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MAS NMR spectroscopy for acidity characterization and olefin reaction monitoring on Zn-modified zeolites

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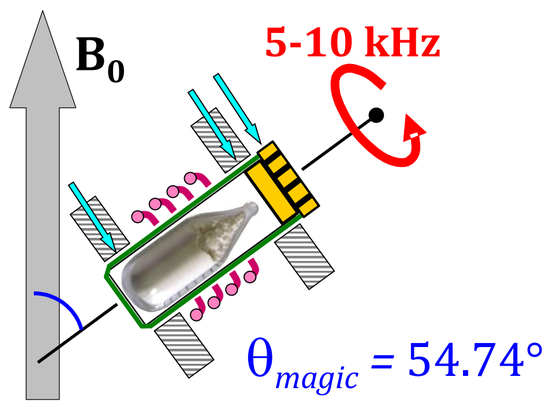
Introduction

Zinc-modified zeolites are effective catalysts for the transformation of light olefins (C_2–C_4), the abundant feedstock produced from naphtha and liquified petroleum gas.[1] However, **the lack of comprehensive information about the nature of the active sites and the reaction mechanism** hinders the implementation of such catalysts on an industrial scale. Here, we demonstrate **the capabilities of MAS NMR** to provide the required data.

Methodology

The key feature of the experimental procedure is the sample preparation in **sealed glass ampoules** acting as microreactors. Such methodology provides reliable data for zeolite catalyst performance under controlled conditions.[2]

Magic Angle Spinning



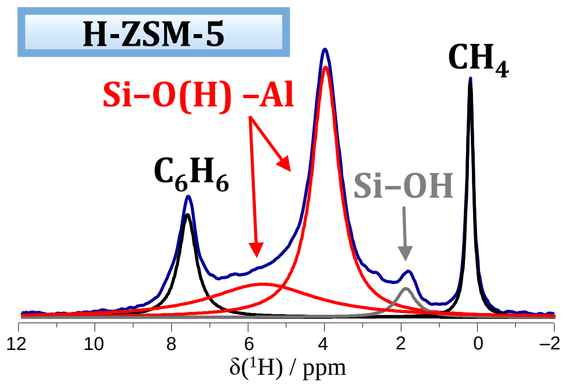
$H_{dd} \sim (3\cos^2\theta - 1)$

^{1}H MAS NMR – OH groups quantification

Internal standard approach

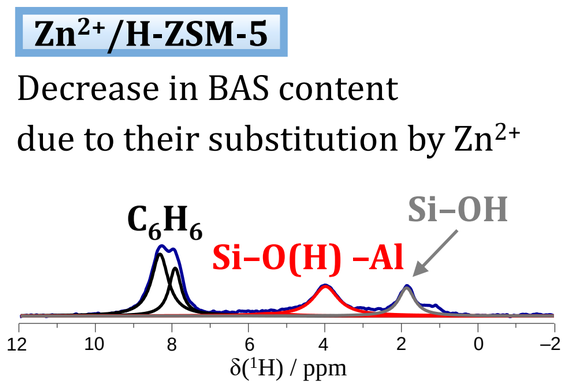
- Chemical shift out of the range of OH groups signals
- No chemical reaction at room temperature

H-ZSM-5



Zn^{2+}/H-ZSM-5

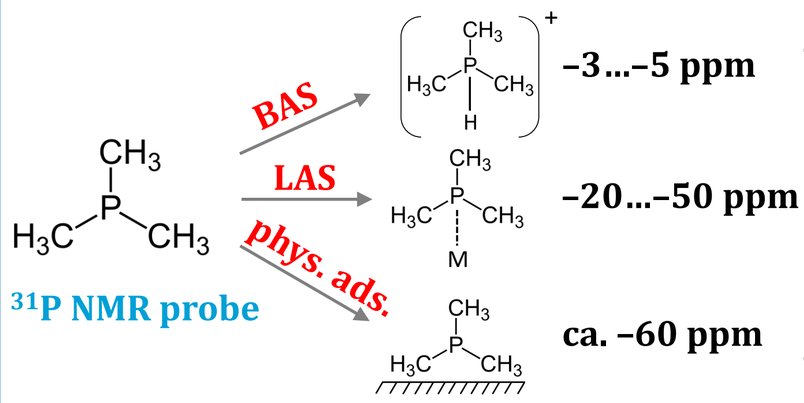
Decrease in BAS content due to their substitution by Zn^{2+}



- Determining various zeolite OH groups concentrations
- Indirect quantification of Zn sites

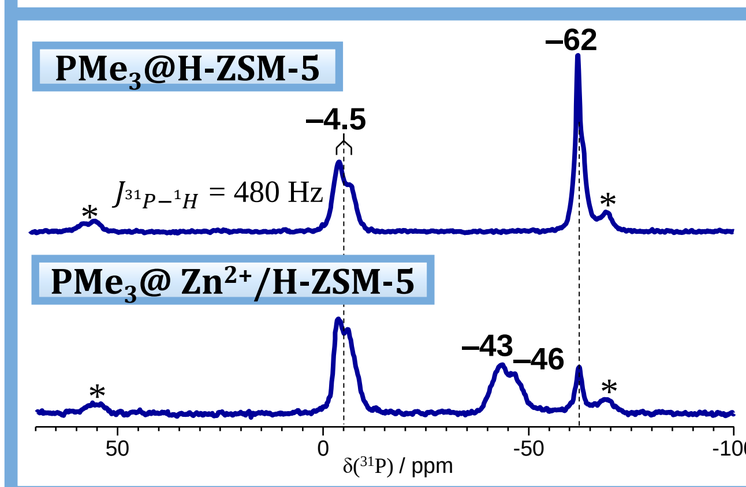
$C_{Zn^{2+}} = [C_{BAS}(\text{H-ZSM-5}) - C_{BAS}(Zn^{2+}/\text{H-ZSM-5})]/2$

