The Initial Stages of Solid Acid–Catalyzed Reactions of Adsorbed Propane. A Mechanistic Study by in Situ MAS NMR

4 AUTHORS, INCLUDING:

Mohamed Haouas
Université de Versailles Saint-Quentin
104 PUBLICATIONS **2,055** CITATIONS

SEE PROFILE

Stéphane Walspurger
Technip B.V., Netherland
49 PUBLICATIONS **780** CITATIONS

SEE PROFILE

Francis Taulelle
Université de Versailles Saint-Quentin
320 PUBLICATIONS **7,606** CITATIONS

SEE PROFILE

The Initial Stages of Solid Acid-Catalyzed Reactions of Adsorbed Propane. A Mechanistic Study by in Situ MAS NMR

Mohamed Haouas,[†] Stéphane Walspurger,[‡] Francis Taulelle,[†] and Jean Sommer*,[‡]

*Contribution from RMN et Chimie du Solide, UMR 7140 CNRS, and
Laboratoire de Physicochimie des Hydrocarbures, UMR 7513, Université Louis Pasteur,
4 rue Blaise Pascal, 67070 Strasbourg Cedex, France*

Received August 5, 2003; E-mail: sommer@chimie.u-strasbg.fr

Abstract: In situ solid-state NMR spectroscopy was employed to study the kinetics of hydrogen/deuterium exchange and scrambling as well as ^{13}C scrambling reactions of labeled propane over Al_2O_3-promoted sulfated zirconia (SZA) catalyst under mild conditions (30−102 °C). Three competitive pathways of isotope redistribution were observed during the course of the reaction: (1) a regioselective H/D exchange between acidic protons of the solid surface and the deuterons of the methyl group of propane-1,1,1,3,3,3-d_6, monitored by in situ ^{1}H MAS NMR; (2) an intramolecular H/D scrambling between methyl deuterons and protons of the methylene group, without exchange with the catalyst surface, monitored by in situ ^{2}H MAS NMR; (3) a intramolecular ^{13}C scrambling, by skeletal rearrangement process, favored at higher temperatures, monitored by in situ ^{13}C MAS NMR. The activation energy of ^{13}C scrambling was estimated to be very close to that of ^{2}H scrambling, suggesting that these two processes imply a common transition state, responsible for both vicinal hydride migration and protonated cyclopropane formation. All pathways are consistent with a classical carbenium ion-type mechanism.

Introduction

Activation of C−H bonds of alkanes on the surface of solid acid catalysts such as zeolites, heteropolyacids, or sulfated zirconia can lead to various reactions including cracking, isomerization, dehydrogenation, and oligomerization.[1−4] Hydron exchange between hydrocarbons and acidic protons of solid acids has often been reported to occur in the early stages of the reactions. Useful information concerning the reaction mechanisms was obtained by isotopic labeling of the starting materials.[5−12] A theoretical approach of H/H exchange has addressed this question.[13] A mechanism based on a trivalent carbenium ion intermediate, hence an intermediary propene, leads to regiospecific H/D exchange following Markovnikov's rule,[14] as observed on methyl hydrons of isobutane at temper-

atures below 150 °C.[15−17] However, in the case of methane and ethane when only primary protons are available, in full analogy with carbonium ions in superacids,[18−21] H/D exchange requires much higher temperatures and proceeds via a direct proton transfer between the solid surface and the alkane in a concerted step involving a pentacoordinated carbon. For propane, a careful study of H/D exchange using labeled material should distinguish these two different cases by considering the regioselectivity of H/D exchange. These steps can therefore be compared to their superacid analogues, for which it has been shown that a carbenium ion mechanism does favor exchange on the methyl hydrons, while a carbonium ion mechanism would favor the methylene hydrons according to the σ-basicity of C−H bonds following the concept developed by Olah,[22] i.e., primary CH < secondary CH < tertiary CH.

Propane activation on solid acids related to aromatization, using isotopic tracers, has been reported in several recent mechanistic studies.[10,23−26] On the basis of extensive H/D exchange, or ^{13}C scrambling, observed by in situ solid state

[†] RMN et Chimie du Solide, UMR 7140 CNRS.

[‡] Laboratoire de Physicochimie des Hydrocarbures, UMR 7513.

(1) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press: New York, 1981.
(2) Olah, G. A.; Molnar, A. *Hydrocarbon Chemistry*; John Wiley: New York, 1995.
(3) Corma, A. *Chem. Rev.* **1995**, *95*, 559.
(4) Corma, A.; Orchilles, A. V. *Microporous Mesoporous Mater.* **2000**, *6*, 21.
(5) Jongepier, R.; Sachtler, W. M. H. *J. Res. Inst. Catal.* **1968**, *16*, 69.
(6) Mota, C. J. A.; Martins, R. L. *J. Chem. Soc., Chem. Comm.* **1991**, 171.
(7) Mota, C. J. A.; Martins, R. L.; Nogueira, W. B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2297.
(8) Mota, C. J. A.; Menezes, S. C.; Nogueira, L.; Kover, W. B. *Appl. Catal. A* **1996**, *146*, 181.
(9) Narbeshuber, T. F.; Stockenhuber, M.; Brait, A.; Seshan, K.; Lercher, J. A. *J. Catal.* **1996**, *160*, 183.
(10) Schoofs, B.; Schuermans, J.; Schoonheydt, R. A. *Microporous Mesoporous Mater.* **2000**, *35−36*, 99.
(11) Schoofs, B., Ph.D. Dissertation, Katholieke Universiteit Leuven: Leuven, Belgium, 2000.
(12) Sommer, J.; Jost, R. *Pure Appl. Chem.* **2000**, *72*, 2309.
(13) Esteves, P. M.; Nascimento, M. A. C.; Mota, C. J. A. *J. Phys. Chem. B* **1999**, *103*, 10417.

(14) Vollhardt, K. P. C. *Organic Chemistry*; Freeman and Co: New York, 1987.
(15) Sommer, J.; Hachoumy, M.; Garin, F.; Barthomeuf, D.; Vedrine, J. *J. Am. Chem. Soc.* **1995**, *117*, 1135.
(16) Sommer, J.; Jost, R.; Hachoumy, M. *Catal. Today* **1997**, *38*, 309.
(17) Essayem, N.; Coudurier, G.; Vedrine, J. C.; Habermacher, D.; Sommer, J. *J. Catal.* **1999**, *183*, 292.
(18) Kramer, G. J.; Van Santen, R. A.; Emeis, C. A.; Nowak, A. K. *Nature* **1993**, *363*, 529.
(19) Schoofs, B.; Martens, J. A.; Jacobs, P. A.; Schoonheydt, R. A. *J. Catal.* **1999**, *183*, 355.
(20) Vollmer, J. M.; Truong, T. N. *J. Phys. Chem. B* **2000**, *104*, 6308.
(21) Hua, W. M.; Goeppert, A.; Sommer, J. *Appl. Catal. A* **2001**, *219*, 201.
(22) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.
(23) Biscardi, J. A.; Iglesia, E. *J. Phys. Chem. B* **1998**, *102*, 9284.
(24) Stepanov, A. G.; Ernst, H.; Freude, D. *Catal. Lett.* **1998**, *54*, 1.
(25) Ivanova, I. I.; Pomakhina, E. B.; Rebrov, A. I.; Derouane, E. G. *Top. Catal.* **1998**, *6*, 49.

