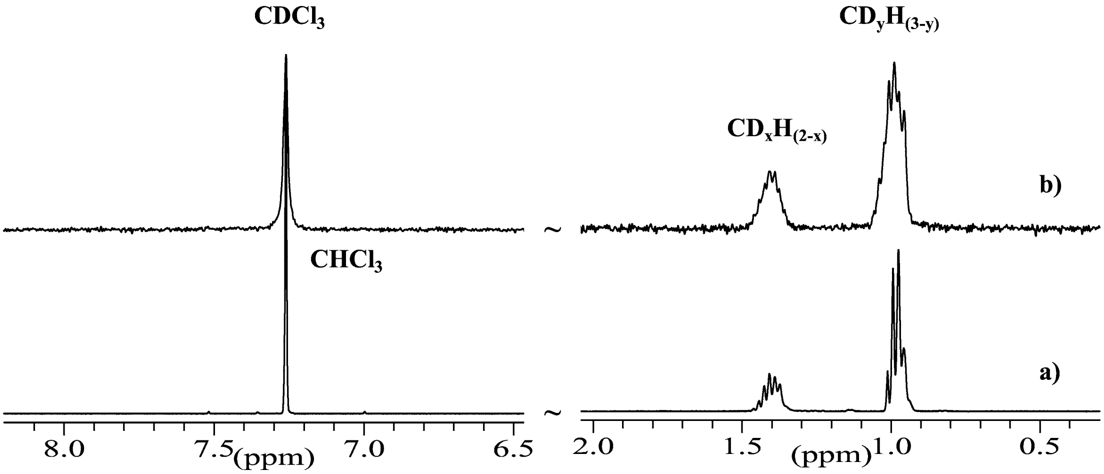

Fig. 1. ^1H (a) and ^2H (b) NMR spectra of propane recovered after H/D exchange with D–ZSM-5 at 300 °C. Signals of $CHCl_3$ and $CDCl_3$ are used as quantitative standards.

magnitude, ca. 91 kJ mol^{-1} for ZSM-5, 90 kJ mol^{-1} for SZ, and 84 kJ mol^{-1} for SZA despite the significant difference in temperature reaction ranges. This finding implies that the exchange mechanism is the same on the three catalysts. On the other hand, for given experimental conditions the extent of H/D exchange was much higher for SZA than for SZ, demonstrating the promoting effect of alumina on the catalyst. Indeed, using a quantitative NMR titration method [21], Brønsted acid sites in SZA were found to be two times more abundant than in SZ.

Although both methyl and methylene hydrons underwent exchange when the reaction was carried out on ZSM-5 [15], a trend for selective exchange can be noticed. It appears clearly from Table 1 that the ability of deuteration in methylene group increases with temperature. The proportion of D in the methylene position relative to the total amount of D in propane increases from 13.2, 22.2, and 26.5% for reaction at 150, 200, and 300 °C, respectively. Accordingly, the relative amount of D in the methylene group increases as well with the extent of exchange reaction. At 300 °C the statistical distribution of 25% ($\frac{2}{8}$) is reached. We can then conclude that in the early stage of reaction the exchange is first favored in the methyl position, while reaching equilibrium the deuterium is distributed statistically in the two positions. This is consistent with the presence of a scrambling process, as will be discussed later, altogether with exchange reaction.

Table 1
Deuterium distribution in propane in at% after H/D exchange on deuterated ZSM-5 at 150, 200, and 300 °C, SZ at 50, 75, and 100 °C, and SZA at 50 and 75 °C[a]

	Methyl hydrons	Methylene hydrons	Propane
ZSM-5/150 °C[b]	2.1	0.9	1.8
ZSM-5/200 °C[c]	7.5	5.7	7.1
ZSM-5/300 °C[d]	23.5	21.2	22.9
SZ/50 °C[b]	2.3	0	1.8
SZ/75 °C[e]	5.8	0	4.4
SZ/100 °C[e]	14.1	1.1	10.9
SZA/50 °C[b]	13.4	0	10.0
SZA/75 °C[e]	20.6	0.6	15.4

[a] Estimated errors within the limit of 3% of the corresponding values.
[b] After 63–64 h of recirculation reaction.
[c] After 58 h of recirculation reaction with redeuteration of the catalyst every 20 h.
[d] After 79 h of recirculation reaction with redeuteration every 24 h.
[e] After 18–23 h of recirculation reaction.

