Journal of Catalysis 339 (2016) 173–185

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

DFT-based microkinetic modeling of ethanol dehydration in H-ZSM-5

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ARTICLE INFO

Article history:
Received 22 January 2016
Revised 5 April 2016
Accepted 26 April 2016
Available online 14 May 2016

Keywords:
DFT
Dispersion energy
Zeolites
Brønsted acid sites
Reaction mechanism
Microkinetic model

ABSTRACT

A detailed reaction network has been constructed for ethanol dehydration in H-ZSM-5 using periodic density functional theory (DFT) calculations with dispersion corrections. Apart from the direct conversion of ethanol to diethyl ether or ethene, where novel mechanisms have been explored, the decomposition of diethyl ether to ethene has also been investigated. Thermodynamic and kinetic parameters were computed using statistical thermodynamics for all elementary steps. By coupling this microkinetic model to a plug-flow reactor model, macroscopic predictions of conversion and selectivity have been obtained at different operating conditions. The results of these simulations have been validated for H-ZSM-5 at different temperatures where experimental data are available. Both theory and experiment show an increase in ethene selectivity with increasing temperature and the experimental conversion agrees very well with the theoretical one. A reaction path analysis for ethanol dehydration in H-ZSM-5 shows that at temperatures above 500 K ethene is mainly produced via the direct dehydration of ethanol, while at temperatures lower than 500 K the reaction path via diethyl ether contributes significantly to ethene formation.

1. Introduction

Owing to its large-scale production, bioethanol can be viewed as a potential renewable feedstock for the production of other chemicals, in the same way that naphtha is used today [1]. In particular, the zeolite-catalyzed conversion of bioethanol offers promising perspectives for the sustainable production of ethene [2,3], butenes [4], and higher liquid hydrocarbons [5]. However, the selection of an appropriate catalyst and process conditions for each of these reactions remains a challenging task, while a fundamental understanding of the lower reactivity of ethanol compared to higher alcohols remains unresolved in the literature [1]. Theoretical studies based on first principles can help to develop an understanding of the reaction mechanisms involved and the parameters responsible for reactivity and selectivity. Moreover, ab initio calculations allow the determination of kinetic and thermodynamic parameters needed for the development of suitable microkinetic models.

Another important aspect in bioethanol conversion over zeolites is the presence of water in the feed. Since bioethanol is produced from fermentation processes, it can contain a variable amount of water. Azeotropic distillation is typically used to recover an aqueous ethanol stream from the fermentation broth. The ethanol–water mixture has an azeotropic composition of 89 and 11 mol % of ethanol and water, respectively. Since further concentration of ethanol is energy intensive, it would be ideal to feed at least the ethanol–water azeotrope for the catalytic process. For this purpose, possible inhibition effects due to the presence of water need to be understood and avoided. Water inhibition can be ascribed to several factors, such as competitive adsorption or co-adsorption of water on the Brønsted acid site of the zeolite, different solvation effect of water on reactants and transition states, and hydrothermal deactivation due to change in catalyst structure.

In this work, an ab initio based microkinetic modeling approach is used to study the reaction mechanism of ethanol dehydration in H-ZSM-5 and to assess the influence of the reaction conditions and water content on conversion and product selectivity. The dehydration reaction is proposed to proceed via two competitive reaction paths [6]. One is the dehydration of ethanol to ethene and water, and the other is the dehydration of ethanol to diethyl ether and water. Moreover, a consecutive path in which diethyl ether is further converted to ethene and ethanol has been reported [7]. Therefore, a parallel-consecutive scheme has been considered in the present study for ethanol dehydration in H-ZSM-5, as shown in Fig. 1. Our study clearly shows that the reaction conditions govern whether ethene is directly generated from ethanol or indirectly generated from ether, or both routes contribute to ethene formation.

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http://dx.doi.org/10.1016/j.jcat.2016.04.020
0021-9517/

2. Methodology

2.1. Catalyst model

H-ZSM-5 is a 3-dimensional medium pore zeolite consisting of 10-membered ring straight and zigzag channels [8]. For the calculations, a Brønsted acid site was created by placing an aluminum at the T12 site and a charge-compensating proton on O_a (see Fig. 2), resulting in a Si/Al ratio of 95. This acid site was chosen because of its location at the channel intersection with maximum accessibility for bulky reactants and transition states [9,10]. The optimized unit cell parameters were $a = 2047.2$ pm, $b = 2010.9$ pm, $c = 1357.6$ pm, $\alpha = 89.97°$, $\beta = 89.88°$, and $\gamma = 89.99°$ [11].