NMR in the 200–300 °C temperature range, several authors suggested that the reaction should be governed by a penta-coordinate carbonium ion intermediate as previously demonstrated in liquid HF-SbF$_5$ superacids.[27,28] However, internal hydron scrambling and isotope redistribution between alkane and catalyst is a rather complex mechanism which may imply several pathways with different rates and activation energies. Monitoring the isotope redistribution directly by in situ solid state NMR experiments can be extremely useful.[29–31] The competitive pathways, having different activation energies, cannot be distinguished when the temperature necessary to activate propane on zeolites passes above all activation energies. In prior studies based on product analysis at low alkane conversion, in the presence of various acidic catalysts including zeolites and sulfated zirconias, we already reported that only methyl hydrons of propane were isotopically exchanged during the initial stages of the H/D exchange process. The regio-selectivity was, however, lost at longer contact times.[15,32,33] The existence of parallel routes was suggested with protonated cyclopropane, as well as primary and secondary propylium ions, in full consistency with classical carbenium ion chemistry.

In the present paper, solid state NMR is used to monitor in situ, inter- and intramolecular H/D exchange as well as ^{13}C scrambling, under the same experimental conditions. Selectively labeled (^{2}H or ^{13}C) propane reacts with alumina-promoted sulfated zirconia. The high reactivity of alumina-promoted sulfated zirconia (SZA),[34–36] in comparison with other solid acids, allowed us to reduce considerably the temperature at which the reactive intermediates start to be generated on the solid. By direct monitoring of the reaction in situ at sufficiently low temperature, differentiation of several pathways became possible: intramolecular isotopic D and ^{13}C scrambling and H/D exchange with the catalyst. These processes are all consistent with a carbenium intermediate pathway.

Experimental Section

Materials and Sample Preparation. Al$_2$O$_3$-promoted sulfated zirconia (SZA) with an alumina content of 3 mol % (Al$_2$O$_3$ + ZrO$_2$) was prepared according to the procedure previously published.[37] Propane-d_8 and propane 1-^{13}C (isotopic purity >99 atom %) were used as purchased from Aldrich Chemical Co. without further purification, while propane-1,1,1,3,3,3-d_6 was synthesized as described elsewhere.[33]

Samples for NMR measurements were prepared by heating about 500 mg of solid catalyst directly into double-bearing Bruker 7 mm zirconia rotors. The temperature was increased at a rate of 2.5 °C min^{-1} under vacuum using a special glass tube in which the NMR rotor was placed at the bottom. Samples were maintained at 200 °C at less than 10^{-3} Pa for 2 h, then loaded at liquid nitrogen temperature with a known

Scheme 1
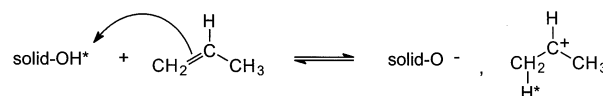
Scheme 2
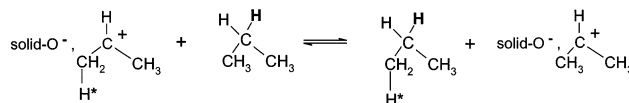
amount of labeled propane ranging from 20 to 70 μmol per gram of dehydrated solid catalyst and finally sealed under vacuum with tightly fitting special double O-ring Torlon caps. Brønsted acid sites in the catalyst were measured according to a quantitative NMR titration method[38] and found to be 660 μmol g^{-1}, which is in large excess relative to exchangeable deuterium of loaded propane. After use, the catalyst was regenerated by pretreating with dry air (40 mL min^{-1}) at 450 °C (10 °C min^{-1}) for 2 h and subsequent exchanging with 3 mol % H$_2$O in N$_2$ at 200 °C for 1 h.

NMR and Treatment of Data. In situ MAS NMR measurements were performed on a Bruker MSL 300 spectrometer at 23–102 °C at a rotation frequency of ca. 1 kHz. The corresponding Larmor frequencies were 300.1, 75.5, and 46.1 MHz for ^{1}H, ^{13}C, and ^{2}H nuclei, respectively. Free induction decays (FID) were recorded with 45° flip angle preparation pulses and 3 s recycle delay for all nuclei. Quantitative conditions were verified. The numbers of scans for accumulation were 40 for ^{1}H and ^{2}H and 400 for ^{13}C. High-power gated proton decoupling was used for ^{13}C and ^{2}H NMR experiments. Scalar couplings (J_{H-C}) were suppressed in ^{13}C spectra; however, no significant change in line broadening of ^{2}H signals was observed. For kinetics experiments, the interval between two steps in the time scale ranged from 2.5 min to 1.5 h depending on temperature and corresponding rate of catalytic reaction. Chemical shifts were referenced to standard TMS (0.0 ppm) for ^{1}H and ^{13}C NMR and to CDCl$_3$ (7.3 ppm) as secondary reference in case of ^{2}H NMR. The measuring temperature was controlled by a Bruker variable-temperature unit. The temperature inside the NMR rotor was calibrated using ethylene glycol as NMR chemical shift thermometer.[39]

An apparent first-order kinetics law was verified for both H/D exchange and isotope scrambling processes. The apparent rates k_i (k_{ex-HD}, k_{S-D}, or k_{S-C} for H/D exchange, D-scrambling, or C-scrambling) were then determined by an exponential fit of the observed integral area of signals as a function of time using the following analytical expression:

$$I(t) = I_{eq}[1 - \exp(-k_i(t + t_0))] \qquad (1)$$

where I_{eq} denotes the integral area of signals at the equilibrium, when no further change is observed, and t_0 denotes a shift in time origin in the case of an induction time ($t_0 > 0$) or a delay ($t_0 < 0$) relative to the kinetics experiments depending on the reaction temperature. Signal areas were determined by deconvolution of the overlapped peaks of CH$_2$ and CH$_3$ using the WinFit NMR simulation program.[40] In the case of ^{1}H kinetics (H/D exchange and D-scrambling) the integrals are reported in term of absolute values as arbitrary units, whereas in the case of ^{13}C kinetics (C-scrambling) the integrals are reported in relative area of total observed signals expressed in percentage. For this later case, I_{eq} was controlled during the simulation and fixed to the expected theoretical value of 33%.

