Hydrogen H/D Exchange and Activation of C_1–*n*-C_4 Alkanes on Ga-Modified Zeolite BEA Studied with ^{1}H MAS NMR In Situ

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Supporting Information

TABLE 1S: Exchange Reactions Used for Simulating the Kinetics of the H/D Exchange for C_2–*n*-C_4 alkanes on H-BEA and Ga/H-BEA Zeolites

no.	Exchange reaction	Rate expression
1	$CD_3CD_3 + OH \leftrightarrows CD_2HCD_3 + OD$	$R_1 = k_a [CD_3CD_3][OH] - (1/6)\, k_a [CD_2HCD_3][OD]$
2	$CD_2HCD_3 + OH \leftrightarrows CDH_2CD_3 + OD$	$R_2 = (1/3)\, k_a [CD_2HCD_3][OH] - (1/3)\, k_a [CDH_2CD_3][OD]$
3	$CD_2HCD_3 + OH \leftrightarrows CD_2HCD_2H + OD$	$R_3 = (1/2)\, k_a [CD_2HCD_3][OH] - (1/3)\, k_a [CD_2HCD_2H][OD]$
4	$CDH_2CD_3 + OH \leftrightarrows CH_3CD_3 + OD$	$R_4 = (1/6)\, k_a [CDH_2CD_3][OH] - (1/2)\, k_a [CH_3CD_3][OD]$
5	$CDH_2CD_3 + OH \leftrightarrows CDH_2CD_2H + OD$	$R_5 = (1/2)\, k_a [CDH_2CD_3][OH] - (1/6)\, k_a [CDH_2CD_2H][OD]$
6	$CH_3CD_3 + OH \leftrightarrows CH_3CD_2H + OD$	$R_6 = (1/2)\, k_a [CH_3CD_3][OH] - (1/6)\, k_a [CH_3CD_2H][OD]$
7	$CH_3CD_2H + OH \leftrightarrows CH_3CDH_2 + OD$	$R_7 = (1/3)\, k_a [CH_3CD_2H][OH] - (1/3)\, k_a [CH_3CDH_2][OD]$
8	$CH_3CDH_2 + OH \leftrightarrows CH_3CH_3 + OD$	$R_8 = (1/6)\, k_a [CH_3CDH_2][OH] - k_a [CH_3CH_3][OD]$
9	$CD_2HCD_2H + OH \leftrightarrows CDH_2CD_2H + OD$	$R_9 = (2/3)\, k_a [CD_2HCD_2H][OH] - (1/3)\, k_a [CDH_2CD_2H][OD]$
10	$CDH_2CD_2H + OH \leftrightarrows CH_3CD_2H + OD$	$R_{10} = (1/6)\, k_a [CDH_2CD_2H][OH] - (1/2)\, k_a [CH_3CD_2H][OD]$
11	$CDH_2CD_2H + OH \leftrightarrows CDH_2CDH_2 + OD$	$R_{11} = (1/3)\, k_a [CDH_2CD_2H][OH] - (2/3)\, k_a [CDH_2CDH_2][OD]$
12	$CDH_2CDH_2 + OH \leftrightarrows CH_3CDH_2 + OD$	$R_{12} = (1/3)\, k_a [CDH_2CDH_2][OH] - (1/2)\, k_a [CH_3CDH_2][OD]$
13	$-CD_2- + OH \leftrightarrows -CDH- + OD$	$R_{13} = k_b [CD_2][OH] - (1/2)\, k_b [CDH][OD]$

