



MAX-PLANCK-GESELLSCHAFT



43. Jahrestreffen Deutscher Katalytiker, (2010) Weimar

## Structure-Activity Relationship Investigation of Pt/H-Mordenite Catalyst for *n*-Butane Isomerization

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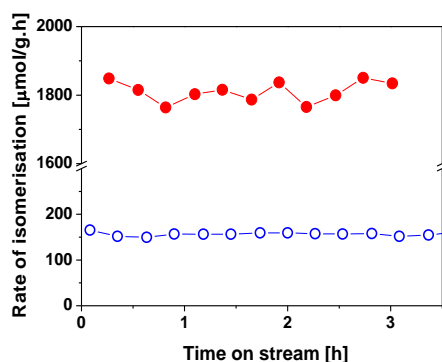
The zeolite H-mordenite doped with a small amount of platinum is used as a solid acid catalyst for the isomerization of light alkanes [1]. Optimization of the acid site distribution and the metal site reactivity of this bi-functional material are necessary for obtaining an active and stable catalyst. Therefore the preparation and even more the activation of the catalyst are very important. To establish correlations between surface sites and catalytic performance a series of Pt/HM materials with differing catalytic properties are compared after various activation procedures. We studied (i) catalytic activity in the isomerization of *n*-butane at 623 K by GC, (ii) *n*-butane adsorption by microcalorimetry and (iii) CO and *n*-butane adsorption by FTIR spectroscopy. Further material characterization includes in situ UV-vis spectroscopy, XRD and TEM.

Pt/HM samples with high dispersion and different state of reduction of the platinum show different (one order of magnitude) rates of *n*-butane isomerization (Fig. 1). In both cases the catalysts have a stable activity with time on stream; hence, enough hydrogenation sites seem to be present to prevent coke formation. The drastic difference in rates may not be attributable only to variations in state of the platinum; thus further investigation of the sites is required.

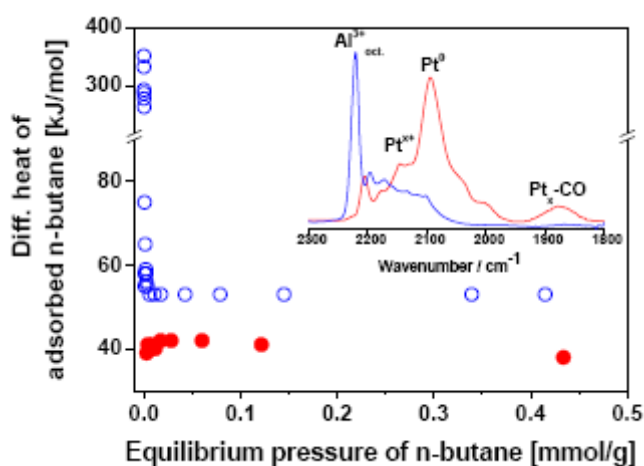
The results from the microcalorimetric study of *n*-butane adsorption show that the majority of sites are energetically uniform on both samples, with heats of approximately 40 kJ/mol (fully H<sub>2</sub>-reduced Pt/HM) and 50 kJ/mol (Pt/HM partially reduced through heating in vacuum), Fig. 2. The weaker interaction with the alkane is apparently favorable for the catalytic performance; perhaps because of easier product desorption. Initial high heats on a partially reduced sample arise from a redox reaction with *n*-butane. The associated adsorption isotherms (not shown) indicate a higher number of *n*-butane adsorption sites for the H<sub>2</sub>-reduced Pt/HM.

The IR spectra of CO adsorption at RT on completely and partially reduced Pt/HM samples (Fig. 2, inset) indicate the presence of Pt<sup>0</sup> (2088 cm<sup>-1</sup>, ~1880 cm<sup>-1</sup>), oxidic moieties Pt<sup>x+</sup> (2200–2100 cm<sup>-1</sup>) and extra framework aluminum (Lewis acid sites, ~2222 cm<sup>-1</sup>) [3]. The H<sub>2</sub>-reduced Pt/HM is characterized by a higher fraction of metallic Pt<sup>0</sup> and a significantly smaller amount of strong Lewis acidic sites. Furthermore,

the IR spectra of Pt/HM after activation in H<sub>2</sub> indicate more bridged Brønsted OH groups (3610 cm<sup>-1</sup>, 3586 cm<sup>-1</sup>) than after activation in vacuum.



**Figure 1:** *n*-Butane isomerization in a flow of 15 kPa *n*-butane in H<sub>2</sub> on a fully H<sub>2</sub>-reduced Pt/HM (●) and partially H<sub>2</sub>-reduced Pt/HM (○) at 623 K.



**Figure 2:** Differential heats of *n*-butane adsorption at 313 K on almost fully H<sub>2</sub>-reduced Pt/HM (●) and partially reduced Pt/HM (○). Inset: IR spectra of CO adsorption at RT on both samples.

Pt/HM catalysts with high platinum dispersion are highly active for *n*-butane isomerization only if activated (reduced) properly. The active state of Pt/HM is characterized through Brønsted acidic bridging OH groups, a small amount of strong Lewis acid sites (Al<sup>3+</sup><sub>oct.</sub>, extra framework alumina), small metallic platinum particles, and an overall weak interaction of the surface acid sites with *n*-butane.

## Acknowledgements

The Max Planck Institute for Coal Research in Mülheim/Ruhr and Åbo Akademi in Turku are kindly acknowledged for providing zeolite samples. The project was financially supported by BMBF grant 03C0307E.

## References

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