

# Pd speciation and support effect for H<sub>2</sub> SCR

<u>Jieling Shao</u><sup>1</sup>, Zhipeng Wang<sup>,2</sup> Phuoc Hoang Ho<sup>1</sup>, Yifei Ren<sup>2</sup>, Derek Creaser<sup>1</sup>, Feng Wang<sup>2</sup> and Louise Olsson<sup>1</sup> <sup>1</sup>Chemistry and Chemical Engineering, Competence Centre of Catalysis, Chalmers University of Technology, Gothenburg S041296, Sweden.

<sup>2</sup> Department of Chemical Engineering, University College London, London WC1E 7JE, United Kingdom \* louise.olsson@chalmers.se

### Significance and Relevance

The catalytic performance of SSZ-13 zeolite and BEA zeolite-supported Pd catalysts was investigated. The degree of ion exchange in the two zeolites and the oxidation states under oxidising and reducing conditions were analysed. Complemented by in situ DRIFTS, the results indicated that palladium is more stable within SSZ-13 compared to BEA zeolite. Additionally, BEA zeolite-supported palladium catalysts with a higher degree of ion exchange compared with the SSZ-13-supported one were proved. The reactivity was further assessed under 6 experimental conditions, the results combined with the XAFS measurement revealing that the Pd metallic state is preferred for the NO reduction activity.

Preferred and 2<sup>nd</sup> choice for the topic: The speciation of Pd on the support of SSZ-13/BEA zeolite for H<sub>2</sub>-SCR application.

Preferred presentation: (Oral preferred or short oral)

### Introduction and Motivations

Hydrogen has been considered as a great alternative fuel for combustion engines to cope with the greenhouse emission (GHG) requirements. However, NO<sub>x</sub> emissions in the exhaust gas are an unavoidable byproduct of the combustion process.<sup>1</sup> Among various approaches, NO<sub>x</sub> selective catalytic reduction with hydrogen (H<sub>2</sub>-SCR) has been widely proposed. It has been highly reported that H<sub>2</sub>-SCR catalysis depends more on the active centres of Pt-group metals.<sup>2</sup> Pd-based catalysts are more promising for H<sub>2</sub>-DeNO<sub>x</sub> due to their superior selectivity towards producing nitrogen, compared to Pt catalysts.<sup>3</sup> While there are many fundamental studies on Pd-zeolite catalysts, few clearly describe the principles underlying their function in H<sub>2</sub>-SCR.<sup>4,5</sup> This study reveals the form of palladium present on the molecular sieve and its dynamic changes during the reaction.

#### **Materials and Methods**

SSZ-13 zeolite was synthesized using a hydrothermal method. Pd-based catalysts were prepared using an incipient wetness impregnation (IWI) technique with a loading of 1 wt% supported on SSZ-13 and BEA zeolites. The powder materials were characterized with various techniques such as elemental analysis, CO chemisorption, N<sub>2</sub> physisorption, XPS, and STEM after the hydrothermal pretreatment. NaCl sodium titration was used to determine the amount of ion-exchanged Pd in the catalysts.<sup>6</sup> Catalytic tests were performed with a flow reactor with the monolith sample at 110°C, 200°C, and 300°C under six sets of reaction conditions including standard H<sub>2</sub>-SCR with various H<sub>2</sub> concentrations, NO oxidation, and NO reduction.

#### **Results and Discussion**

It has been reported that Pd loading on zeolite exists in a variety of forms, including ionic  $Pd^{2+}$  in the zeolite framework (Z<sub>2</sub>Pd and ZPdOH) depending upon the Al distribution, PdO<sub>x</sub> clusters and smaller Pd particles on the zeolite.<sup>7</sup> With the NaCl titration method, the results indicated that 40% of Pd in Pd/BEA can be exchanged over the calcined IWI synthesized catalyst, while only 4.3% in the Pd/SSZ-13 catalysts which agrees with the results has been reported in the literature.<sup>8</sup> This is due to the larger pore openings of the BEA zeolite compared to SSZ-13. After the hydrothermal pretreatment, the degree of ion exchange increased. Pd oxides and smaller particles on the catalyst surface were further identified by XRD measurements following pretreatment of the samples. Faint characteristic peaks of PdO were observed on the SSZ-13-supported catalysts, due to the fewer Pd ions inside the framework.



In situ DRIFTS measurements of CO and NO adsorption profiles demonstrated that Pd remains more stable in SSZ-13 zeolite compared to BEA zeolite, as indicated by a slower CO-induced reduction and slower transfer of surface intermediate species by NO.



**Figure.1** Gas concentrations (N<sub>2</sub>O, NO, NO<sub>2</sub>, NH<sub>3</sub>,N<sub>2</sub>) and NO conversion of H<sub>2</sub>-SCR at 200  $^{\circ}$ C on (a) Pd/SSZ-13 (b) Pd/BEA catalysts under 6 reaction condition steps (Table, S1-S6) and their LCF results (c-d).

It is shown in Fig.1 that the standard  $H_2$ -SCR for the first three steps at 200°C with increasing  $H_2$  concentration. The NO oxidation reaction in steps 4 and 6 is more reactive on Pd/BEA than Pd/SSZ-13. Step 5 is NO reduction in an anaerobic environment, using a 10-fold excess of hydrogen. The reduction of NO by hydrogen is accompanied by the reduction of Pd to its metallic state. The in-situ dynamic oxidation state change of Pd was measured and verified using the XAFS synchrotron technique. The first three steps have better performances on Pd/SSZ-13 than Pd/BEA, with more Pd metallic states which is proved by LCF analysis in Fig.1c and Fid.1d. There are more Pd oxides on Pd/BEA at Step 4 and Step 6 compared to Pd/SSZ-13, with higher NO oxidation activity. From this, it is clear that the metallic state of palladium favors  $H_2SCR$  and the oxidized state is more favorable for NO oxidation reactions. And the BEA-loaded catalyst is more easily oxidized and reduced under the corresponding reaction conditions.

#### References

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## Acknowledgements

This study has been funded by the Swedish Energy Agency and carried out in collaboration with Volvo AB, Scania CV, and Johnson Matthey via a strategic vehicle research and innovation (FFI) project (P51458-1). We also appreciate the assistance for Flow-reactor support from Lennart Norberg and Lasse Urholm.