(26) Ivanova, I. I.; Rebrov, A. I.; Pomakhina, E. B.; Derouane, E. G. *J. Mol. Catal. A* **1999**, *141*, 107.
(27) Olah, G. A.; Sommer, J.; Prakash, S. K. *Superacids*; J. Wiley: New York, 1985.
(28) Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370.
(29) Anderson, M. W.; Klinowski, J. *Nature* **1989**, *339*, 200.
(30) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1996**, *29*, 259.
(31) Hunger, M.; Horvath, T. *J. Catal.* **1997**, *167*, 187.
(32) Sommer, J.; Hachoumy, M.; Habermacher, D.; Reynaud, A.; Jost, R. In *Proceeding of the DGMK–Conference, Catalysis on Solid Acids and Bases*; Berlin (Germany); 1996; p 33.
(33) Haouas, M.; Walspurger, S.; Sommer, J. *J. Catal.* **2003**, *215*, 122.
(34) Gao, Z.; Xia, Y. D.; Hua, W. M.; Miao, C. X. *Top. Catal.* **1998**, *6*, 101.
(35) Lei, T.; Xu, J. S.; Gao, Z. *Chem. Lett.* **1999**, *6*, 509.
(36) Lei, T.; Xu, J. S.; Hua, W. M.; Tang, Y.; Gao, Z. *Catal. Lett.* **1999**, *61*, 213.
(37) Hua, W.; Goeppert, A.; Sommer, J. *J. Catal.* **2001**, *197*, 406.

(38) Olindo, R.; Goeppert, A.; Habermacher, D.; Sommer, J.; Pinna, F. *J. Catal.* **2001**, *197*, 344.
(39) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.
(40) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calve, S.; Alonso, B.; Durand, J. O.; Bujoli, B.; Gan, Z. H.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70.
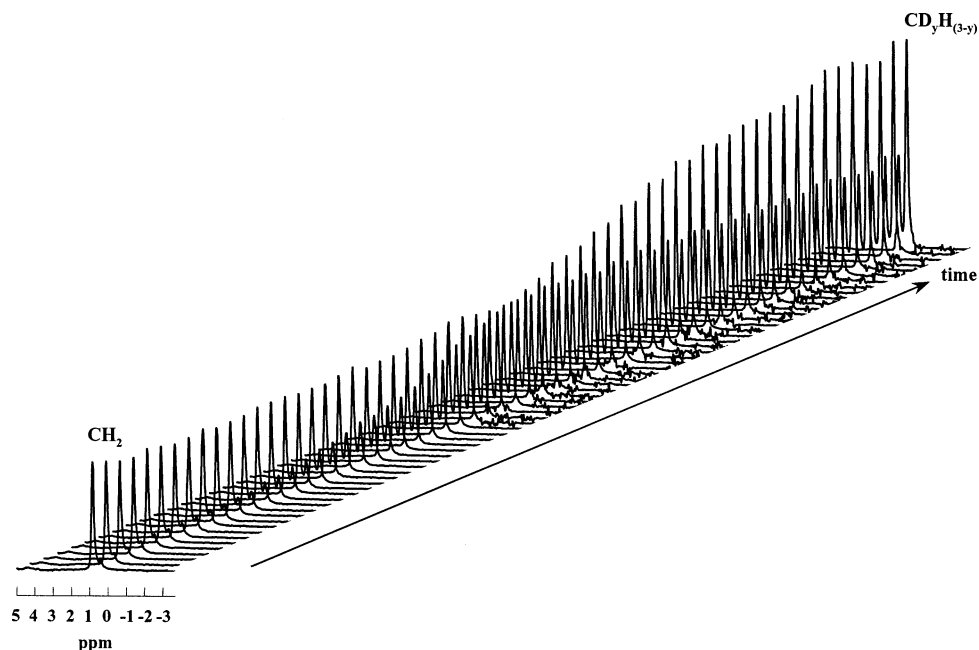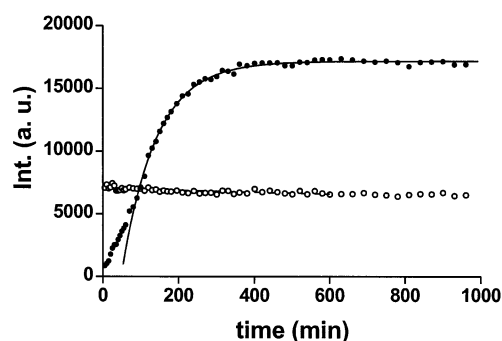
Figure 1. Stack plot of the ^{1}H MAS NMR spectra during the H/D exchange reaction between propane-1,1,1,3,3,3-d_6 and Al$_2$O$_3$-promoted sulfated zirconia catalyst (SZA) at 48 °C.

Results and Discussion

Despite several decades of efforts to understand the initial step of alkane activation on solid acids such as zeolites, heteropolyacids, or sulfated zirconias, it is still not clear how the initial adsorbed carbenium ions are generated from saturated hydrocarbon: σ-bond protolysis by superacidic sites, hydride abstraction by strong Lewis acid sites, and oxidative dehydrogenation followed by protonation have all been suggested but not univocally demonstrated.[41–43] However, the recent literature seems to indicate that the activation mechanism may be quite different depending on the solid acid, one-electron oxidation for sulfated zirconias[44,45] and the Haag–Dessau (protolysis) mechanism on zeolites.[46,47] Once generated, the adsorbed carbenium ion may undergo all well-documented competitive reactions such as deprotonation, β-scission, alkylation, and oligomerization.

In the case of propane, the initial activation step involves the OH hydrons of the catalyst and the methyl hydrons and leads to propene and/or adsorbed 2-propylium ion (Scheme 1). The true nature of the ions, isolated or not, cannot only be obtained from rate and product distribution studies. But it is well known that even in the strongest acid media, carbenium does exist as ion pairs. On solid oxides, stabilization (or solvation) occurs at the surface, most probably via the oxygen lone pairs available, generating oxonium-type ions also called alkoxy species. We suggest that at the temperature at which our reactions occur, no free carbenium ions are generated, but that the reactions occur rather in a concerted way in which the transition states never carry a full positive charge, the incipient

(41) Lercher, J. A.; Van Santen, R. A.; Vinek, H. *Catal. Lett.* **1994**, *27*, 1.
(42) Farcasiu, D.; Lukinskas, P. *Rev. Roummaine. Chem.* **1999**, *44*, 1091.
(43) Farcasiu, D. *Catal. Lett.* **2001**, *71*, 95.
(44) Ghenciu, A.; Farcasiu, D. *Chem. Commun.* **1996**, 169.
(45) Zhang, J. H.; Nicholas, J. B.; Haw, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3302.
(46) Haag, W. O.; Dessau, R. M. In *Proceedings of the 8th International Congress on Catalysis, Berlin*; 1984; p 305.
(47) Jentoft, F. C.; Gates, B. C. *Catal. Lett.* **1997**, *4*, 1.