It is interesting to note that, in the case of sulfated zirconia catalysts, regiospecific H/D exchange was observed at low temperatures. Only methyl hydrons were exchanged for deuterium with SZ and SZA at 50–75 and 50 °C, respectively. Since SZA is more reactive than SZ, a trace of deuterium was detected in the methylene position of propane after reaction with SZA at 75 °C. Therefore, for SZ, a higher temperature, i.e., 100 °C, was required to observe deuterium in the methylene group in a ^2H NMR spectrum, albeit in a very small amount, cf. Fig. 2. These results confirm unambiguously the selective H/D exchange of a methyl group of propane over solid catalysts at moderate temperatures, as already shown in a one-pass mode reaction study with a very low degree of deuteration [18,19].

Since the exchange process is regioselective, the most probable mechanism would be based on formation of stabilized isopropyl cation as an intermediate. Stabilization of the formed trivalent carbocation as a surface-adsorbed alkoxy species in equilibrium with alkene during the exchange reaction is generally suggested [22]. The occurrence of carbenium ions as reaction intermediates is strongly supported by the observation that the isotopic exchange between alkanes and solid acid catalysts can be totally suppressed in the presence of carbon monoxide [3,23]. Regarding the loss of the regioselectivity at temperatures above 100 °C, a second process could occur jointly with the exchange reaction.

3.2. Reactions with labeled propane 1,1,1,3,3,3-d_6 and 2,2-d_2

To check the occurrence of a possible scrambling process, further experiments using partially deuterium labeled pro-

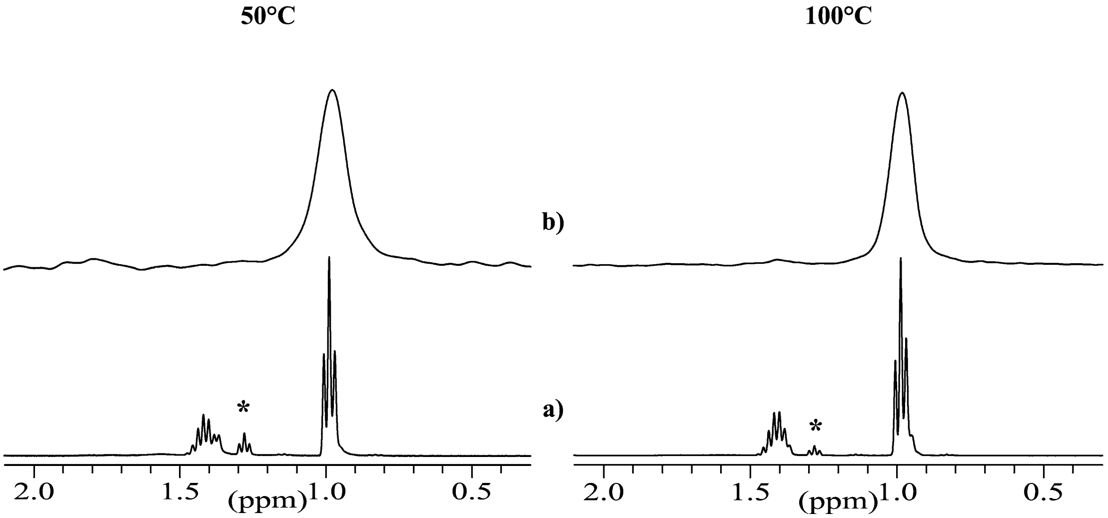

Fig. 2. ^1H (a) and ^2H (b) NMR spectra of propane recovered after H/D exchange with deuterated SZ at 50 and 100 °C. $*$ denotes ethanol in the internal standard mixture.