^{31}P MAS NMR – probing the acid strength



Additionally: correlation between $\delta(^{31}P)$ and Brønsted acid strength

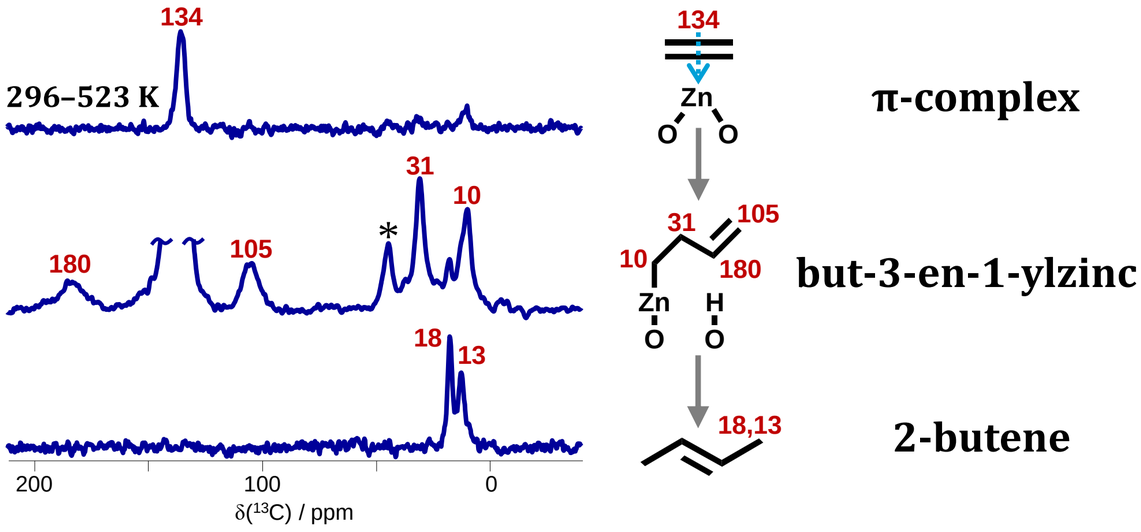
PMe_3@H-ZSM-5



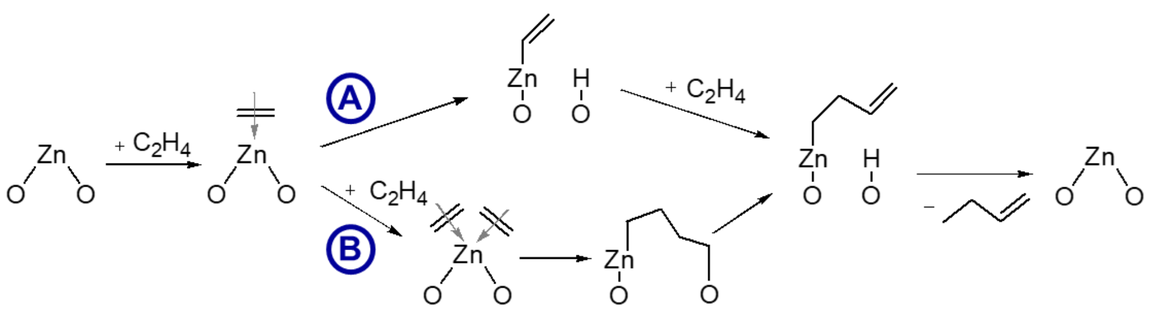
1. The strength of BAS is identical in H-ZSM-5 and Zn^{2+}/H-ZSM-5.
2. Two types of LAS are present in Zn^{2+}/H-ZSM-5.

^{13}C MAS NMR – reaction mechanism

Selective dimerization of ethene on Zn^{2+}/H-ZSM-5[4]



Alternative reaction pathways



Conclusions

1. Surface **OH groups** of Zn-zeolites can be **quantified** with **^{1}H MAS NMR** using internal standard approach.
2. **^{31}P MAS NMR** study of adsorbed $P(CH_3)_3$ revealed **two types of Lewis acid sites** in Zn^{2+}/H-ZSM-5 and **no change in zeolite acid strength** upon modification with Zn.
3. **Selective ethene dimerization** to 2-butene on Zn^{2+}/H-ZSM-5 was discovered with **^{13}C MAS NMR**. The **mechanism** of the dimerization reaction was established.

References

1. Y. Ono, *Catal. Rev.-Sci. Eng.* **1992**, 34, 179.
2. A.A. Gabrienko, et al., *J. Phys. Chem. C* **2015**, 119, 24910.
3. A.A. Gabrienko, et al., *ChemCatChem* **2020**, 12, 478.
4. Z.N. Lashchinskaya, et al., *J. Phys. Chem. C* **2022**, 126 (15), 6570.

Acknowledgements

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