Figure 2. Change in intensity of the ^{1}H NMR signals of the methyl (●) and methylene (○) hydrons during the reaction of adsorbed propane-1,1,1,3,3,3-d_6 on SZA at 65 °C. Solid lines represent the fits using eq 1 for the methyl group and a linear regression for the methylene group.

rearranged ions being already solvated by an other oxygen lone pair. The relative importance of alkoxy or ion pair structure depends of course on the structure of the ion and the nucleophilicity of its environment.[48] A recent theoretical work by Farcasiu and Hancu[42] stresses the importance of the counterion on the relative stability of the propylium ions. As the propylium ion desorbs via hydride transfer from propane, this leaves the methylene hydrons unchanged (Scheme 2). Earlier reports[11,24] suggesting that both methyl and methylene hydrons are equally involved via direct hydron exchange with the catalyst were rather surprising. It was particularly noticed that at low alkane conversion, in the same temperature range, the exchange was regioselective.[32] Other suggestions involving pentacoordinated carbonium intermediates have also been made.[11,25] Actually, the exchange process is complex and implies several competitive pathways, which can be sufficiently slowed to be distinguished by in situ NMR in the temperature range 48–90 °C.

Regioselective H/D Exchange and Intramolecular Hydride Shifts. When propane-1,1,1,3,3,3-d_6 was contacted with SZA

(48) Song, W. G.; Nicholas, J. B.; Haw, J. F. *J. Phys. Chem. B* **2001**, *105*, 4317.

¹H NMR
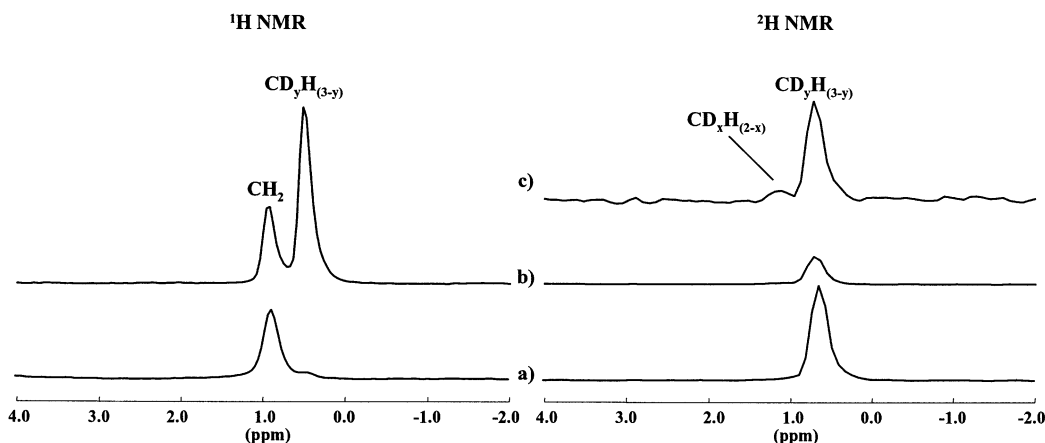
²H NMR

Figure 3. ¹H (left) and ²H (right) MAS NMR spectra of adsorbed propane-1,1,1,3,3,3-d_6 on SZA (a) before reaction and (b) after heating to 48 °C for 20 h. The ²H NMR spectrum (c) after reaction at 90 °C for 9.5 h is also included. Intensities of (a) and (b) are on same scale.

at 48 °C, the signal of methylene protons was observed at the start at 1.0 ppm in the ¹H MAS NMR spectrum (Figure 1). Later, as the reaction proceeds, the signal of the methyl hydrons at 0.5 ppm appears and increases, as a consequence of progressive substitution of deuterons by protons. MAS conditions were necessary to distinguish between the two signals, since the static NMR experiment showed a unique broad, nonresolved, signal of adsorbed propane. A rotation of a few hundred hertz was found sufficient to remove the chemical shift and diamagnetic susceptibility anisotropies of the surface-adsorbed molecule.

When the equilibrium between methyl hydrons and catalyst was reached, the intensity of the methyl signal in the spectra showed a plateau, as shown in the example at 65 °C (Figure 2). The kinetics of the H/D exchange between acidic protons of the surface and the methyl deuterons of propane-1,1,1,3,3,3-d_6 were determined by fitting the curve of the NMR signal intensity as a function of time with the first-order rate equation, eq 1. The deviation of the initial points is consistent with a short induction period, often reported to occur when alkanes are activated on solid acids.[49−52] This induction is generally suggested to correspond with the initial step, i.e., the generation of the adsorbed carbenium intermediates from the starting alkane via oxidation,[53,54] protolysis,[55] or hydride abstraction.[56,57] Such an induction period is not observed when the hydron exchange takes place directly between the acid and the alkane.[37]

The linear regression fit of the methylene signal intensity as a function of time provided a negative slope, indicating a small but continuous decrease of this signal which accounts for an internal D-scrambling between methyl and methylene positions via hydride(deuteride) shifts in the isomeric adsorbed propylium ions (Scheme 3). As expected due to the low reactivity (or higher solvation) of adsorbed primary ions, this process is favored at high temperatures, as shown by an increase of the negative slope (α) (Table 1). This table summarizes the ¹H NMR kinetics

Scheme 3
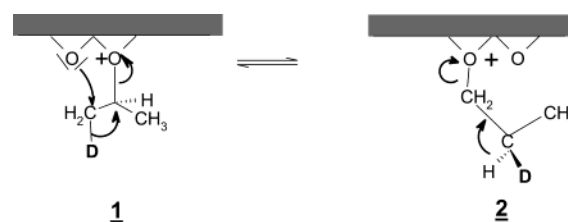
Table 1. Rates ($k_{ex−HD}$) and Induction Times (t_0) of H/D Exchange on Methyl Hydrons (CH₃) and Slopes (α) of Decrease of Methylene (CH₂) ¹H NMR Signal during the Reaction of Propane-1,1,1,3,3,3-d_6 with SZA

	CH₃		CH₂
T (°C)	$k_{ex−HD}$ (1000 min⁻¹)	t_0 (min)[a]	α (min⁻¹)
48	3.33 ± 0.12	92	−0.50 ± 0.05
65	11.0 ± 0.2	48	−0.76 ± 0.12
73	21.2 ± 0.7	16	−0.93 ± 0.06
90	46.2 ± 0.8	0	−2.9 ± 0.4

[a] Estimated errors within the limit of 5% of the corresponding values.

results of hydrogen/deuterium exchange of methyl groups as well as the decrease of the methylene signal during the reaction of propane-1,1,1,3,3,3-d_6 over SZA.

