

# Contribution of Brønsted acid sites to the ring opening of cis-decalin on noble metal-containing zeolites Y

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## INTRODUCTION

Ring opening of polynuclear aromatic hydrocarbons in Diesel fuels is an interesting route for improving their cetane number and cold-flow properties. In the present work, zeolites Y loaded with the noble metals iridium and platinum were applied for the ring opening of cis-decalin as a model compound. For all the zeolite catalysts under study, the density and strength of the bridging OH groups, the so called SiOHAI groups, acting as Brønsted acid sites, were investigated and discussed in relation to the observed selectivities to ring opening products (ROPs) and open-chain decanes (OCDs). For improving the cetane number the OCDs are the desired reaction products.

## **REACTION SCHEME**

ring opening products (ROPs)

open-chain decanes (OCDs)

## **RESULTS AND DISCUSSION**

Three characteristic performances of zeolite catalysts in the catalytic ring opening of cis-decalin

The catalytic properties for selected noble-metal containing zeolites Y are shown in Fig. 3. These three catalysts show characteristic performances for all the iridium- and platinum-containing zeolites Y, which were studied in the present work.

#### 0.9 w% lr/Na-Y:

- Shows moderate activity in the cis-decalin conversion.
- All types of reaction products are formed in a large temperature range.
- Probably, the reaction route from cis-decalin to OCDs proceeds via different intermediates, such as



## EXPERIMENTAL SECTION

Commercial zeolite Na-Y (Strem Chemicals Inc., USA) was loaded with different amounts of  $[Ir(NH_3)_5CI]CI_2$  (0.6 to 4.7 wt% Ir on Na-Y) and  $[Pt(NH_3)_4]CI_2$  (0.9 to 4.5 wt% Pt on Na-Y) via ion exchange in aqueous suspension. The catalysts were calcined in synthetic air for 3 h (1.5 MPa, 300 °C) and subsequently reduced in H<sub>2</sub> for 2 h (5.0 MPa, 350 °C) in a fixed-bed reactor. Assuming a stoichiometric factor of 2 : 1 (H / metal), the noble metals on all above-mentioned zeolites reached a dispersion of 45 to 65 %. The catalytic experiments were performed in the activation reactor under flowing hydrogen saturated with cis-decalin at 250 – 370 °C (5.0 MPa, 130 mL/min). The Brønsted acid sites (SiOHAI groups) were characterized by <sup>1</sup>H MAS NMR spectroscopy via an evaluation of the integral intensity (density of acid sites) and via the determination of the low field shift  $\Delta \delta_{1H}$  of the SiOHAI signal, observed upon adsorption of acetonitrile- $d_3$  (strength of the acid sites).

various sk-Isos and ROPs.

#### 4.7 wt% lr/Na-Y:

- Shows high activity in the cis-decalin conversion.
- ROPs are the main reaction products, already at 250 °C.
- Maximum OCD formation occurs at 290 °C, after strong decrease of the selectivity for ROPs.

#### 4.5 wt% Pt/Na-Y:

- Requires a much higher reaction temperature for reaching the maximum ROP- and OCD-formation (ca. 320 and 350 °C, respectively) as the 4.7 wt% Ir/Na-Y.
- Skeletal isomers are the main reaction products at low and moderate temperatures (250 to 300 °C) like for the 0.9 wt% Ir/Na-Y.



## **RESULTS AND DISCUSSION**

#### Strength and density of Brønsted acid sites

Strength of Brønsted acid sites:

- The strength of the Brønsted acid sites is described by the difference  $\Delta \delta_{1H}$  between the chemical shift of the SiOHAI groups (around 3.5 ppm, see Fig. 2) before loading and their shift value after loading of acetonitrile-d<sub>3</sub>, i.e. for the interacting protons of the SiOHAI groups. The <sup>1</sup>H MAS NMR spectra before (bottom) and after (top) loading with acetonitrile- $d_3$  for the 0.9 wt% lr/Na-Y are depicted in Fig. 2.
- The range of the differences  $\Delta \delta_{1H}$  in this work is between 4.2 and 5.2 ppm (see Tab. 1, column 3). Pure zeolite H-Y has a difference of  $\Delta \delta_{1H} = 5.2 \text{ ppm}.^{[1]}$
- The acid sites in the different catalysts with the same type of metal are stronger when the metal content is higher. The dispersion of the metal is less relevant.

