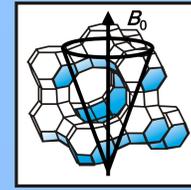


# Modification of Co-FCC Catalysts and Their Characterization by Solid-State NMR Spectroscopy

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## INTRODUCTION

Zeolites are the main component of fluid catalytic cracking (FCC) catalyst. A goal in the project FAST CARD is, to increase the amount of bio oil in the so called Co-FCC. The feed of the Co-FCC process is a mixture of vacuum gas oil consisting of crude oil and bio oil, made from lignin-based bio mass. The reason to implement bio oil in the Co-FCC are the 20-20-20 targets from the European Union [1]. A point in these targets is that the whole EU should increase the amount of renewable energy sources by 20% until the year 2020.

Hydrodeoxygenated bio oil molecules are sterically demanding and, depending to their deoxygenating level, contain much more oxygen than fossil-based feed. Because of the high effort of the hydrodeoxygenation, the FCC catalysts have to tolerate coking caused by the high oxygen content of the feed. For that, it is necessary to improve the zeolitic component in the Co-FCC catalyst. Next to high hydrothermal stability and high catalytic activity, the pore structure is a critical factor for the cracking performance of a zeolitic catalyst suitable for the bio-based feed.

## EXPERIMENTAL SECTION

Commercially available ultra stable zeolite Y (Grace GmbH & Co.KG, Germany) was either stirred in hydrochloric acid (sample name USY-Cl) at room temperature or in aluminum nitrate aqueous solution at 80 °C (sample name USY-AI) over night. The leaching was carried out with a 0.1 M HCl solution and a 0.5 M Al(NO<sub>3</sub>)<sub>3</sub> solution. After the leaching, the samples were washed with deionized water until the pH value was near neutral or there were nitrate free.

Furthermore, the USY zeolite was covered with AlCl<sub>3</sub> (sample name USY-Sub). In a long flask, connected via a quick-fit to a valve, was AlCl<sub>3</sub> filled and upon glass wool and the zeolite sample. The flask was evacuated and lowest part heated to 140 °C for 16 h. The AlCl<sub>3</sub> sublimated through the sample and re-sublimated on the cold glass of the flask.

The <sup>1</sup>H and <sup>29</sup>Si MAS NMR studies were performed on a Bruker Avance III 400 WB, while the <sup>27</sup>Al MAS NMR investigations were done on a Bruker Avance III 700 HD equipment. For the <sup>1</sup>H MAS NMR studies, the samples were evacuated and activated at 450 °C in glass tubes. Then, the tubes were sealed and transferred in a glovebox, flushed with dry N<sub>2</sub>. In the glovebox, the samples were filled into the rotors.

For loading with NH<sub>3</sub>, the rotors were opened and placed in a glass tube, connected to a vacuum line. After the loading, the samples were evacuated and heated at 180 °C for 2 h.

For the *in situ* H/D exchange experiments, the samples were evacuated and loaded with deuterated benzene-d<sub>6</sub> over the gas phase. The rotors with the loaded samples were inserted into the MAS NMR probe already heated at 70 °C. The H/D studies were carried out at 100 °C.

The samples used for catalytic studies were aged at 700 °C in pure water steam for 5 h (sample name + 700) inside a fixed-bed quartz glass reactor to obtain equilibrated and aged catalysts.

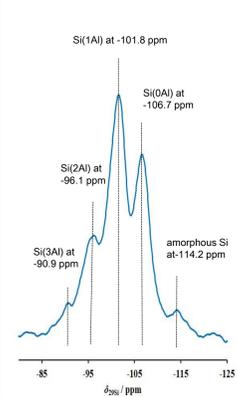
The surface areas and micro/mesoporous volumes were determined by N<sub>2</sub> physisorption experiments at -196 °C.

The catalytic studies were performed with a 90 wt.-%/10 wt.-% mixture of n-decane and 2-ethylphenol as model compounds for the vacuum gas oil and the hydrodeoxygenated oil, respectively. These studies were done by M. Heuchel and F. Reinhardt (University of Stuttgart).