The rates of exchange were found to be on the same order of magnitude as measured with ZSM-5 zeolite in the temperature range184−270 °C,[24] confirming our previous findings.[33,37] However this does not necessarily imply that both systems present identical activation processes. The apparent activation energy obtained by the Arrhenius plot was determined as 61 ± 4 kJ mol⁻¹, a value much lower than that reported for ZSM-5 (108 kJ mol⁻¹). This difference may result both from the higher acidity of SZA and from a weaker stability of the alkoxy intermediates. To verify the occurrence of such D-scrambling, ²H MAS NMR measurements were carried out after each H/D exchange experiment. Figure 3 shows ²H MAS NMR spectra of propane-1,1,1,3,3,3-d_6 before and after reaction for 20 and 9.5 h at 48 and 90 °C, respectively. For comparison, ¹H MAS NMR spectra were included. The decrease of the ²H NMR signal and the simultaneous increase of the ¹H NMR signal of methyl

(49) Coelho, M. A.; Alvarez, W. E.; Sikabwe, E. C.; White, R. L.; Resasco, D. E. *Catal. Today* **1996**, *28*, 415.
(50) Hong, Z.; Fogash, K. B.; Dumesic, J. A. *Catal. Today* **1999**, *51*, 269.
(51) Hong, Z.; Fogash, K. B.; Watwe, R. M.; Kim, B.; Masquedajimenez, B. I.; Natalsantiago, M. A.; Hill, J. M.; Dumesic, J. A. *J. Catal.* **1998**, *178*, 489.
(52) Hammache, S.; Goodwin, J. J. G. *J. Catal.* **2003**, *218*, 258.
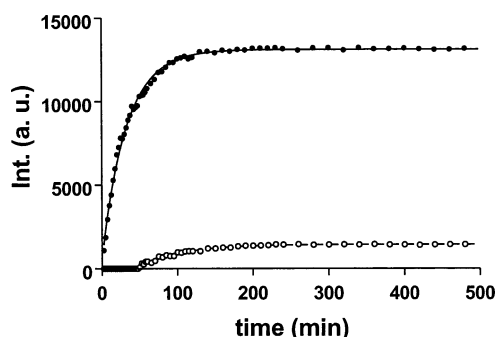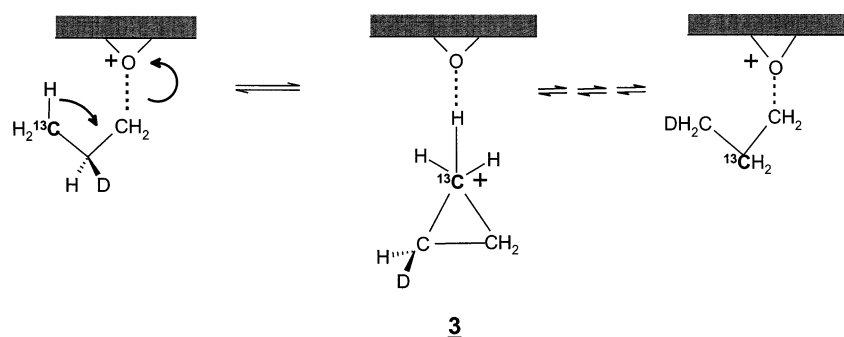(53) Farcasiu, D.; Ghenciu, A.; Li, J. Q. *J. Catal.* **1996**, *158*.
(54) Vera, C. R.; Yori, J. C.; Parera, J. M. *Appl. Catal. A* **1998**, *167*, 75.
(55) Kotrel, S.; Knozinger, H.; Gates, B. C. *Microporous Mesoporous Mater.* **2000**, *6*, 11.

(56) Pinna, F.; Signoretto, M.; Strukul, G.; Cerrato, G.; Morterra, C. *Catal. Lett.* **1994**, *26*, 3.
(57) Matsuhashi, H.; Shibata, H.; Nakamura, H.; Arata, K. *Appl. Catal. A* **1999**, *187*, 99.

Scheme 4

3

Figure 4. Change in intensity of the ^1H NMR signals of the methyl ($\bullet$) and methylene ($\bigcirc$) hydrons of adsorbed propane-d_8 on SZA at 82 °C. Solid line represents the fits using eq 1.

Table 2. Kinetic Parameters of the Reactions of Adsorbed Propane-d_8 on SZA: H/D Exchange and D-Scrambling Rates (k_{ex-HD}, k_{S-D}) on Methyl and Methylene Hydrons, Respectively, and Induction Period of D-Scrambling Relative to H/D Exchange

T (°C)	k_{ex-HD} (1000 min^{-1}) CH$_3$	k_{S-D} (1000 min^{-1}) CH$_2$	k_{ex-HD}/k_{S-D}	Δt_0 (min)^a
30	1.28 ± 0.02	0.19 ± 0.05	6.7	141
48	3.18 ± 0.04	1.34 ± 0.02	2.4	134
62	5.10 ± 0.08	2.20 ± 0.32	2.3	128
71	21.5 ± 0.5	10.2 ± 0.4	2.1	87
82	30.3 ± 0.6	17.6 ± 0.8	1.7	45

^{a} Estimated errors within the limit of 5% of the corresponding values.

Figure 5. Arrhenius plots of ($\bullet$) the apparent H/D exchange rate between the methyl group of propane and SZA and ($\bigcirc$) the apparent intramolecular D-scrambling rate on the methylene groups.
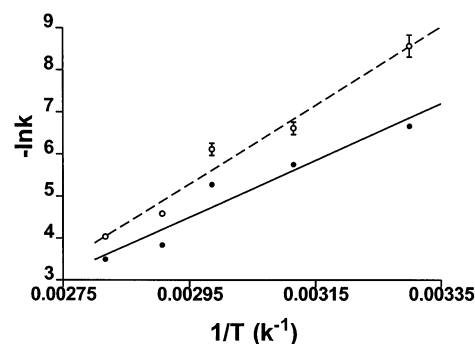
hydrons show the transfer of protons from acidic catalyst to the deuterated methyl group of the propane molecule. The appearance of a methylene resonance in ^2H spectra especially noticeable at higher temperature constitutes a good indication of the intramolecular D-scrambling since catalyst surface was free of exchangeable deuterium. Moreover, in the carbonium ion mechanism methylene hydrons would exchange faster than the primary hydrons.

