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ISLE Isotherm: a "dual-energy" single-site approach to modelling SAR and Cu-loading effects on NH_3 adsorption/desorption over Cu-exchanged chabazites

N.Usberti[1], U.Iacobone[1], I.Nova[1]*, E.Tronconi[1], M.P.Ruggeri[2], J.E.Collier[2], A.P.E.York[2]

1 Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano (Italy)

2 Johnson Matthey Technology Centre, Sonning Common (United Kingdom)

**Corresponding author: isabella.nova@polimi.it*

Highlights

- NH_3 adsorption/desorption on Cu-CHA is affected by SiO_2/Al_2O_3 ratio, Cu loading and H_2O.
- Cu-CHA catalysts exhibit two NH_3 desorption peaks, while bare CHA shows one.
- Empirical ISLE coverage dependence provides satisfactory fit of SAR and Cu loading effects

1. Introduction

Cu-exchanged chabazites (Cu-CHA) show high activity and stability over a wide range of temperatures in NH_3-SCR, the state of art technology for NO_X abatement from heavy duty Diesel engines. Several studies were performed in order to investigate the relationship between Cu-CHA structure and SCR activity: in particular, it was found that the SiO_2/Al_2O_3 ratio (SAR) of the chabazite affects the interaction between Cu ions and the NH_3 adsorption/desorption process. The aim of this work is to elucidate this effect with a dedicated experimental campaign and to derive an accurate kinetic model of the NH_3 storage over Cu-exchanged chabazites, which is the first step for a better understanding and for the quantitative description of the NH_3-SCR process.

2. Methods

In order to investigate NH_3 storage on the catalysts, NH_3-TPD experiments were run over different Cu-CHA samples and the corresponding parent zeolites (CHA), varying the SAR from 10 to 25 (same Cu content, 2% w/w), and over Cu-CHA samples with different Cu loadings from 1 to 3% (same SAR=25). Sample powders were saturated with 500 ppm of NH_3 at 150°C, then NH_3 desorption was measured increasing temperature up to 550°C with a rate of 15°C/min in He [1].

3. Results and discussion

NH_3 desorption profiles during temperature ramp up to 550°C collected over a bare chabazite (CHA 13) and over two Cu-CHA samples (SAR = 13 and 17), are shown in figures 1A, 1B and 1C (symbols), respectively.

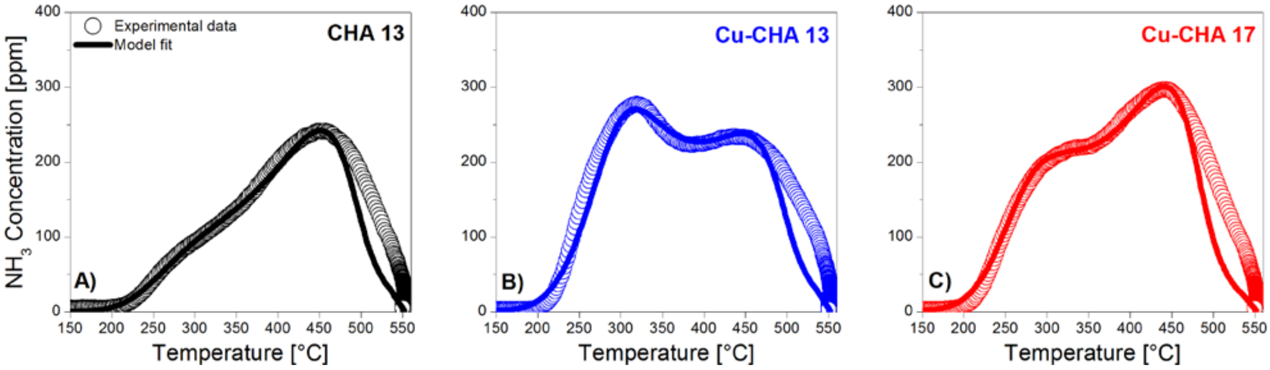

Figure 1. NH_3-TPD exp. data and model fit over CHA13 (A), Cu-CHA13 (B) and Cu-CHA17 (C)

CHA 13 shows one main NH_3 desorption peak centered at 450°C, ascribed to the contribution of Brønsted acid sites. Differently, Cu-CHA 13 exhibits a more complicated NH_3 desorption trend with temperature: two

NH_3 peaks were detected at 320ºC and at 450ºC [2]. While the high temperature peak is in line with the one observed over CHA 13, the additional low temperature peak is associated with Lewis acid sites [1], due to the presence of Cu ions and Al located outside of the framework. Similar NH_3 desorption dynamics were obtained over Cu-CHA 17, highlighting the presence of two families of acid sites on zeolites surface. However, compared to the results of Cu-CHA 13, Cu-CHA 17 shows a different distribution of desorbed ammonia, with a decrease of the low-T NH_3 peak and an increase of NH_3 released at high temperature. This is due to the complex effect of the SAR on the speciation of the Cu cations in the zeolite, as will be explained in more detail in the full presentation. In experiments performed over Cu-CHA 25 with Cu loading varying from 1% to 3% w/w, increasing the Cu loading promoted Lewis acidity of the catalysts, resulting in increasing the low temperature NH_3 desorption peak.

Experimental data collected over powdered catalysts have been analyzed according to a heterogeneous one-dimensional plug-flow dynamic reactor model, assuming the catalyst bed to be isothermal. In order to model ammonia adsorption/desorption kinetics, a non-activated adsorption process was incorporated combined, with different coverage dependences of the NH_3 desorption energy $E°_{DES}$ (Langmuir or Temkin-type), resulting in the following desorption rate expressions:

$$r_{ADS} = k_{ADS}\, C_{NH_3}\, (1-\theta_{NH_3})$$

$$r_{DES} = k_{ADS}\, exp[-E_{DES}/RT]\, \theta_{NH_3} \qquad with\ E_{DES} = E^0_{DES}\ [Langmuir]\ ;\ = E^0_{DES}(1-\alpha\theta_{NH_3})\ [Temkin]$$

Both the Langmuir and Temkin approaches, widely accepted and used in the literature on SCR kinetic mechanisms, were unable to fit the "dual sites" experimental trend over Cu-CHA. A new approach was then developed: an empirical coverage dependence was included in the model, representative of the existence of two adsorption sites on the catalyst surface having different acid strengths and NH_3 adsorption energies:

ISLE isotherm: $E_{DES} = E^0_{DES}(1 - A(1 + tanh(\alpha(\theta_{NH_3} - \theta_m))))$

The model fit is shown in figure 1 in solid lines. It is clear that with this new approach a fairly good description of the desorption phase is obtained for the whole set of catalysts tested, thus including an accurate description of the SAR effect.

4. Conclusions

The accurate description of NH_3 adsorption/desorption step is the basis for the analysis and design of the NH_3-SCR catalytic process. An experimental and modeling analysis was performed in order to investigate the NH_3 adsorption/desorption process over copper exchanged zeolites. Experimental tests showed a clear "dual site" NH_3 desorption dynamics over temperature, affected by the structure and composition of the catalyst (SAR, Cu loading) and by the experimental conditions (presence of H_2O during NH_3 adsorption). The modeling analysis clearly shows that both Langmuir and Temkin coverage dependences fail to describe the experimental trends, thus an improved dual-site modelling approach is implemented: incorporating the ISLE isotherm in the reactor model provides a very good fit of the NH_3 desorption peaks, specifically including an accurate description of the SAR effect, too.

References

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Keywords
SCR; Cu-CHA; SAR; dual-site NH_3 adsorption/desorption.