14	-CDH- + OH ⇆ -CH_2- + OD	$R_{14} = (1/2)\, k_b\, [CDH][OH] - k_b\, [CH_2][OD]$
15	-CD_2CD_2- + OH ⇆ -$CDHCD_2$-+ OD	$R_{15} = k_c\, [CD_2CD_2][OH] - (1/4)\, k_c\, [CDHCD_2][OD]$
16	-$CDHCD_2$- + OH ⇆ -CH_2CD_2- + OD	$R_{16} = (1/4)\, k_c\, [CDHCD_2][OH] - (1/2)\, k_c\, [CH_2CD_2][OD]$
17	-$CDHCD_2$- + OH ⇆ -CDHCDH- + OD	$R_{17} = (1/2)\, k_c\, [CDHCD_2][OH] - (1/2)\, k_c\, [CDHCDH][OD]$
18	-CH_2CD_2- + OH ⇆ -CH_2CDH- + OD	$R_{18} = (1/2)\, k_c\, [CH_2CD_2][OH] - (1/4)\, k_c\, [CH_2CDH][OD]$
19	-CH_2CDH- + OH ⇆ -CH_2CH_2- + OD	$R_{19} = (1/4)\, k_c\, [CH_2CDH][OH] - k_c\, [CH_2CH_2][OD]$
20	-CDHCDH- + OH ⇆ -CH_2CDH- + OD	$R_{20} = (1/2)\, k_c\, [CDHCDH][OH] - (1/2)\, k_c\, [CH_2CDH][OD]$

For kinetics modeling the H/D exchange in alkanes the following reactions from Table 1S were taken into account:

- **ethane-d_6:** reactions 1-12 with OH represented by SiOHAl ($k_a = k_{SiOHAl}$) and the same reactions 1-12 with OH represented by SiOH (i.e. $k_a = k_{SiOH}$);
- **propane-d_8:** reactions 1-12 to describe the exchange in the methyl groups ($k_a = k_{CH3}$) and reactions 13-14 to describe the exchange in the methylene groups ($k_b = k_{CH2}$);
- ***n*-butane-d_{10}:** reactions 1-12 to describe the exchange in the methyl groups ($k_a = k_{CH3}$) and reactions 15-20 to describe the exchange in the methylene groups ($k_c = k_{CH2}$);

(1) H/D exchange in C_1,C_2 alkanes.

On the base of correspondent reactions from Table1 and Table 1S the following kinetic equations are derived for SiODAl and SiOD groups

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{SiODAl}]}{\mathrm{d}t} &= k_{\mathrm{SiOHAl}}\left\{[\mathrm{CD_n}]_0[\mathrm{SiOHAl}]_0 - [\mathrm{CD_n}]_0[\mathrm{SiODAl}] - \frac{1}{n}[\mathrm{X_{CHn}}][\mathrm{SiOHAl}]_0\right\}\\ \frac{\mathrm{d}[\mathrm{SiOD}]}{\mathrm{d}t} &= k_{\mathrm{SiOH}}\left\{[\mathrm{CD_n}]_0[\mathrm{SiOH}]_0 - [\mathrm{CD_n}]_0[\mathrm{SiOD}] - \frac{1}{n}[\mathrm{X_{CHn}}][\mathrm{SiOH}]_0\right\}\end{aligned} \qquad (1S)$$

where $[CD_n]_0$ is the initial concentrations of alkane; $[X]_{CHn}$ is the concentration of protium in alkane calculated as following

$$[\mathrm{X_{CHn}}] = \sum_{k=1}^{n} k[\mathrm{CD}_{n-k}\mathrm{H}_k]$$

The system of differential equations (1S) is easily transformed into system (2), assuming that $[X_{CHn}]=[SiODAl]+[SiOD]$ and mole fractions of D isotope are determined via equalities

$$F_{SiODAl}=\frac{[SiODAl]}{[SiOHAl]_0}, \qquad F_{SiOD}=\frac{[SiOD]}{[SiOH]_0}.$$

(2) H/D exchange in C_3, *n*-C_4 alkanes.

