ELSEVIER

Catalysis Today 50 (1999) 511–515

CATALYSIS TODAY

Theory, spectroscopy and kinetics of zeolite catalysed reactions

Rutger A. van Santen*

Laboratory of Inorganic Chemistry and Catalysis, Schuit Institute of Catalysis, Eindhoven University of Technology,
PO Box 513, 5600 MB, Eindhoven, Netherlands

Abstract

The combined use of quantum chemistry and spectroscopy to provide a basis of microkinetics modelling is discussed.

© 1999 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Quantum chemistry; Spectroscopy

1. Introduction

One of the major challenges in theoretical catalysis is to predict the performance of a catalyst based on the knowledge of the reactive site.

Important to end this are computational tools to predict reaction rate constants and the nature of the intermediate complexes. Essential is the availability of in situ spectroscopic techniques that enable verification of predictions on a molecular level. This is especially important since the quantum-chemical calculations usually involve the choice of approximate models.

The cluster approximation of the protonic zeolitic sites is to be used for the computation of transition state geometries and energies [1]. The main requirement to the first-principle electronic structure calculation is the availability of accurate geometry optimization and accurate energies computation. Current density functional theory based techniques predict interaction energy with an accuracy of ±20 kJ/mol.

A major drawback of the cluster approximation of the protonic sites is that it cannot be used to describe the properties that relate to the activity size or shape. Hence to predict the catalytic activity of zeolites one has to add information on the interaction with cavities as can be obtained from adsorption studies or theoretical simulation [2].

We will summarize the highlights of theoretical results of protonation and proton activation.

Results will be related to infrared and NMR spectroscopic data used as input to a microkinetic analysis of the hydroisomerisation of *n*-hexane.

2. Quantum-chemical studies of reaction mechanism

Each cluster choice of the zeolitic protonic sites corresponds to different values of deprotonation energy and hence acidity. This can be varied also by different choices of cluster termination. A useful way to use cluster models to predict activation ener-

---

*Tel.: +31-040-247-3082; fax: +31-040-247-5054; e-mail: tgtarsechem.tue.nl

0920-5861/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(98)00485-4

gies is to extrapolate activation energies found for different clusters as a function of deprotonation energy.

This is an example of the use of the Brønsted–Polanyi relationship that relates changes in activation energy (ΔE_{act}) to changes in reaction ($\Delta E_{\mathrm{reaction}}$):

$$\Delta E_{\mathrm{act}_4} \approx \tfrac{1}{2}\Delta E_{\mathrm{reaction}}$$

A comparison of the relative changes in computed activation energies for the dehydrogenation of ethane, cracking of ethane and hydride transfer between methane and methoxide is made [3–5].

The computed values refer to cluster calculations with deprotonation energies of 317.5 and 302.3 kcal/mol, respectively.

Protonation of intermediates occurs only in the transition states that behave as carbonium or carbenium ions electrostatically balanced against the negative change of zeolite cluster. The activated complexes convert to alkoxy species in the groundstate. In Fig. 1 the value of 295.4 kcal/mol refers to the experimentally determined deprotonation energy of low aluminium ZSM-5 [6].

The ΔE_{act} versus $\Delta H_{\mathrm{deprotonation}}$ curves enable to estimate the change in activation energy with proton acidity. Compared to the results obtained for the single tertrahedral cluster, the activation energy for the embedded cluster have decreased by 30 kJ/mol whereas the deprotonation energy has changed by 60 kJ/mol. Brønsted–Polanyi's proportionality is seen to be confirmed.

Graphs as shown in Fig. 1 enable in principle the prediction of activation energy for any chosen acidity.

We discussed earlier [7] how the potential energy field based on the embedding models enable the computation of deprotonation energies as a function of proton position in the zeolite lattice.