2.2. Electronic energy calculations

Dispersion corrected periodic DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) using plane wave basis sets [12–15]. The electron–ion interactions were described using the projector–augmented wave (PAW) method [16,17] with a plane-wave energy cutoff value of 600 eV. The exchange–correlation energies were calculated on the basis of the generalized gradient approximation (GGA) according to Perdew, Burke and Ernzerhof (PBE) [18]. Brillouin zone sampling was restricted to the Γ-point. A maximum force convergence criterion of 0.02 eV $Å^{-1}$ was used and each self-consistency loop was iterated until a convergence level of 10^{-8} eV was achieved. Dispersive corrections for the van der Waals interactions were included by adding a pairwise interaction term to the Kohn–Sham energy using the DFT-D2 approach proposed by Grimme [19] and extended by Kerber et al. [20] for periodic calculations. The electronic charge on atoms and fragments was calculated using Bader analysis [21] as implemented by Henkelman et al. [22]. Transition state search was performed using nudged elastic band [23] and dimer [24] calculations. The nudged elastic band calculation, connecting the proposed reactant to the proposed product, was used to find an initial guess for the minimal energy path, which was used as a starting point for the dimer calculations.

2.3. Frequency calculations

Normal mode analysis was performed using a Partial Hessian Vibrational Analysis (PHVA), considering the T5 cluster (HAl$(SiO_4)_4$) of the zeolite framework and the adsorbate molecule to be free for the numerical Hessian calculation. Previous studies for physisorption and chemisorption in zeolites have shown that the partial hessian approach leads to a marginal difference in the result as compared to a Full Hessian Vibrational Analysis (FVHA) [25]. The low-lying frequencies (<50 cm^{-1}) associated with the frustrated motions of the surface bound species (such as translation or rotation of the molecule within the zeolite pore) can lead to significant errors in the entropy calculations [26–29]. Although a more accurate estimation of the entropic contributions can be obtained by accounting for anharmonicities [30–32], this requires significant computational efforts for large systems. Another approach to treat the low-lying modes is the use of a frequency cutoff [26,27,33,34]. De Moor et al. [34] studied the entropy contributions of these frequencies for alkanes and alkenes in FAU and suggested their replacement with 50 cm^{-1} when using the immobile adsorbate approach. Therefore, in order to obtain consistent results, the immobile adsorbate approach was used for all surface species and the low-lying frequencies were replaced by normal modes of 50 cm^{-1} [34].

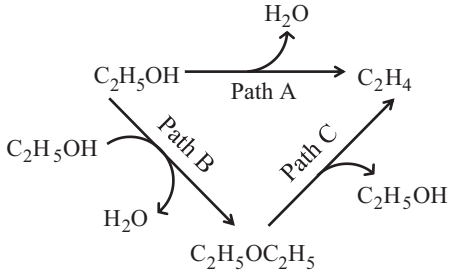

Fig. 1. Parallel-consecutive reaction scheme for ethanol dehydration. Path A: direct ethanol dehydration to ethene, Path B: ethanol dehydration to diethyl ether, Path C: decomposition of diethyl ether to ethene and ethanol.

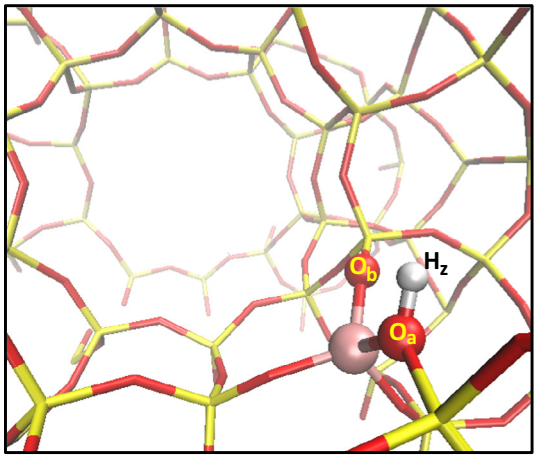

Fig. 2. Location of the Brønsted acid site in the unit cell of the H-ZSM-5 structure. Color code: silicon – yellow, aluminum – pink, oxygen – red, hydrogen – white.

2.4. Statistical thermodynamics

Enthalpies, entropies, and Gibbs free energies for reactants, products, and transition states were calculated using statistical thermodynamics [35]. The partition functions for the gas-phase species included vibrational, rotational and translational degrees of freedom, while only the vibrational contributions were taken into account for the surface species. The standard pressure used for all gas phase species was taken to be 100 kPa. Equilibrium coefficients for each elementary reaction were obtained using the following formula:

$$K = \exp\left(-\frac{\Delta H^0 - T\Delta S^0}{RT}\right) = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (1)$$

where R is the gas constant, T the temperature, ΔH^0 the standard enthalpy of reaction, ΔS^0 the standard entropy of reaction, and ΔG^0 the standard Gibbs free energy of reaction. Rate coefficients for each elementary reaction were calculated on the basis of transition state theory:

$$k = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{0,\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{0,\ddagger}}{RT}\right) = \frac{k_b T}{h}\exp\left(-\frac{\Delta G^{0,\ddagger}}{RT}\right) \quad (2)$$

where k_B is the Boltzmann constant, h the Planck constant, $\Delta H^{0,\ddagger}$ the standard enthalpy of activation, $\Delta S^{0,\ddagger}$ the standard entropy of activation, and $\Delta G^{0,\ddagger}$ the standard Gibbs free energy of activation. Arrhenius pre-exponential factors (A) and activation energies (E_a) for the activated elementary steps were obtained by regression of Eq. (2) in the temperature range of 300–800 K.

At the investigated conditions, adsorption/desorption steps are always quasi-equilibrated and, hence, the absolute value of the