On the base of correspondent reactions from Table 1S the following kinetic equations are derived for concentration of protium in the methyl groups $[H]_{CH3}$ and the methylene groups $[H]_{CH2}$:

$$\begin{aligned}\frac{d[X_H^a]}{dt}&=k_{CH3}\left\{[RD_a^{(CH3)}]_0[OH]_0-[RD_a^{(CH3)}]_0[OD]-\frac{1}{a}[X_H^a][OH]_0\right\}\\ \frac{d[X_H^b]}{dt}&=k_{CH2}\left\{[RD_b^{(CH2)}]_0[OH]_0-[RD_b^{(CH2)}]_0[OD]-\frac{1}{b}[X_H^b][OH]_0\right\}\end{aligned} \qquad (2S)$$

where $[RD_a^{(CH3)}]_0$ and $[RD_b^{(CH2)}]_0$ represent the initial concentrations of the methyl and the methylene groups (in μmol g^{-1}), respectively; *a* and *b* is the total number of hydrogen atoms in methyl groups and methylene groups of a hydrocarbon, respectively; $[OH]_0=[SiOHAl]_0+[SiOH]_0$ is the total initial concentration of zeolitic OH groups.

Protium concentrations $[H]_{CH3}$, $[H]_{CH2}$ correspond to

$$[H]_{CH3}=\sum_{k=1}^{a}k[RD_{a-k}H_k], \qquad [H]_{CH2}=\sum_{l=1}^{b}l[RD_{b-l}H_l]$$

The system of differential equations (2S) is easily transformed into system (6), assuming that $[OD]=[H]_{CH3}+[H]_{CH2}$ and mole fractions of H isotope are determined via equalities

$$F_H^a=\frac{[H]_{CH3}}{a[RD_a^{(CH3)}]_0}, \qquad F_H^b=\frac{[H]_{CH2}}{b[RD_b^{(CH2)}]_0}.$$

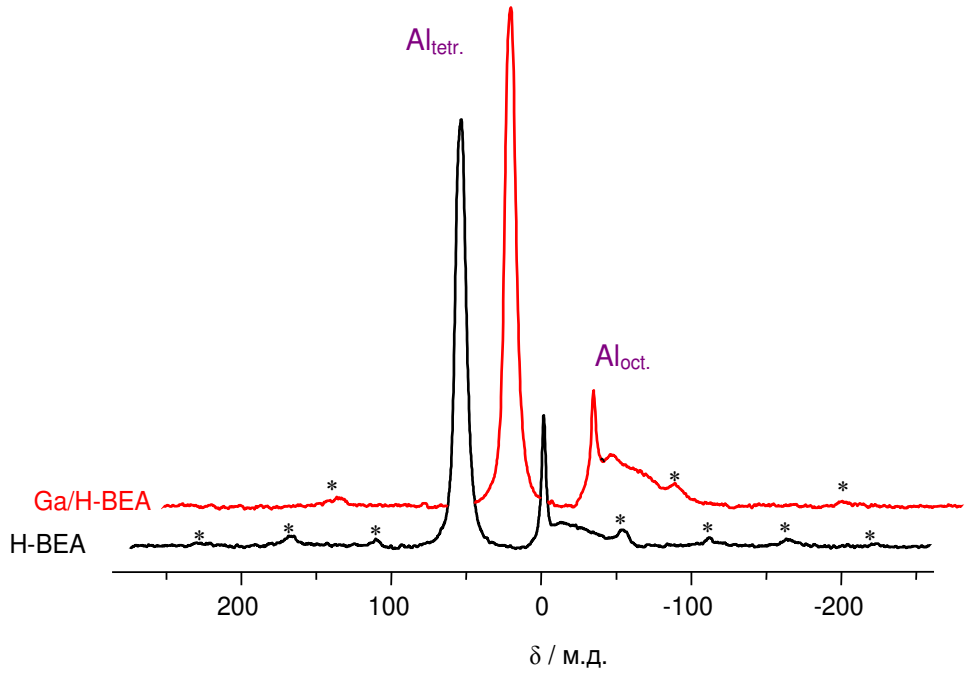

Figure 1S. ^{27}Al MAS NMR spectra of zeolites H-BEA and Ga/H-BEA. Asterisks * belong to spinning sidebands.