Intramolecular Hydron Scrambling. Time-resolved ^1H MAS NMR experiments during the reaction of propane-d_8 (perdeuterated) with H-SZA were carried out at different temperatures, i.e., 30, 48, 62, 71, and 82 °C. The change in ^1H NMR signal intensities of methyl and methylene protons as a function of time at 82 °C is shown in Figure 4. A fast increase of the methyl proton's signal was observed as a consequence of the rapid H/D exchange with the catalyst following Scheme 1. The methylene hydrons appeared much later, in agreement with the vicinal hydride shift following Scheme 3. This type of scrambling is well documented in the stable propylium cation in liquid superacid media[58,59] but absent in carbonium ions, as demonstrated in the case of propane-1,1,1,3,3,3-d_6 in HF-SbF$_5$ superacids.[60] Moreover, acid strength of metal-modified sulfated ZrO$_2$ is far from that of HF-SbF$_5$ superacids.[61] The delay between the two processes (Table 2) is expected for two reasons: (i) the internal scrambling can proceed only once the methyl group is enriched in protons, (ii) internal scrambling needs the

involvement of an adsorbed primary carbenium ion intermediate, and thus a higher energy of activation (see above).

Activation energies for the H/D exchange process of the methyl group and D-scrambling of the methylene group in the reaction of SZA and propane-d_8 were determined from Arrhenius plots (Figure 5) as 54 ± 9 and 78 ± 8 kJ mol^{-1}, respectively. This difference of ca. 24 kJ mol^{-1} could account for the additional energy required to generate the adsorbed 1-propylium cation. The activation energy for intramolecular proton interchange in the propylium ion in SbF$_5$-SO$_2$ClF mixtures was reported to be 69 ± 2 kJ mol^{-1}.[62] Two competing mechanisms were proposed for the intramolecular proton interchange: via the reversible 1–2 hydride shift between 1- and 2-propylium ions and via a protonated cyclopropane (PCP) intermediate (Scheme 4). In contrast with vicinal hydride shifts, the ring closure leading to PCP is less direct, as it requires a preliminary rotation of the C$_1$–C$_2$ bond in order to allow the overlapping of the empty p-orbital on C$_1$ with the C$_3$–H σ bond. Moreover, it may also lead to skeletal rearrangement after ring opening. In analogy with these mechanistic proposals we suggest

(58) Saunders: M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53.
(59) Saunders: M.; Hewett, A. P.; Kronja, O. *Croat. Chem. Acta* **1992**, *65*, 673.
(60) Goeppert, A.; Sassi, A.; Sommer, J.; Esteves, P. M.; Mota, C. J. A.; Karlsson, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1999**, *121*, 10628.
(61) Haw, J. F.; Zhang, J. H.; Shimizu, K.; Venkatraman, T. N.; Luigi, D. P.; Song, W. G.; Barich, D. H.; Nicholas, J. B. *J. Am. Chem. Soc.* **2000**, *122*, 12561.

(62) Saunders: M.; Hagen, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 6881.
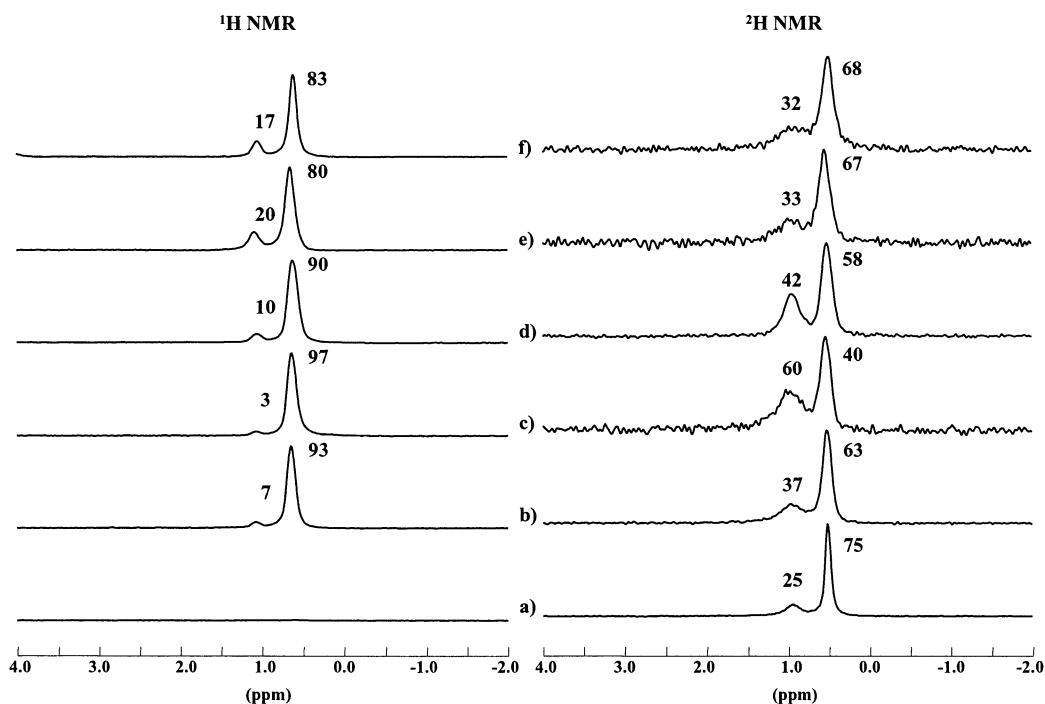
Figure 6. [1]H (left) and ^{2}H (right) MAS NMR spectra of adsorbed propane-d_8 on SZA (a) before reaction and after (b) 50 h at 30 °C, (c) 25 h at 48 °C, (d) 25 h at 62 °C, (e) 16 h at 71 °C, and (f) 8 h at 82 °C. Values of proton and deuteron proportions in the methyl and methylene groups are indicated in each spectrum.
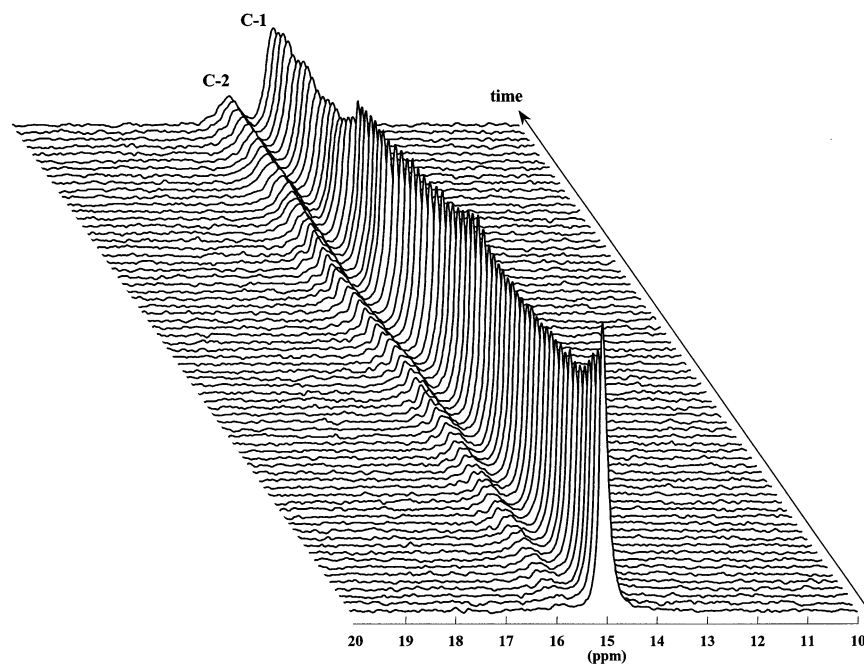

Figure 7. Stack plot of the ^{13}C MAS NMR spectra observed during reaction of propane 1-^{13}C on Al$_2$O$_3$-promoted sulfated zirconia catalyst at 82 °C. The time between subsequent spectra was 15 min for the first series of spectra, 30 min for the following one, and 45 min for the last one.

a similar process on the solid but with more strongly solvated intermediates, as shown in Scheme 4.

