Calculation of reaction rate constants for hydrogen–deuterium exchange reactions of methane catalysed by acid zeolites

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Hydrogen–deuterium exchange between methane and an acid zeolite is a model reaction (refs. 1–6) for which experimental rate constants and activation energies can be compared with theoretical values, obtained with Eyring's transition state theory (ref. 7).

Obtaining rate constants for zeolite catalysed reactions, is neither experimentally nor theoretically straightforward. Experimentally, the apparent reaction rates are influenced by the adsorption behaviour of the molecules.[8,9] Intrinsic reaction parameters can only be obtained by fitting the reaction rate data to a model. Another problem is the uncertainty about the exact number of acid sites in a zeolite, due to the existence of extra-framework Al and lattice defects. The accuracy of theoretically calculated rate constants depends strongly on the model used to represent the zeolite. Usually a fully relaxed cluster,[3,4] which can only model the local environment of the acid site, is employed. Thus adsorption, and structural, long range effects cannot be accounted for in model cluster calculations.

The aim of the present paper is to check the validity of calculated rate constants. Therefore we compared them with reliable experimental values.[6] The kinetics of hydrogen–deuterium exchange between methane and deuterated acid FAU- and MFI-type zeolites have been determined in a circulation batch reactor with on-line mass spectrometric product analysis, in the temperature range 450–550 °C. The apparent activation energy was in the range 122–150 kJ mol^{-1} and a kinetic isotope effect ($k_{OH/CD}/k_{OD/CH}$, see Fig. 1) of *ca.* 1.7 was found for MFI catalysts. This was explained by suggesting that the O–D/O–H bond dissociation is the rate determining step or that the mechanism is not concerted.

Rate constants can be calculated when all the steps involved in the reaction are characterised. The reactants, transition states, and products are localised with cluster type calculations as used successfully before.[10] During the geometry optimisation we look for a local minimum for reactants, and products and for a first-order saddle point for transition states. The cluster we used consists of three T-atoms (one Al and two Si) and was allowed to relax completely during the optimisations. The DFT calculations used the B3LYP functional[11] and a 6-31G* basis set. They were done with Gaussian98.[12]
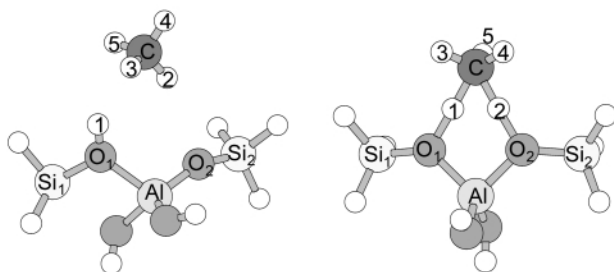
We found a symmetrical transition state with the exchanging hydrogens in the middle between the methane carbon and the cluster oxygen, as can be seen in Fig. 1. The interatomic distances are given in Table 1 along with the values obtained in previous studies using another level of calculations.[1,3,4]

The reaction rate constants are evaluated by using the canonical transition state theory of Eyring, Evans and Polanyi.[7] The general expression for the reaction rate constant k_r is:

$$k_r = \frac{k_B T}{h} \cdot \frac{Q^\ddagger}{\prod_i Q_i} \cdot e^{-\frac{E_{bar}}{k_B T}} \tag{1}$$

where k_B and h are respectively Boltzman's and Planck's constants, T is the temperature. E_{bar} is the activation barrier of the reaction. It is the energy difference between energies of reactants and transition-state and contains the zero point energy corrections. Q_i and $Q^\ddagger$ represent the partition function of reactants and transition-state (the index i running over all reactants). For the evaluation of eqn. (1) we use molecular partition functions.[7] With the assumption that rotational (r), vibrational (v) and electronic (e) movements are independent of each other, the molecular partition function Q is given by $Q=Q_t Q_r Q_v Q_e$, Q_t being the translational partition function.

For the H–D exchange reaction of methane, the reaction rate constant per acid proton becomes:

$$k_r = (N_A V)\left(\frac{k_B T}{h}\right) \cdot \frac{\left(Q_v^\ddagger Q_r Q_t\right)_{TS}}{\left(Q_v Q_r Q_t\right)_{CH_4}\left(Q_v Q_r Q_t\right)_{HZ}} \cdot e^{-\frac{E_{bar}}{k_B T}} \tag{2}$$

N_A is Avogadro's number and V is the volume of one mol under the considered P and T. It appears because of the use of concentrations in the rate laws.