pane 1,1,1,3,3,3-d_6 and 2,2-d_2 were run on deuterated and non-deuterated SZA at 100 °C. All results summarized in Table 2 were consistent with evidence of intramolecular scrambling between hydrogen and deuterium of the two positions in the molecule of propane. The lack of exchange at the methylene carbon was observed at low temperatures and the scrambling between methyl and methylene hydrogens occurred at higher temperatures. When propane 1,1,1,3,3,3-d_6 was reacted with deuterated SZA, no further deuteration of the propane molecule occurred, whereas when it reacted with non-deuterated catalyst, H/D exchange was observed between the deuterium of the molecule and the proton of the surface, demonstrating that only methyl hydrons are really involved in the exchange. The scrambling process was evidenced by the decrease of the D percentage in the methyl position and the increase in the same time of that in the methylene position, especially in the case of reaction with a deuterated catalyst. Fig. 3 shows clearly the increases of NMR signal intensities of both methyl and methylene groups in ^1H and ^2H spectra, respectively, as a consequence of scrambling between the two positions. The presence of deuterium in the methylene position in case of reaction with the non-deuterated catalyst, on the other hand, is also direct proof of deuterium scrambling since the catalyst was free of deuterium. The same findings were observed again using propane 2,2-d_2, which showed a decrease of deuterium content in the methylene position when it reacted with deuterated SZA and, on the other hand, the appearance of deuterium in the methyl position upon reaction with a non-deuterated catalyst. The scrambling phenomena in the propyl cation formed in a liquid superacid medium was extensively studied by Saunders and co-workers [24–26]. Nevertheless, the absence of intramolecular scrambling in propane in liquid superacids was also reported [9]. The authors concluded that, in contrast with well-documented carbenium rearrangements, intramolecular hydron scrambling or skeletal rearrangement does not occur in H-carbonium ions or protonated alkanes. Accordingly, the presence of a scrambling process in our experiments would be in agreement with the formation of carbenium ions [18] as intermediates during the exchange process, rather than nonclassical pentacoordinated carbonium ions [15,17].

Table 2
Deuterium distribution in propane in at% after H/D exchange of propane 1,1,1,3,3,3-d_6 and 2,2-d_2 on deuterated and nondeuterated SZA at 100 °C[a]

	Methyl hydrons	Methylene hydrons	Propane
$CD_3CH_2CD_3$[b]	97.3	0	73.0
$CD_3CH_2CD_3$ + SZA-D[c]	85.1	19.7	68.8
$CD_3CH_2CD_3$ + SZA-H[c]	45.5	40.9	44.4
$CH_3CD_2CH_3$[b]	0	93.2	23.3
$CH_3CD_2CH_3$ + SZA-D[c]	37.9	42.9	39.2
$CH_3CD_2CH_3$ + SZA-H[c]	4.4	35.1	12.1

[a] Estimated errors within the limit of 3% of the corresponding values.
[b] Starting reagent.
[c] After 15–17 h of recirculation reaction.

Beside the H/D exchange between the surface of the solid catalyst and the adsorbed molecule, it appears clearly that other processes are also involved additionally at higher temperatures. The observed hydron scrambling can be obtained following two different processes, i.e., intramolecular H/D exchange or skeletal rearrangement. The intramolecular exchange implies hydride migration to a vicinal carbocation center. The skeletal rearrangement reaction allows a complete change in the hydrocarbon chain via a protonated cyclopropane intermediate. The experiments with regiospecifically deuterated propanes, 1,1,1,3,3,3-d_6 and 2,2-d_2, do not allow one to distinguish between the two processes as both routes could proceed also simultaneously.

3.3. *Reactions with labeled propane 1-^{13}C*

To verify whether skeletal rearrangement occurs and participates in the observed hydron scrambling, an experiment