Figure 6 shows ^{1}H and ^{2}H NMR spectra of adsorbed propane-d_8 on SZA after longer contact times at different temperatures. ^{2}H NMR spectra before heating and just after sample preparation (Figure 6a) showed signals of CD$_3$ and CD$_2$ in a ratio of 3:1, respectively, in agreement with the ^{1}H NMR, whereas no significant ^{1}H signal was present. After reaction, a substantial decrease of ^{2}H NMR signal intensity was observed with

CD$_y$H$_{(3-y)}$/CD$_x$H$_{(2-x)}$ ratios below 3, while ^{1}H NMR exhibits the corresponding signals in ratios much larger than 3 at all temperatures, in agreement with the rapid exchange of the methyl hydrons with the protons of the catalyst. A maximum is reached at 62 °C (Figure 6d), when the CD$_y$H$_{(3-y)}$/CD$_x$H$_{(2-x)}$ ratio is below 1. At higher temperatures increasing participation of intramolecular scrambling leads progressively to a distribution closer to statistical, which would only be attainable at this temperature after much longer contact times. As both skeletal
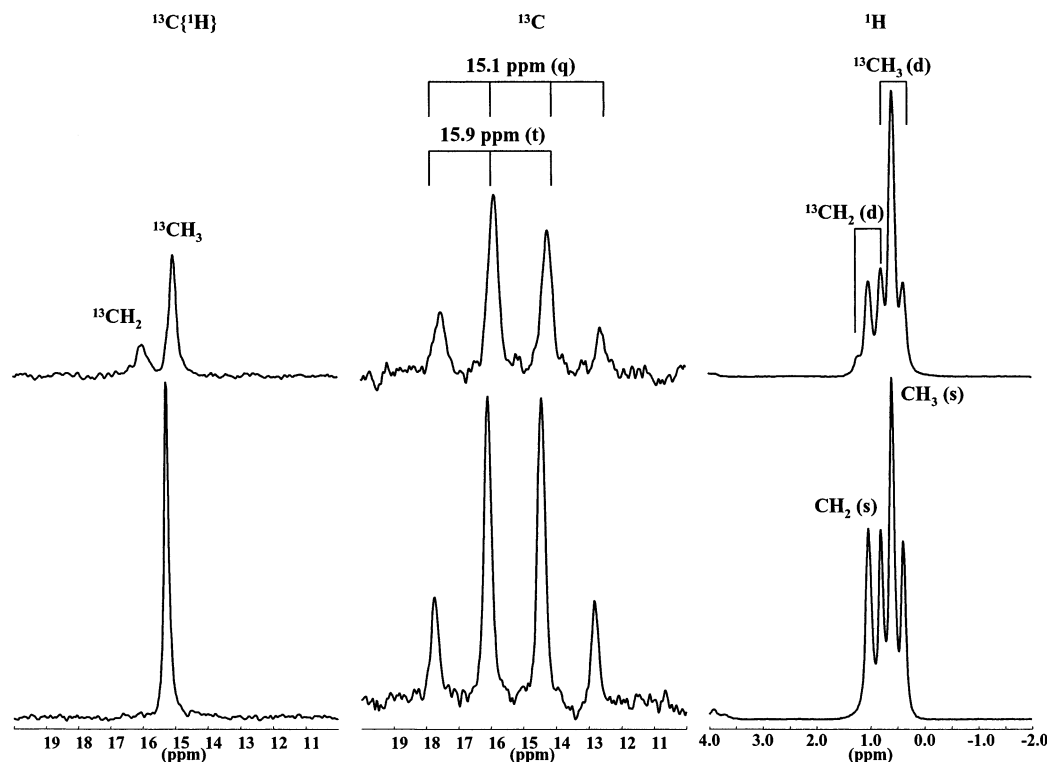
Figure 8. ^1H and ^{13}C with and without proton high-power decoupling MAS NMR spectra of adsorbed propane 1-^{13}C on SZA before reaction (bottom) and after heating to 82 °C for 34.5 h (top).

rearrangement and vicinal hydride shifts may contribute to scrambling at these temperatures, a simultaneous study with ^{13}C-labeled propane was imperative.

Carbon-13 Scrambling. Carbon-13 scrambling in the isopropyl cation was originally observed under stable ion conditions in liquid superacid media and was rationalized by the formation of a protonated cyclopropane intermediate.[58,59] Similar conclusions have been reached in the carbon scrambling in the *tert*-butyl cation based on rearrangement via the primary isobutyl cation involving the delocalized protonated methylcyclopropane as intermediate or transition state.[63] Carbon-13 scrambling in propane at temperatures as low as 300 °C was also reported over H-ZSM-5 zeolites.[25,64] It was suggested that a nonclassical C-ethanemethonium ion-type transition state could be involved after protonation of the alkane by strong Brønsted sites. However, protonation of propane in liquid superacids did not lead to intramolecular ^{13}C scrambling.[60]

As a PCP-type intermediate seemed more plausible and in order to clarify the mechanism, we monitored in situ the scrambling process using proton-decoupled ^{13}C MAS NMR with propane 1-^{13}C over SZA. Figure 7 shows the change in ^{13}C spectra during the reaction at 82 °C. The spectrum of adsorbed molecule before heating (Figure 8 left) showed a single resonance at 15.1 ppm, corresponding to the labeled methyl group of propane. A second line appeared at 16.0 ppm upon heating and grew up progressively with increasing contact time. These resonances are only slightly high-field-shifted (1 ppm) relative to adsorbed propane on ZSM-5 zeolites.[65−67] Proton-
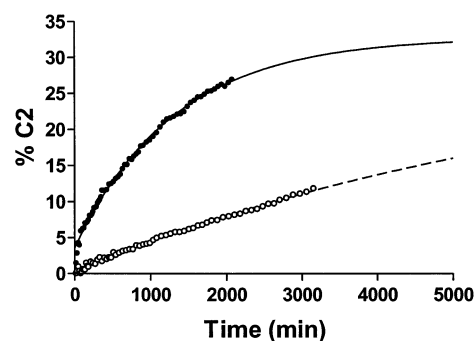
Figure 9. Relative intensity of methylene ^{13}C NMR signal as a function of reaction time of adsorbed propane 1-^{13}C on SZA (●) at 82 °C and (○) 62 °C. Solid lines represent the fits using $I_{eq} = 33\%$ for eq 1.