Numerical values for the rigid rotor, harmonic oscillator partition functions are obtained after a frequency calculation by Gaussian98.[12,13] Eqn. (2) was used to calculate the rate constants for a temperature ranging from 300 to 800 K. An Arrhenius-plot gives an apparent activation energy of 157.0 kJ mol^{-1}, in close agreement with the experimental value.[6]

A comparison between the experimentally measured values of the exchange rate and the theoretically calculated ones can be found in Fig. 2. The rate constant depends on both the zeolite structure type and the Al content of the zeolite. Since our cluster contains two Si and one Al the Si/Al ratio is two. The calculated reaction rate constant $k_{OH/CD}$ of 1.97×10^{-7} s^{-1} agrees well with the experimentally obtained values at low Si/Al ratio.[6]

On deuteration, the reaction rate will decrease. In Table 1 rate constants for reaction of non-deuterated/deuterated zeolite (indicated with subscript OH or OD, respectively) with non-deuterated/deuterated methane (indicated subscript with CH or CD, respectively) are given. Deuteration of one of the exchanging atoms has a larger impact than deuteration of the non-exchanging atoms of methane: $k_{OH/CH}/k_{OD/CH} \approx k_{OH/CD}/$

Fig. 1 Geometry of (a) CH$_4$ adsorbed on acid site of zeolite, (b) transition state, with the labelling of the atoms as in Table 1. For $k_{OH/CD}$: 1 = H, 2–5 = D and for $k_{OD/CH}$: 1 = D, 2–5 = H.

Table 1 Selected geometrical and energetical parameters, with **ADS** = adsorption of CH_4 on cluster, **TS** = transition state, $E_{bar} = E(TS) - E(cluster) - E(CH_4)$ including ZPE

	ADS	TS	ADS	TS	ADS	TS	ADS	TS
Method	B3LYP/6-31G*		MP2/6-31++G** // HF/6-31G*		HF/6-31G**		PB86/DZPV	
Cluster	$AlSi_2O_4H_9$		AlO_2H_5		$AlSi_2O_4H_9$		$AlSi_2O_4H_9$	
Reference	This work		1		3		4	
Distances/Å AlO$_1$	1.901	1.836	—	1.860	1.942	1.801	—	1.883
AlO$_2$	1.720	1.836	—	1.860	1.706	1.801	—	1.883
O$_1$H$_1$	0.970	1.330	—	1.156	0.949	1.399	—	1.332
CH$_1$	2.477	1.332	—	1.496	—	1.282	—	1.356
E_{bar}/kJ mol^{-1}		159.71	166.94		—		—	
Imaginary frequency/cm^{-1}		−1745.64	−2095		−1423.38		−1389.4	
$k_{OH/CH}$/s^{-1}		$3.36 \times 10^{-7\,a}$	—		—		$3.38 \times 10^{-6\,b}$	
$k_{OH/CD}$/s^{-1}		$1.97 \times 10^{-7\,a}$	—		—		—	
$k_{OD/CH}$/s^{-1}		$1.92 \times 10^{-7\,a}$	—		—		—	
$k_{OD/CD}$/s^{-1}		$1.09 \times 10^{-7\,a}$	—		—		—	

^{a} At 750 K. ^{b} At 673 K.
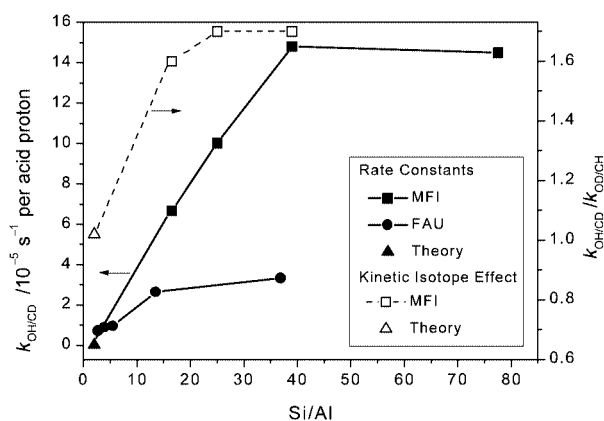
Fig. 2 Solid line and symbols: rate constants, $k_{OH/CD}$, at 700 K in function of Al-content. Dashed line and open symbols: kinetic isotope effect, $k_{OH/CD}/k_{OD/CH}$, at 700 K. Experimental values are taken from ref. 6.

$k_{OD/CD} \approx 1.7$ whereas $k_{OH/CD}/k_{OD/CH} = 1.02$. This is a consequence of the symmetrical transition state.

The experimental values for the kinetic isotope effect, $k_{OH/CD}/k_{OD/CH}$, are larger than the theoretical values (see Fig. 2). Unfortunately there are not enough experimental data to extrapolate to lower Si/Al ratios to validate the theoretical prediction.

It is promising to see that present day quantum chemical techniques allow the evaluation of rate constants of a simple zeolite catalysed reaction as they are yielding a lower limit for high alumina zeolites. Feasible differences between theory and experiment can be explained in several ways: (1) the cluster is only an approximation to a real zeolite lattice and does not include structural and long range effects; (2) different Si/Al ratio compared to real zeolites; (3) uncertainty on the obtained frequencies. We will use our method of calculation of rate constants for more complex reactions, *e.g.* acid zeolite catalysed methylation of toluene to form xylene[14] to check its validity.

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