## RESULTS AND DISCUSSION

### Density of Brønsted Acid Sites

The aim of the catalyst modification was an increased hydrothermal stability and amount of mesopores without a loss of Brønsted acid sites. The mesopores are necessary to decrease the coking during the cracking. Figure 1 shows a <sup>29</sup>Si MAS NMR spectrum of USY Grace. By simulation of the <sup>29</sup>Si MAS NMR spectra it is possible to



determine the framework Si/Al ratio. The bulk and Si/Al ratios are given in Table 1. The framework aluminum decreases rapidly by the aging treatment. The modification with hydrochloric acid and aluminum nitrate shows no significant effect to the aluminum content. It is important to note that the framework aluminum content decreases after the aging of the samples, especially for aluminum nitrate-treated catalysts.

To determine the density of Brønsted acid sites (Si(OH)Al), the <sup>1</sup>H MAS NMR signal intensity at 3.8 ppm (signal at 6.2 ppm in Figure 3) was compared with that of a zeolite HY standard with known density of Brønsted acid sites (Figure 2).

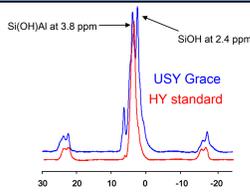


Fig. 2 <sup>1</sup>H MAS NMR spectrum of zeolite USY Grace and the HY standard.

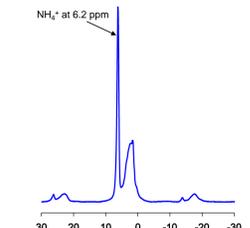


Fig. 3 <sup>1</sup>H MAS NMR spectrum of zeolite USY Grace aged at 700 °C, loaded with NH<sub>3</sub>.

Upon loading with ammonia, the accessible Brønsted acid sites chemisorb the probe molecules leading to ammonium ions (signal at 6.2 ppm in Figure 3). The determine density of Brønsted acid sites of samples under study are given in Table 1. The largest density has the unmodified zeolite USY. After the modification, the samples lose active sites or they are no longer accessible for the probe molecule NH<sub>3</sub>.

The hydrothermal stability is studied by the remaining micropore volume after the aging, determined via N<sub>2</sub>-physisorption. No increased stability of the modified samples was observed. The mesopore volume of the modified samples increases instead, except for zeolite USY coated with AlCl<sub>3</sub> (Figure 4).

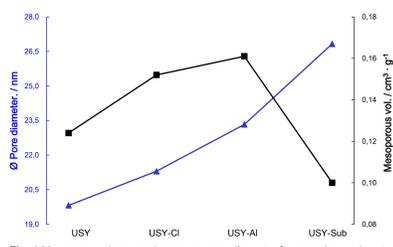


Fig. 4 Mesopore volume and average pore diameter for samples under study.

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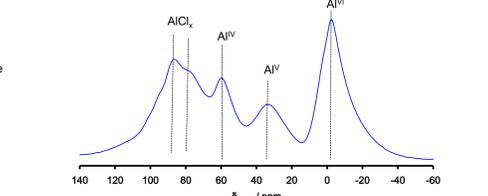


Fig. 5 <sup>27</sup>Al MAS NMR spectrum of zeolite USY-Sub.

In the <sup>27</sup>Al MAS NMR spectrum of the sample USY-Sub consists of signals due to tetrahedral framework Al at 58.8 ppm, penta-coordinated Al at 33.7 ppm, octahedral extra-framework Al at -2.4 ppm, and signals at 77.8 ppm and 86.5 ppm. The latter two signals are caused by AlCl<sub>x</sub> species. The remaining AlCl<sub>x</sub> may block the mesopores and is responsible for the low mesopore volume. After the aging treatment, the AlCl<sub>x</sub> species are removed from the zeolite and the mesopore volume is in the expected range.

Tab. 1 Si/Al ratios and densities of Brønsted acid sites of the samples under study.

	USY	USY700	USY-Cl	USY-Cl700	USY-AI	USY-AI700	USY-Sub	USY-Sub700
ICP-OES Si/Al	3.1	3.4	3.8	3.5	4.2	3.5	2.0	(-)
NMR Si/Al	4.4	9.5	4.5	11.6	4.6	17.2	4.6	10.6
$\frac{n_{Si(OH)Al}}{mmol \cdot g^{-1}}$	1.12	0.12	0.92	0.08	1.08	0.06	0.78	0.02

### H/D Exchange Experiments

With deuterated model compounds it is possible to investigate the protonation step on acidic catalyst loaded with organic molecule. In Figure 6, the H/D exchange of benzene-d<sub>6</sub> by zeolite USY is shown. In the spectra, the <sup>1</sup>H MAS NMR signal of benzene-d<sub>6</sub> increases, while the signal of Brønsted acid sites at 3.8 ppm decreases as a function of time.