coupled ^{13}C NMR spectra (Figure 8 middle) showed scalar coupling with the proton linked to the labeled carbon center, whereas a quadruplet and triplet were observed for the methyl and methine carbon. Since $^1J_{CH}$ for both CH_3 and CH_2 were close to the difference between the respective chemical shifts, an overlapping pattern was obtained. ^1H NMR of adsorbed propane 1-^{13}C (Figure 8 right) allowed to distinguish between the three kinds of protons: methine protons (singlet at 0.6 ppm), the methyl protons linked to the labeled C (doublet at 1.0 ppm), and the second methyl protons (singlet at 1.0 ppm). After reaction, an additional doublet around the methine signal appeared due to coupling with ^{13}C in this position as a result of scrambling. No further significant signals appeared at these moderate temperatures (30−82 °C). Nevertheless, increasing temperature up to 102 °C led to an additional new signal around

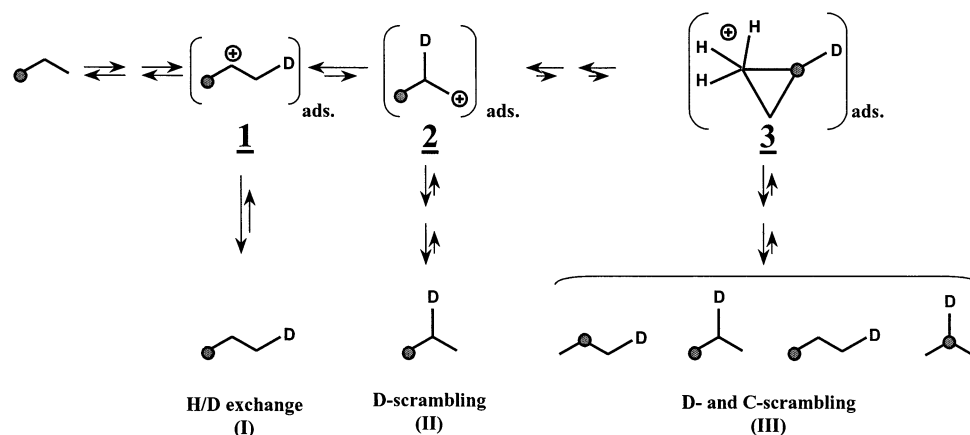(63) Prakash, G. K. S.; Husain, A.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 50.
(64) Ivanova, I. I.; Blom, N.; Derouane, E. G. *J. Mol. Catal. A* **1996**, *109*, 157.
(65) Derouane, E. G.; Abdul Hamid, S. B.; Ivanova, I. I.; Blom, N.; Hojlund-Nielsen, P.-E. *J. Mol. Catal.* **1994**, *86*, 371.

(66) Ivanova, I. I.; Blom, N.; Abdul Hamid, S. B.; Derouane, E. G. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 454.
(67) Luzgin, M. V.; Stepanov, A. G.; Sassi, A.; Sommer, J. *Chem.-Eur. J.* **2000**, *6*, 2368.

Figure 10. Initial products and intermediates resulting from H/D exchange of propane 1-^{13}C over SZA.

23.5 ppm that corresponds to isobutane as the side product of oligomerization-cracking.[25,64]

Figure 9 shows the change in intensity of the C-2 carbon NMR signal during the reaction of propane 1-^{13}C on SZA at 62 and 82 °C. First-order kinetics was verified using eq 1 to simulate the experimental data with controlled parameter for I_{eq}, fixed to the expected value at the equilibrium, i.e., 33% (one methine carbon of three total carbons). The C-scrambling process appeared extremely slow relative to the H/D exchange. Indeed, the calculated rates of C-scrambling from fits for eq 1 were $(76 \pm 4) \times 10^{-5}$ and $(15 \pm 2) \times 10^{-5}$ min^{-1} for 82 and 62 °C, respectively, 2 orders of magnitude slower than H/D exchange with the catalyst. The difference in rate between these two processes may be associated with the relative stability of the corresponding alkoxy species. The equilibrium can then be expected to be reached after 3 and 16 days of reaction at 82 and 62 °C, respectively. No significant ^{13}C scrambling was observed at 48 °C within 19 h of reaction. Above 82 °C, after prolonged contact times, side reactions, i.e., oligomerization-cracking, were observed. The apparent activation energy for ^{13}C scrambling within the temperature range 62−82 °C was determined as 80 kJ mol^{-1}. This value is much lower than the corresponding activation energy obtained on ZSM-5 zeolite (ca. 118 kJ mol^{-1}).[65] It is also interesting to note that the activation energy of the D-scrambling process (77 kJ mol^{-1}) was close to that of C-scrambling. This is in line with a common intermediate, **2**.

The various exchange and scrambling mechanisms consistent with our results and with previous studies of isopropyl cation in liquid superacids can be summarized as follows (Figure 10). (I) Hydron exchange with the catalyst introduces a deuteron in the methyl group of adsorbed 2-propylium ion **1**. (II) When enough energy is available with temperature, a vicinal deuteride shift occurs to form adsorbed 2-deutero-1-propylium ion, **2**. This is the first step for the intramolecular H/D scrambling. (III) The

formation of an adsorbed protonated cyclopropane intermediate **3** constitutes the second intramolecular scrambling process, leading to a complete statistical redistribution of the isotopes. It should be kept in mind that the reactive intermediates are represented as ions for the sake of graphical simplicity.

Conclusion

Using highly reactive alumina-promoted sulfated zirconia catalyst (SZA), selectively labeled propane, and in situ solid state NMR techniques at moderate temperature, the various solid acid-catalyzed inter- and intramolecular hydron exchange processes of propane were characterized. The sequence of reaction steps was established in terms of reaction rates. A selective H/D exchange between catalyst and propane involving exclusively methyl hydrons occurred first. At higher temperature H/D scrambling occurs between methyl and methylene hydrons. A third quite slower process led to complete H/D and ^{13}C isotope scrambling via skeletal rearrangement. The apparent activation energy for H/D exchange with the catalyst is significantly lower than that of both scrambling processes. Activation energies for D- and C-scrambling were roughly comparable, indicating that both processes involved a common intermediate: adsorbed 1-propylium ion. The mechanism of exchange/scrambling has been described previously, for zeolites, as a single-step mechanism. It appears here as a three-step reaction: first the H/D regioselective exchange, H/D selective scrambling, and further H/D and C scrambling. For each of the three reaction steps demonstrated in this study, a mechanism based on similarities with classical carbenium ion chemistry provides the best rationale for these observations.