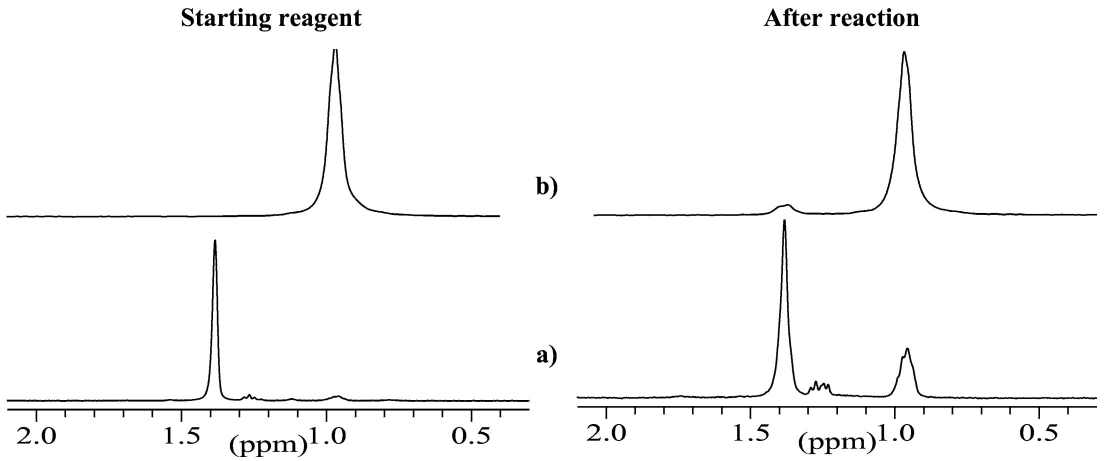

Fig. 3. ^1H (a) and ^2H (b) NMR spectra of propane 1,1,1,3,3,3-d_6 before and after H/D exchange with deuterated SZA at 100 °C.

using labeled propane 1-^{13}C on SZA was monitored under the same experimental conditions at 100 °C as for H/D exchange. The recovered recirculated propane for 15 h was analyzed by means of NMR spectroscopy. The proton spectra acquired with and without ^{13}C decoupling are given in Fig. 4. The ^{13}C-decoupled proton NMR (Fig. 4b) showed the conventional propane spectrum, i.e., a triplet and a septet for methyl and methylene protons, respectively, whereas the non-decoupled spectrum (Fig. 4a) showed additional scalar coupling with the ^{13}C isotope.

Based on comparison with the spectrum of the starting reagent, the satellite triplets around the main signal of methyls are due to the labeled ^{13}C methyl group ($^1J_{HC} =$ 125 Hz), whereas the nonlabeled ^{13}C methyl group presents a doublet of triplet that appears like a quadruplet due to close values of decoupling constants ($^3J_{HC} = 6.56$ Hz; $^3J_{HH} = 7.25$ Hz). Methylene protons showed also satellites around its main signal, which accounts for 16% of the total methylene signal, which were absent originally in the spectrum of the starting reagent, indicating the presence of the ^{13}C label in the methylene position. This is unequivocally direct proof of ^{13}C scrambling after contact with the catalyst, which was also confirmed by ^{13}C NMR. Ivanova et al. [17] proposed a mechanism for ^{13}C scrambling in propane over H–ZSM-5 catalysts involving propane protonation on strong Brønsted sites leading to C-ethanemethonium non-classical transition. Theoretical calculations, nevertheless, indicated that this species is not favored among the possible protonated propane species [9]. The energies of protonated cyclopropanes, however, are known to be far below the energy of the transition state for proton scrambling [26–28], which could better rationalize the observed ^{13}C scrambling.

A general scheme is then proposed, illustrated in Fig. 5, which accounts for our experimental results with respect to regiospecific H/D exchange and hydron and/or carbon scrambling in propane over solid acids. In this mechanism we propose that formation of propene would be a common

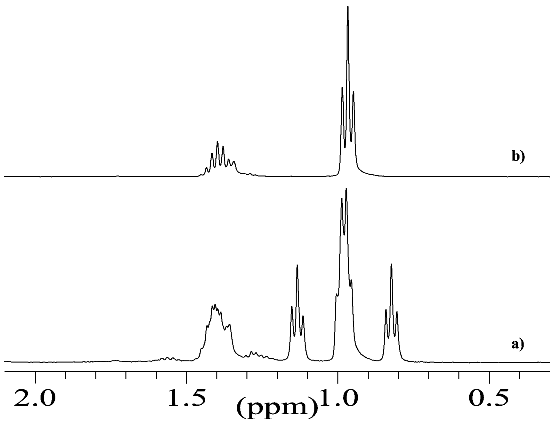

Fig. 4. ^1H (a) and ^{13}C decoupled ^1H (b) NMR spectra of propane 1-^{13}C recovered after recirculation reaction with SZA at 100 °C for 15 h.