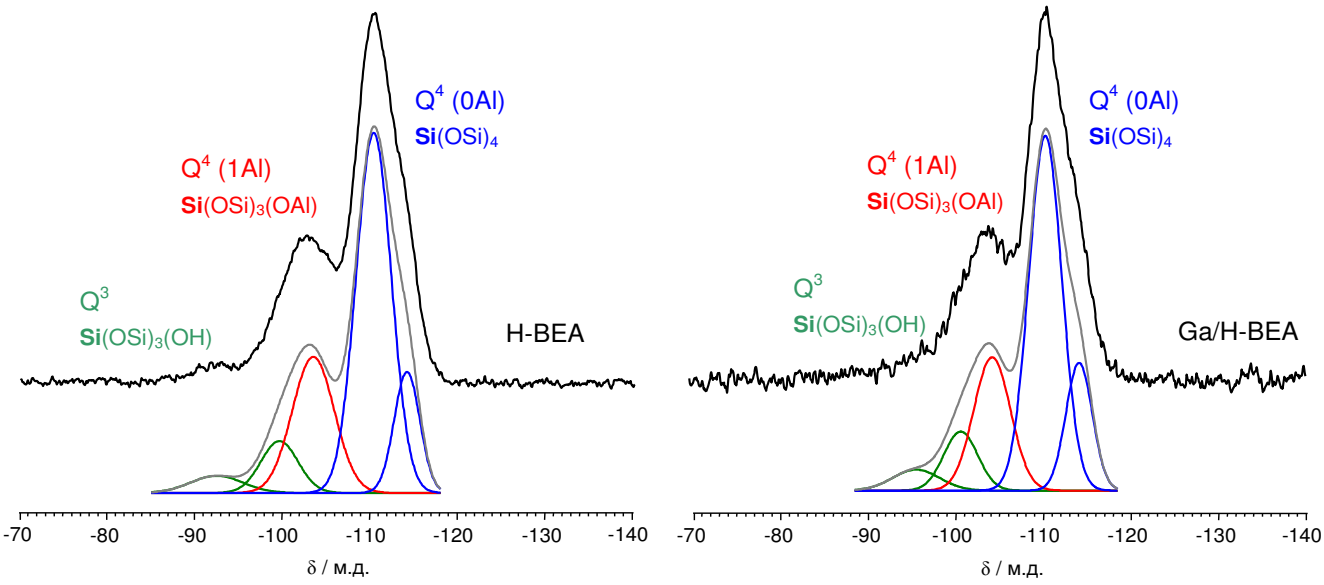

Figure 2S. ^{29}Si MAS NMR spectra of zeolites H-BEA and Ga/H-BEA.

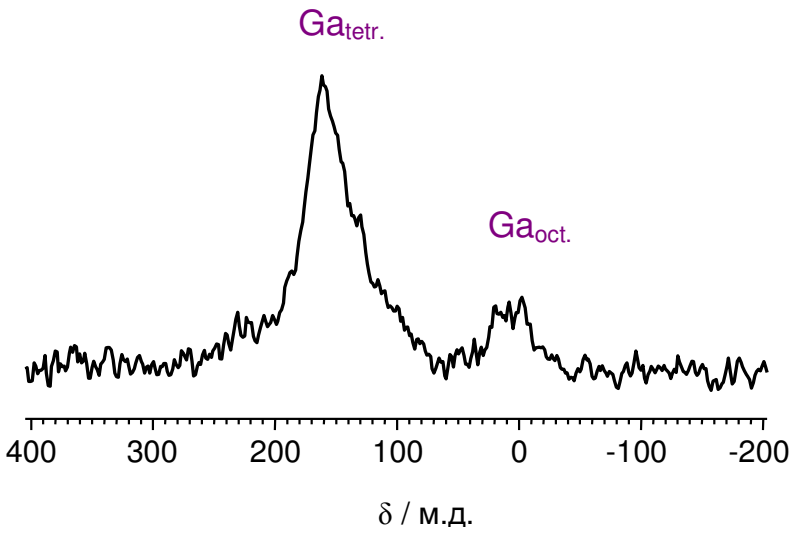

Figure 3S. ^{71}Ga MAS NMR spectrum of zeolite Ga/H-BEA .