Not all zeolite catalysed reactions proceed via an intermediate. Typical examples are internal hydrogen shift reactions of olefin [8] or associative reaction paths that for instance occur in the formation of dimethylether from adsorbed methanol dimer. Also alkylation and transalkylation reactions of substituted aromatic molecules have been found to circumvent the alkoxy mediated path [11]. Whereas alkoxy species may be formed during the reaction, their non-participation in the actual reaction chain gives them the status of inert spectator species.

Studies using clusters have also shown the dramatic influence of coadsorbed spectator molecules such as

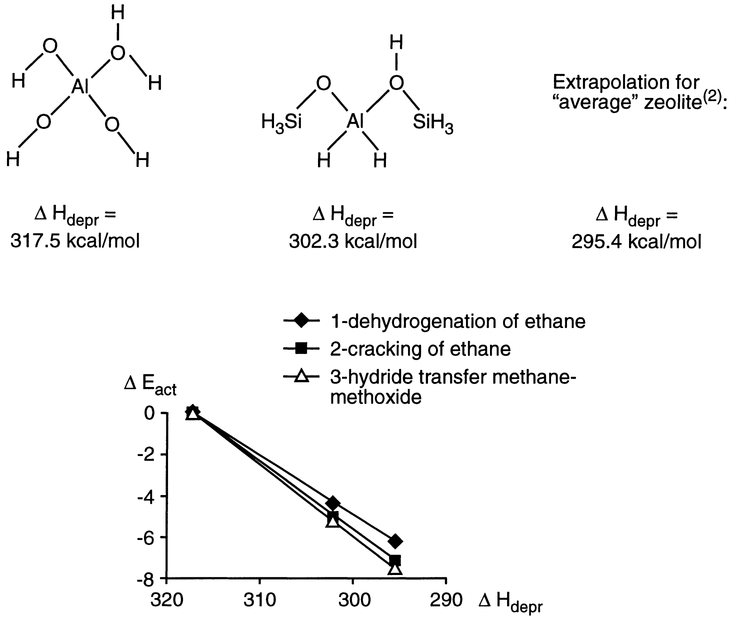

Fig. 1. Extrapolation of activation energies computed for reactions on small clusters towards zeolitic values. The value 295.4 kcal/mol is that from the experiment.

H_2O or CH_3OH on the height of activation barriers of elementary [9–12] reactions.

For instance the conversion of methanol to ethanol proceeds via an intermediate complex of three methanol molecules, with one of the molecules being an adsorbed spectator molecule [12]. Its presence results in a dramatic lowering of the activation barrier of the relevant elementary reaction step. Many reactivity calculations using clusters such that one Al-containing tetrahedron surrounded with two or more terminating Si-containing tetrahedron were used. All computational results reported were performed using non-local exchange-correlation gradient corrections by Becke and Perdew. More details on the calculations were reported elsewhere [1–5,7–12].

3. Spectroscopy

One of the most important spectroscopies to probe the nature of adsorption complexes is infrared spectroscopy [13]. NMR spectroscopy has also contributed significantly to the analysis of the reaction intermediates [14]. An interesting subject of recent debate is the question whether methanol or water is protonated or not, when adsorbed to a zeolitic proton [1].

Theory based on cluster calculations, predicts that the isolated proton adsorbed molecules are not protonated. The ground state is a strongly interacting hydrogen bonded molecule in which the zeolite proton has become significantly weakened and polarized. Experimental confirmation had been based on many different data. The hydrogen bonded state became recognizable in infrared spectroscopy once the interpretation of the doubly or triply split broadened spectral feature of the downward shifted zeolite proton stretch frequency became generally recognized.

The splitting arises from band bleaching due to Fermi-resonance with upwards shift in plane and out plane zeolite proton bending modes [15,16]. A theoretical approach towards the simulation of such spectra has been developed [17].

Broad line NMR data appear to agree with this conclusion for chemisorbed methanol. Interpretation of solid state NMR data is less straightforward. The downward shifted proton chemical shift cannot readily be used as a distinguishing marker of protonated versus hydrogen bonded methanol. Also Al quadrupole coupling constant NMR measurements do not give a unique interpretation. Whereas the hydrogen bonded methanol state still creates an asymmetric environment to Al, it is significantly less asymmetric than when proton transfer occurs and an unambiguous assignment between the two states is not possible [18].