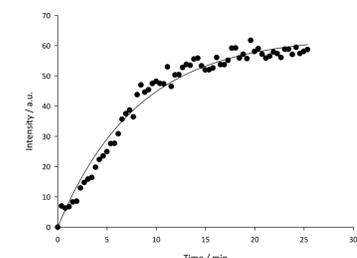


Fig. 7 <sup>1</sup>H MAS NMR signal intensity of aromatic hydrogen atoms plotted as a function of time.

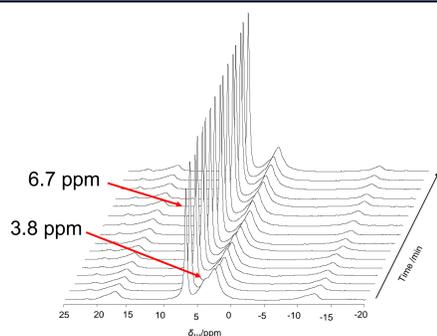


Fig. 6 Stack plot of *in situ* <sup>1</sup>H MAS NMR spectra recorded during the H/D exchange between benzene-d<sub>6</sub> and zeolite USY.

By plotting of the signals due to the aromatic hydrogen atoms as a function of time (Figure 7), the H/D exchange rate can be obtained. Via this kinetic rate constant, determined for different H/D exchange temperatures, the activation energy of the protonation step can be calculated.

### Catalytic Studies

The conversion of the n-decane/2-ethylphenol mixture (90 wt.-%/10 wt.-%) require zeolites with large pores. Catalytic studies with zeolites having a 10-ring pore system led to lower conversions of the reaction mixture after a short time on stream (Figure 8). Zeolite Fe-ZSM-5, e.g., could not reach a same high reactant conversion, like zeolites with a 12-ring pore system. This is a hint, that the bio oil component 2-ethylphenol causes a rapid blocking of the acid sites, which deactivates the catalyst.

Experiments with pure n-decane showed a higher conversion and a lower deactivation of the 10-ring zeolite catalysts [2]. It is obvious, that a modification by leaching of zeolite USY results in a negative effect considering the activity loss.

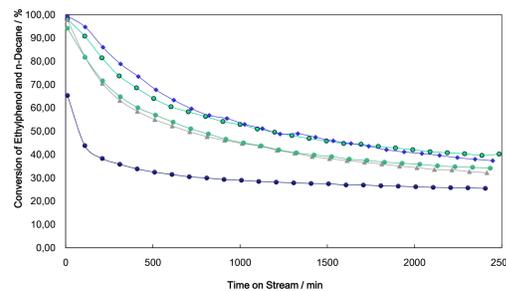


Fig. 8 Co-conversion of the n-decane/2-ethylphenol mixture (90 wt.-%/10 wt.-%) at 480 °C plotted as a function of time on stream. The catalysts were hydrothermally aged at 700 °C in pure water steam for 5 h before the catalytic experiments.

The hydrothermal stability has increased not noticeable. Simultaneously, the density of Brønsted acid sites is reduced. This results in a lower conversion of the reaction mixture.

## Summary

- The catalyst modification by acid leaching creates mesopores, but causes a decrease of the density of Brønsted acid sites. At the same time, the hydrothermal stability remains unaltered.
- The hydrothermal aging treatment has a strong influence on the Si/Al ratio and the density of Brønsted acid sites. This effect is much higher for the aged samples than for the samples modified by acid leaching.
- The loading of zeolite catalysts with AlCl<sub>3</sub> leads to a decrease of the framework aluminum content, while an increase of the framework aluminum species was found after the hydrothermal treatment of these materials. That could be a way to create mesopores and keeping the framework Si/Al ratio low.
- In the catalytic experiments, the modified samples shown a lower activity than the original zeolite USY. This activity loss is caused by the decreased density of Brønsted acid sites.

## References

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