

## O04.15. SINGLE Ni IONS HOSTED IN ZEOLITES AS ACTIVE SITES FOR SELECTIVE DIMERIZATION OF BUTENES

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### Introduction

Light linear and monobranched olefins have attracted growing industrial attention as a basic feedstock and important intermediate in the production of polyethylene and plasticizers. Butene dimerization on heterogeneous Ni based catalysts represents an appealing route to synthesize linear octenes from undervalued cracking fractions. Zeolites well-ordered microporous structure offers an opportunity to direct the selectivity towards the linear dimers [1,2]. Different active sites have been proposed in solid Ni-based catalysts ranging from Ni-hydride species, Ni<sup>2+</sup> and Ni<sup>+</sup> ions to [NiOH]<sup>+</sup> species[3]. Identifying the nature of the active site as well as the mechanistic steps in the dimerization cycle are key for designing highly active and selective catalysts for butene dimerization. However, the effect of the chemical environment on the Ni speciation and activity needs to be tackled in order to achieve understanding of the dimerization reaction mechanism.

In this work, we studied catalysts based on ion exchanged Ni in CHA, MFI, and FAU, with different Ni loadings. The different pore sizes and interconnectivities of the selected frameworks will allow us to determine the influence of spatial constraints and local environment on the activity and selectivity of Ni sites in butene dimerization.

### Experimental

Na-forms of the zeolites were prepared by three ion exchanges of the H-form with 0.06 M aqueous NaOAc overnight at 80 °C. After the last ion exchange, the zeolite was calcined for 6 h at 500 °C resulting in the Na-form. The introduction of Ni<sup>2+</sup> is carried out as a Ni/Na co-exchange with varying concentrations of exchange solutions of Na and Ni acetate. The pH of the solution is kept in the region 6-7 during the total time of the ion exchange. The solid was washed thoroughly with doubly deionized water, dried at 80 °C for several hours and calcined in flowing synthetic air for 6 h at 500 °C.

The catalytic tests in butene dimerization are performed in a downstream fixed bed flow reactor at 50 bar, 160 °C and weight hour space velocities between 6 and 2000 h<sup>-1</sup>.

Ni-zeolites and their parent zeolites have been studied by different characterization techniques. Among them, results of IR spectroscopy, including CO adsorption

measurements at 77 K and X-ray absorption spectroscopy (XAS) provide the most relevant information.

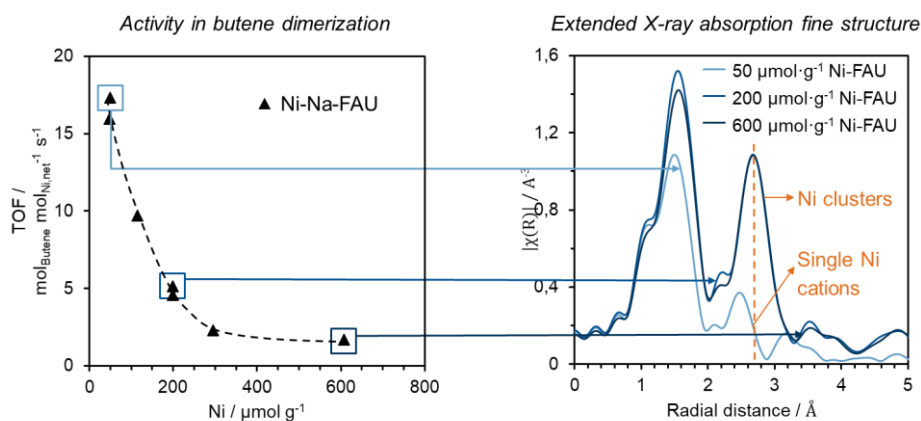
### Results and Discussion

The activity and nature of Ni species in zeolites have been studied by several spectroscopic techniques and catalytic tests at differential conversions. In order to rule out any strong effect of the Bronsted acidity of the zeolites, reference samples consisting in H-form zeolites without any Ni (or Na) loading have been tested in the same reaction conditions. It is concluded that the activity of Bronsted acid sites contributes to less than 10 % of the total activity of the Ni-Na-zeolites tested.