However, pico second infrared laser spectroscopy can be used to probe the state of adsorbed water or methanol at a time scale short compared to the proton exchange of the adsorbed molecules.

The pico second laser infrared spectrum measured for adsorbed water or methanol to denterated mordenite gives a fingerprint spectrum that can only be assigned to hydrogen bonded water [19].

To probe the concentration of adsorbed reactants and products at in situ condition, recently a new radiochemical tracer technique has been developed using position emission profiling (PEP) [20]. This is a relatively slow technique but satisfactory on kinetic timescale. Through the reactor bed concentration profiles can be imaged with millimetre spatial resolution and seconds time resolution.

4. Microkinetics

Heats of adsorption of hydrocarbons can be computed using configurationally biased Monte Carlo techniques [21,22].

The heat of adsorption of alkanes appear to be a strong function of micropore dimension.

Adsorption isotherms can be computed as a function of pressure and temperature. When zeolites, such as ferririete are studied, the distribution of hydrocarbons over the different micropores appear to be a strong function of hydrocarbon chain length as well as micropore filling [21,22]. Such data are very important to the overall modelling of zeolite kinetics. The degree of micropore filling affects the rate of micropore diffusion dramatically, that may influence the overall rate of the reaction to a considerable extent [23].

Using theoretical values of the adsorption energies of alkanes experimental measurements of the apparent by *y*Pt promoted acidic zeolites have been modelled [23] using an approximate micropore concentration dependent diffusion model.

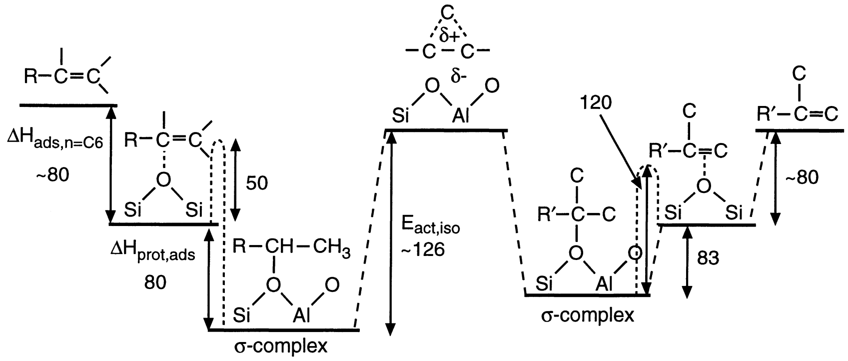

Fig. 2. Reaction energy diagram (kJ/mol) of isomerization of an olefin catalysed by ZSM-5 with a low aluminium content.

Comparison with experiment has been made at conditions where the hexane and the hexane re-equilibrated reaction can be considered rate limited by the activation of olefin by zeolitic protons.

The reaction energy diagram for isomerization of hexene constructed from a combination of experimental and theoretical data is shown in Fig. 2.

Most important is the realization that the results of cluster calculations should be used by not assuming as reference state gas phase olefin and free zeolite cluster, but olefin adsorbed on the siliceous part of the micropore. The protonation energy then is the sum of two terms: heat of adsorption of olefin and protonation energy. The latter is computed from cluster calculations. Most interesting is the predicted activation energy for the isomeration of *n*-alkoxy to *i*-alkoxy. The value we deduce equals 126 kJ/mol. This value should be independent from zeolite type and generally applicable as long as $Al/Si \ll 0.1$.

Predicted micropore concentrations and PEP data are in good agreement and provide for mordenite a porefilling of 60% at reaction conditions (240°C, 1 atm) [24].

5. Conclusions

In order to predict the kinetics of a catalytic reaction based on molecular data, one requires adequate theory and experiment to probe the events at different length and timescales.