#### Density of Brønsted acid sites:

 $\Delta \delta_{1H} = 4.4 \text{ ppm}$ 

- The density of the Brønsted acid sites was detected via loading the catalysts with NH<sub>3</sub>. The spectra were simulated and quantitatively evaluated. The results are shown in Tab. 1, column 4.
- In this work the range of the density of Brønsted acid sites is between 0.7 and 6.6 SiOHAI groups per unit cell (u.c.).
- As shown in Tab. 1, the 4.5 wt% Pt/Na-Y has less SiOHAI groups per u.c. (2.5 SiOHAI/u.c.) than e.g. the 4.7 wt% Ir/Na-Y (6.6 SiOHAI/u.c.), which has a similar metal content and only a slightly higher dispersion (Tab. 1, column 2).
- For all catalysts under study, the iridium statistically forms around 1.2 SiOHAI groups per metal atom, while platinum only forms between 0.5 and 0.8 SiOHAI groups per metal atom.

#### Y<sub>OCDs</sub> in dependence on acidic properties

Two series of Ir/Na-Y catalysts containing different metal loadings with significant varied metal dispersions (Tab. 1, column 2) were studied for their catalytic properties (Fig. 4).

- Upper curve: Well dispersed Ir/Na-Y catalysts.
- Lower curve: Poorly dispersed Ir/Na-Y catalysts.
- Both curves show a maximum for the catalyst with the medium metal loading and a medium strength of the Brønsted acid sites in comparison with the other catalysts.
- Zeolite 4.5 wt% Pt/Na-Y (▼) with well dispersed platinum also has Brønsted sites with medium acid strength.
- For catalysts with similar metal dispersion, the maximum yield of OCDs is obtained using medium strength Brønsted acid sites (Fig. 4).
- The amount of loaded metals and the density of the less dispersed (●) iridium atoms, and the Brønsted acid sites seem to play a secondary role.



**Fig. 4** Yields of OCDs ( $Y_{OCDs}$ ) for two series of Ir/Na-Y catalysts with well dispersed (O) and catalyst 4.5 wt% Pt/Na-Y ( $\mathbf{\nabla}$ ). The numbers at the data points indicate the low-field shifts,  $\Delta \delta_{1H}$ , correlating with the acid site strength.



<sup>1</sup>H MAS NMR spectra of the catalyst 0.9 wt% Ir/Na-Y Fig. 2 before (bottom) and after (top) loading with acetonitrile- $d_3$ . The shift difference  $\Delta \delta_{1H} = 4.4$  ppm between the signals at 3.5 and 7.9 ppm correlate with the strength of the Brønsted acid sites (SiOHAI groups).<sup>[2]</sup>

3.5 ppm

Tab. 1 Summary of the results for the measurements of dispersion and strength and density of the Brønsted acid sites for zeolites Y loaded with iridium and platinum.

## REFERENCES

- D. Santi, S. Rabl, V. Calemma, M. Dyballa, M. Hunger, J. Weitkamp, *ChemCatChem* 5 (2013) 1524-1530
- U. Obenaus, *Diploma Thesis*, Faculty of Chemistry, University of Stuttgart (2013) [2]

# Conclusions

- Zeolites with a medium acid strength of their Brønsted sites ( $\Delta \delta_{1H} = 4.6 5.0$  ppm) and with well dispersed metal atoms show the highest yields of open-chain decanes.
- In case of the iridium-containing catalysts, the maximum yields of open-chain decanes decrease in the presence of strong Brønsted acid sites ( $\Delta \delta_{1H} = 5.2$  ppm), which promote the cracking of ring opening products and open-chain decanes to short-chained hydrocarbons.
- High selectivities to skeletal isomers occur for catalysts with weak Brønsted acid sites ( $\Delta \delta_{1H} < 4.5$  ppm) and/or platinum as the metal component.
- The density of the SiOHAI groups on 4.5 wt% Pt/Na-Y (2.5 SiOHAI/u.c.) is much lower than those of 4.7 wt% Ir/Na-Y (6.6 SiOHAl/u.c.), and these sites have a much lower acid strength ( $\Delta \delta_{1H} = 4.7$  ppm) than those of 4.7 wt% lr/Na-Y ( $\Delta \delta_{1H} = 5.2$  ppm).
- The above-mentioned finding could be a hint that a low density of SiOHAI groups with a low to medium acid strength promote reaction routes via skeletal isomers.
- In contrast, a high density of strong Brønsted acid sites may promote the direct formation of ring opening products already at low reaction temperatures.
- For highly selective ring opening catalysts, a good correlations between the strength and density of Brønsted acid sites is important.