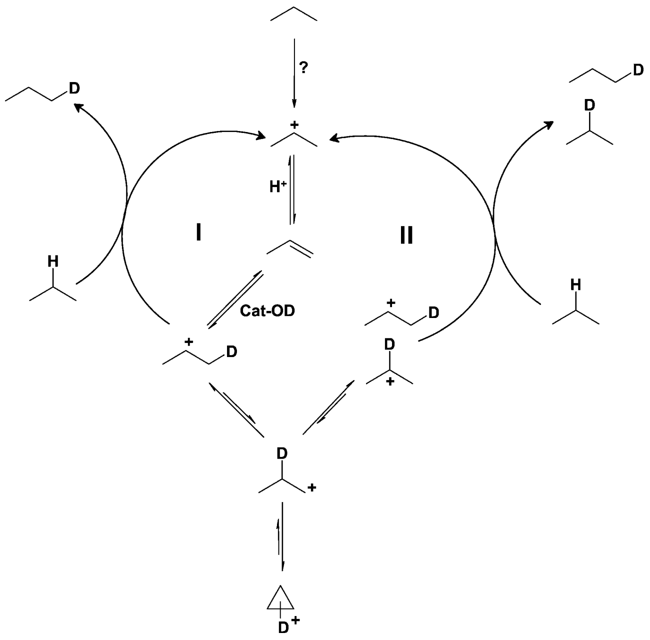

Fig. 5. Proposed catalytic cycle of regiospecific H/D exchange (process I) and skeletal rearrangement (process II) of propane on solid acids.

reaction intermediate for both a selective H/D exchange process (route I) and a skeletal rearrangement reaction (route II).

The reaction mechanism that is proposed involves proton transfer and the formation of intermediate carbenium ions, although the first step in the activation of the propane molecule, i.e., the formation of the initial isopropyl cation, still remains undetermined. Some hypotheses are generally suggested, such as hydride abstraction by Lewis acid sites, oxidation by electron acceptor sites, protonation of trace olefins by acidic sites, or direct protonation of the alkane by strong Brønsted acid sites. This last scheme is in fact the carbonium ion mechanism to initiate a carbenium ion mechanism. The formation of propene via oxidative dehydrogenation cannot be excluded [29]. Once the propylium ion is formed, it can either deprotonate, directly generating propene, or be stabilized as an alkoxy species for which deprotonation can occur in a concerted way on the surface. In both cases, regarding the highly reactive catalyst, propene will be reprotonated and so on, leading to a complete exchange of the methyl hydrons between the catalyst and the alkane. Therefore, protonation with Brønsted acid sites should be regioselective according to the Markovnikov addition rule. At this stage, two reaction pathways could be encountered following the experimental conditions. Below 75 °C, skeletal rearrangement is avoided and hydride abstraction from incoming propane closes the catalytic cycle of regioselective H/D exchange (route I). At higher temperatures, above 75 °C, formation of protonated cyclopropane is favored, presumably via the primary carbenium ion. In addition to the H/D exchange process, skeletal rearrangement leads to both carbon and deuteron scrambling (route II) and hydride abstraction from incoming propane allows desorption of propane deuterated in both methyl and methylene positions. This carbenium ion mechanism is supported by the observation of regiospecific H/D exchange observed only at moderate temperatures with sulfated zirconia-based catalysts. With zeolites that require higher temperatures for occurrence of the H/D exchange the observation of this selectivity is more difficult due to the extensive H/D exchange at the temperature at which it occurs. The second argument for the proposed mechanism is the evidence for the skeletal rearrangement at high temperature, responsible for the deuteron and carbon scrambling and therefore the loss of the regioselectivity. The carbonium ion mechanism would neither justify nor favor scrambling processes. Extended work by means of in situ solid state NMR is in progress to better separate and quantify the rate of the two processes: the H/D exchange and the skeletal rearrangement.

4. Conclusion

With use of a recirculation reaction mode facilitating long contact times, hydrogen/deuterium exchange reaction of propane over sulfated zirconia-based catalysts was observed within the temperature range of 50–100 °C without significant side products from oligomerization-cracking reactions. Zeolite ZSM-5 requires quite higher temperatures, i.e., 150–300 °C. At temperatures below 75 °C, the H/D exchange occurring between the deuteron of D_2O-exchanged solid acid catalysts and propane was found to be regioselective, involving the methyl protons only. At higher temperatures with ZSM-5, the methylene hydrons were also exchanged, however, to a lesser extent than methyl hydrons at low H/D exchange. The presence of deuterium in the methylene position at higher temperatures is rationalized by intramolecular rearrangements, which were evidenced using labeled molecules, i.e., propane 1-^{13}C as well as propane 1,1,1,3,3,3-d_6 and propane 2,2-d_2. Both regioselective H/D exchange and skeletal rearrangement processes are in agreement with an activation mechanism involving trivalent carbenium-ion-type intermediates rather than pentavalent carbonium ion intermediates.

Acknowledgments

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