While shape selectivity towards the linear dimers is observed for the small-pore zeolite CHA, the highest rates per Ni are obtained for Ni-exchanged FAU. The butene consumption rates per mol Ni obtained for Ni-Na-FAU series suggest an exponential decrease of activity with Ni loading (Figure 1A). This indicates that the increase of Ni loading leads to smaller fractions of Ni atoms being active, either because of the formation of multinuclear Ni species or because of limited accessibility of Ni sites. XAFS measurements of the Ni-Na-FAU series (Figure 1B) shows for samples with Ni loadings above 200  $\mu\text{mol}\cdot\text{g}^{-1}$ , the appearance of Ni-Ni scattering indicative of the presence of multinuclear Ni clusters. Conversely, the sample with 50  $\mu\text{mol}\cdot\text{g}^{-1}$  Ni does not feature any signal at the Ni-Ni distance, leading to the conclusion that Ni is present as isolated  $\text{Ni}^{2+}$  ions.

Next, we have compared the dimerization activity of Ni exchanged CHA materials with similar Si/Al ratios but significantly different concentrations of Al pairs. It has been found that, for each series of Ni-CHA catalysts, the activity increases linearly with Ni loading up to the point all Al pairs are exchanged. Once the concentration of Al pairs is surpassed, the introduction of Ni does not lead to any additional activity. This is strong evidence of the nature of the active site being a single  $\text{Ni}^{2+}$  ion exchanged on Al pairs.

Finally, studies of Ni on MFI show that both single  $\text{Ni}^{2+}$  ions and larger clusters can be hosted by this framework. The sample with the highest activity features a Ni loading corresponding to the exchange of  $\text{Ni}^{2+}$  for the total concentration of Al pairs. This implies that the activity is associated with single Ni cations on Al pairs, which agrees well with the observations in CHA. IR spectroscopy of adsorbed CO shows a main band at 2212  $\text{cm}^{-1}$ , which is attributed to the  $\text{Ni}^{2+}$ -monocarbonyl species adsorbed on isolated  $\text{Ni}^{2+}$  sites exchanged in zeolites [4]. In addition, a shoulder at 2194  $\text{cm}^{-1}$  arises for MFI samples with high Ni content, which is attributed to CO on  $\text{Ni}^{2+}$  grafted onto a surface or  $\text{Ni}^{2+}$  of NiO nanoparticles. The catalytic activity of Ni-Na-MFI samples in butene dimerization correlates with the integral of the  $\text{Ni}^{2+}$ -CO vibration band at 2212  $\text{cm}^{-1}$  at low CO pressures (0.01 mbar). This provides further evidence of  $\text{Ni}^{2+}$  cations functioning as the active species in butene dimerization.



**Figure 1** A) Butene consumption rates and octene formation rates per mol Ni for Ni-Na-FAU series, measured at 50 bar, 160°C and WHSV between 6-2000 h<sup>-1</sup>. B) XAFS spectra of samples of the Ni-Na-FAU series. Dashed line at ca. 2.7 Å indicates Ni-Ni-scattering.

## Conclusions

In this work, we have identified single Ni<sup>2+</sup> cations as the catalytically active sites in butene dimerization on Ni-zeolite catalysts. The performance of three Ni-Na-CHA types with different concentrations of Al pairs indicates that the active site in butene dimerization correlates with single Ni<sup>2+</sup> cations on Al pairs. XAFS measurements corroborated that the high activity in Ni-Na-FAU samples with low Ni loadings stems from accessible single Ni<sup>2+</sup> cations. Finally, CO adsorption monitored by IR on Ni-Na-MFI catalysts supported this observation by showing the correlation of activity with the concentration of CO adsorbed on single Ni<sup>2+</sup> ions. The performance of the different zeolite constraints in butene dimerization also revealed higher linear octene selectivities for smaller pore sizes following the principle of shape selectivity.

Overall, our study provides relevant information on the speciation of transition metal ions in different zeolite frameworks and on how catalytic activity of such metal ions is affected by their local environment and accessibility. The comparison of different zeolite constraints allows more profound insights into the influence of Ni immediate environment. Zeolite properties such as Al pairs and pore size are shown to have an important impact on the activity and selectivity of Ni-zeolite catalysts in butene dimerization.

## References

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