Spectroscopic measurements are needed to test theoretical predictions based on quantum-chemical calculations.

Data on diffusion and adsorption are required in order to bridge the gap between microscopic dynamics and microscopic kinetics.

This short paper summarizes current research aiming to complete a program as sketched above.

References

[1] R.A. van Santen, G.J. Kramer, Chem. Rev. 95(3) (1995) 637.
[2] R.A. van Santen, J. Mol. A 405 (1996) 1307.
[3] V.B. Kazansky, I.N. Senchenya, M.V. Frash, R.A. van Santen, Catal. Lett. 27 (1994) 345.
[4] V.B. Kazansky, M.V. Frash, R.A. van Santen, Catal. Lett. 28 (1994) 211.
[5] S.R. Blaszkowski, M.A.C. Nascimento, R.A. van Santen, J. Phys. Chem. 100 (1996) 3463.
[6] E.A. Paukshtis, E.N. Turchenko, Russ. Chem. Rev. 52 (1983) 426.
[7] G.J. Kramer, R.A. van Santen, J. Am. Chem. Soc. 117 (1995) 1766.
[8] A.M. Rigby, G.J. Kramer, R.A. van Santen, J. Catal. 1 (1997) 117.
[9] S.R. Blaszkowski, R.A. van Santen, J. Am. Chem. Soc. 118 (1996) 5152.
[10] S.R. Blaszkowski, R.A. van Santen, J. Phys. Chem. B. 101 (1997) 2292.
[11] S.R. Blaszkowski, R.A. van Santen. Proc. AcS Symposium, Theoretical Chemistry, Dallas 1998, in press.
[12] S.R. Blaszkowski, R.A. van Santen, J. Am. Chem. Soc. 119 (1997) 5020.
[13] G. Mirth, J.A. Anderson, M.N. Klinowski, J. Chem. Soc., Faraday. Trans. 1 86(17) (1990) 3039.
[14] E.J. Munson, N.D. Lazo, M.E. Moelenhoff, J.F. Haw, J. Am. Chem. Soc. 113 (1993) 2783.
[15] A.G. Pelmenschikov, R.A. van Santen, J. Phys. Chem. 97 (1993) 10678.
[16] A.G. Pelmenschikov, A.G. van Wolput, J.H.M.C. Jänchen, R.A. van Santen, J. Phys. Chem. 99 (1995) 3612.

[17] E.L. Meijer, R.A. van Santen, A.P.J. Jansen, J. Phys. Chem. 100 (1996) 9282.

[18] H. Koller, E.L. Meijer, R.A. van Santen, Solid State Nucl. Magn. Reson. 9 (1997) 165.

[19] M. Bonn, H. Bakker, K. Domen, C. Hirose, A.W. Kleijn, R.A. van Santen, Catal. Rev.-Sci. Eng. 40 (1998) 127–173.

[20] R.A. van Santen, B.G. Anderson, R.H. Cunningham, A.V.G. Magnus, L.J. IJzendoorn, M.J.A. Voigt, Ang. Chem. 108 (1996) 2964.

[21] S.P. Bates, W.J.M. van Well, R.A. van Santen, B.J. Smit, J. Am. Chem. Soc. 28 (1996) 6753.

[22] S.P. Bates, W.J.M. van Well, R.A. van Santen, B.J. Smit, J. Phys. Chem. 100(44) (1996) 17573.

[23] A.v.d. Runstraat, J. van Grondelle, R.A. van Santen, Ind. Eng. Chem. Res. 36 (1997) 3116.

[24] R.A. van Santen, B.G. Anderson, R.H. Cunningham, A.V.G. Magnus, J. van Grondelle, L.J. van IJzendoorn, in: J.W. Hightower, W.N. Delglass, E. Iglesia, A.T. Bell (Eds.), Proceedings of the 11th International Congress on Catalysis – 40th anniversary, Stud. Surf. Sci. Catal. 101 (1996) 791.