

Supporting Information

Methane Activation on In-Modified ZSM-5 Zeolite. H/D Hydrogen Exchange of the Alkane with Brønsted Acid Sites

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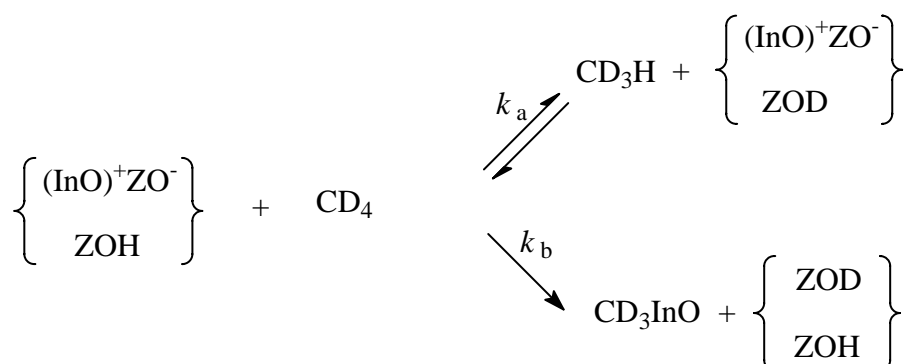
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Analysis of the kinetics for H/D exchange of methane-*d*₄ on InO⁺/H-ZSM-5 zeolite.

Kinetic curves for the reaction of methane-*d*₄ on InO⁺/H-ZSM-5 zeolite were analyzed on the base of the following (also see Scheme 1 in the manuscript):



The scheme involves H/D exchange between methane-*d*₄ and Brønsted acid site (BAS) of the zeolite (pathway 1) and irreversible conversion of methane into oxyindium–methyl species (pathway 2). Corresponding rate constants, *k*_a (for pathway 1) and *k*_b (for pathway 2), were

estimated by fitting the simulated kinetic curve to the experimental one, while treating k_a and k_b as free parameters. Reactions 1-14 (Table 1S) were used to calculate the simulated kinetic curve. In these reactions, {OH} and {OD} terms represent active sites capable of both exchanging hydrogen (protium or deuterium) in methane and transforming methane into side product (oxyindium–methyl). The set of formal kinetic equations derived on the base of reactions 1-14 was solved numerically by the Runge-Kutta method (Villadsen, J.; Michelsen, M. L. *Solution of Differential Equation Models by Polynomial Approximation*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1978). The initial concentration for {OH} was set to 270 $\mu\text{mol/g}$ in accordance with the stated zeolite unit cell composition $(\text{In}_2\text{O}_3)_{0.65} (\text{InO}^+)_{3.0} \text{H}_{1.7} \text{Al}_{4.7} \text{Al}^{\text{nonfr}}_{0.7} \text{Si}_{90.6} \text{O}_{192}$. The presence of the residual protium (1%) in methane- d_4 was taken into account by assuming binomial distribution through the CD_3H , CD_2H_2 , CDH_3 , and CH_4 isotope molecules, while the sum of all isotope molecules $\text{CH}_n\text{D}_{4-n}$ ($n=0\div 4$) was equated to the amount of methane adsorption (202 $\mu\text{mol/g}$). As the intensity of the ^1H MAS NMR spectrum is proportional to protium content, the experimental kinetic curves on Figure 5 were fitted to the function

$$[H] = \sum_{n=1}^4 n \cdot [\text{CH}_n\text{D}_{4-n}]$$

where $[H]$ represents protium concentration in methane ($\mu\text{mol/g}$) and $[\text{CH}_n\text{D}_{4-n}]$ is time-dependent concentration of the $\text{CH}_n\text{D}_{4-n}$ isotope molecule from Runge-Kutta numerical solution. Errors were estimated for the values of rate constants (k_a , k_b) assuming that position of each point in the kinetics is affected by spectrum integration error of 5%.

TABLE 1S: Reactions used for simulating the kinetics curves for the H/D exchange of methane- d_4 on $\text{InO}^+/\text{H-ZSM-5}$ zeolite

No.	Reaction	Rate constant	Equilibrium constant
1	$\text{CD}_4 + \{\text{OH}\} \rightleftharpoons \text{CD}_3\text{H} + \{\text{OD}\}$	k_a	$K_1 = 4$
2	$\text{CD}_3\text{H} + \{\text{OH}\} \rightleftharpoons \text{CD}_2\text{H}_2 + \{\text{OD}\}$	k_a	$K_2 = 3/2$
3	$\text{CD}_2\text{H}_2 + \{\text{OH}\} \rightleftharpoons \text{CDH}_3 + \{\text{OD}\}$	k_a	$K_3 = 2/3$
4	$\text{CDH}_3 + \{\text{OH}\} \rightleftharpoons \text{CH}_4 + \{\text{OD}\}$	k_a	$K_4 = 1/4$
5	$\text{CD}_4 + \{\text{OH}\} \rightarrow \text{methyl-InO}$	k_b	—
6	$\text{CD}_3\text{H} + \{\text{OH}\} \rightarrow \text{methyl-InO}$	k_b	—
7	$\text{CD}_2\text{H}_2 + \{\text{OH}\} \rightarrow \text{methyl-InO}$	k_b	—
8	$\text{CDH}_3 + \{\text{OH}\} \rightarrow \text{methyl-InO}$	k_b	—
9	$\text{CH}_4 + \{\text{OH}\} \rightarrow \text{methyl-InO}$	k_b	—
10	$\text{CD}_4 + \{\text{OD}\} \rightarrow \text{methyl-InO}$	k_b	—
11	$\text{CD}_3\text{H} + \{\text{OD}\} \rightarrow \text{methyl-InO}$	k_b	—
12	$\text{CD}_2\text{H}_2 + \{\text{OD}\} \rightarrow \text{methyl-InO}$	k_b	—
13	$\text{CDH}_3 + \{\text{OD}\} \rightarrow \text{methyl-InO}$	k_b	—
14	$\text{CH}_4 + \{\text{OD}\} \rightarrow \text{methyl-InO}$	k_b	—