

## Alkane activation over lanthanum exchanged zeolite X

Carsten Sievers<sup>1,2,\*</sup>, Ayumu Onda<sup>1</sup>, Alexander Guzman<sup>1</sup>, Roberta Olindo<sup>1</sup> and Johannes A. Lercher<sup>1</sup>

<sup>1</sup>Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

<sup>2</sup>Present address: Georgia Institute of Technology, School of Biomolecular and Chemical Engineering, 311 Ferst Drive, N.W., Atlanta, GA 30332; USA, \* carsten.sievers@mytum.de

### Introduction

Acidic zeolite catalysts have a wide range of applications for reactions like catalytic cracking, alkylation, hydrocracking and isomerization. Lanthanum exchange is among the most important methods for increasing the hydrothermal stability of large pore zeolites. Additionally, it has been suggested that the presence of lanthanum cations increases the strength of the Brønsted acid sites in the zeolite [1]. Alkane activation on zeolites is usually triggered by protolytic cracking [2]. Alternatively, olefin impurities or hydride abstraction by soft Lewis acid sites have been reported [3]. The protolytic route is only observed at high temperatures [4]. Recently, the activation of alkanes over zeolites at ambient conditions has been demonstrated for the first time [5].

### Materials and Methods

Lanthanum exchanged zeolite X was prepared by ion exchange with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  from NaX (Si/Al = 1.2), which was purchased from Chemische Werke Bad Köstritz. Prior to adsorption, the catalyst was activated at 180 °C leaving small amounts of residual water. For the IR experiments a Bruker IF 66v/S spectrometer was used. The NMR spectra were measured on a Bruker AV500 spectrometer using cross polarization for sensitivity enhancement.

### Results and Discussion

The acidity of the catalyst was determined by pyridine IR resulting in concentrations of Brønsted and Lewis acid sites of 0.294 and 0.098 mmol/g, respectively. Moreover, <sup>27</sup>Al MQMAS NMR was used to demonstrate that the lanthanum cations lead to a distortion of the local environment of most of the framework Al atoms.

Alkanes interact with zeolites primarily via dispersive van-der-Waals forces [6]. In addition to these, interactions with Brønsted acid sites contribute to the heat of adsorption. When small amounts of alkanes were adsorbed on LaX, unusually high extinction coefficients were observed for the CH vibrations in the IR spectra (Figure 1). It has been suggested that the extinction coefficients of IR vibrations are a good indicator for the polarization of the sorbate [7]. A more detailed understanding was obtained by <sup>13</sup>C CP MAS NMR spectroscopy. In the spectrum of 2-methylheptane adsorbed on LaX an upfield shift was observed for the methyl groups, while the peaks of the methylene and methine groups shifted downfield (Figure 2). These changes indicate that a partial positive charge is induced to methylene and methine groups upon adsorption on LaX.

When di- or tri-branched octane isomers were adsorbed on the zeolite, the alkanes were activated once a critical loading was reached. It is suggested that the activation occurs via hydride abstraction from a tertiary carbon atom. The abstracted hydride recombines with a Brønsted acidic proton forming dihydrogen, while the activated hydrocarbon is present as carbenium ion / alkoxy group. Once these species are formed they participate in a variety of reactions including β-scission, isomerization, alkene addition and hydride transfer. The observation of a critical loading can be explained by the fact that the adsorbed alkanes need to be present in an entropically unfavorable position in order to be activated. Alternatively, it is possible that reaction products are only observed once a sufficient concentration of mobile alkanes exists within the zeolite pores.

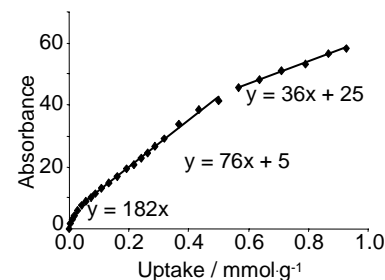


Figure 1. Absorbance for  $\nu_{\text{CH}}$  of adsorbed 2-methylpentane on LaX

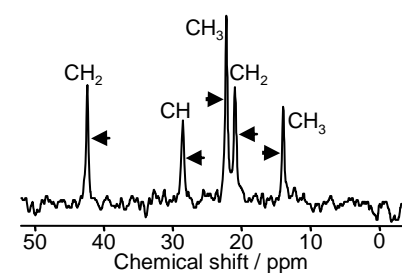


Figure 2. <sup>13</sup>C CP MAS NMR spectrum of 2-methylpentane adsorbed on zeolite LaX (arrows indicated shift upon adsorption)

### Significance

For the first time we observed the low temperature activation of branched octane isomers over LaX. Activation of alkanes at low temperatures is desirable for economical reasons. Moreover, it might alter the selectivity of a reaction and open new pathways for synthesis.

### References

1. van Bokhoven, J.A., Roest, A.L., Königsberger, D.C., Miller, J.T.; Nachttegaal, G.H., and Kentgens, A.P.M. *J. Phys. Chem. B* 104, 6743 (2000).
2. Haag, W.O., and Dessau, R.M. in "Proc. 8th Int. Congress on Catalysis, Berlin" Vol. 2 p. 305. Dechema, Frankfurt am Main, 1984.
3. Schoofs, B., Schuermans, J., and Schoonheydt, R.A. *Micropor. Mesopor. Mater.* 99, 35 (2000).
4. Narbeshuber, T.F., Vinek, H., and Lercher, J.A. *J. Catal.* 157, 388 (1995).
5. Sievers, C., Onda, A., Guzman, A., Otilliner, K., Olindo, R., and Lercher, J.A. *J. Phys. Chem.* accepted for publication.
6. Eder, F., and Lercher, J.A. *Zeolites* 18, 75 (1997).
7. Kazansky, V.B., and Pidko, E.A. *J. Phys. Chem. B* 109, 2103 (2005).