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Cu-CHA material efficient in the SCR process in the presence of water and CO_2

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A reproducible method for the synthesis of SCR active Cu-CHA materials has been developed, which allows the incorporation of up to 4% of copper inside the cavities of the zeolite. These materials are highly efficient in the removal of NO_x by reaction with ammonia, even in the presence of water and CO_2 in the reaction atmosphere. Cu^{2+} species are the active species in the reaction and in contact with water and CO_2, the hydrated-carbonate Cu^{2+} species placed in the 8-rings were identified as the responsible for the improvement in the activity.

1. Scope

With the intention of placing an SCR catalytic bed in the coupling of technologies to obtain zero emission at the outlet gas of a diesel engine, Cu-CHA zeolitic materials are presented as a suitable option. Therefore, the aim of this contribution is focused on the improved synthesis of Cu-SAPO-34 materials active in the SCR process even in the presence of water and CO_2, identifying the copper active species and their location in the structure.

2. Results and discussion

The synthesis of these materials was carried out using an ultrasound assisted method that improves the crystallinity and reduces the synthesis time. All the materials have been well-characterized and their morphological and structural properties depend on the synthesis conditions, although are in line with those reported by other authors[1,2]. The activity in the SCR process was studied in a fix bed reactor loaded with the catalyst in powder form and feeding 750ppm NH_3 + 750ppm NO + 3% of O_2 in Helium or in 1.5% of H_2O and 0.3% of CO_2 atmosphere. In Figure 1, the results in both atmospheres in terms of NO and ammonia conversion and nitrogen selectivity at three different temperatures are summarized. In dry conditions, at low temperatures, the conversion values are almost identical indicating the reaction by the standard SCR reaction. As the temperature increases, the ammonia conversion values are higher than NO conversion, meaning that a parallel reaction is taking place and associated with the ammonia oxidation. In addition, the selectivity to nitrogen decreases due to the increment in the N_2O production, with a maximum around 300ºC, related to nitrate decomposition.

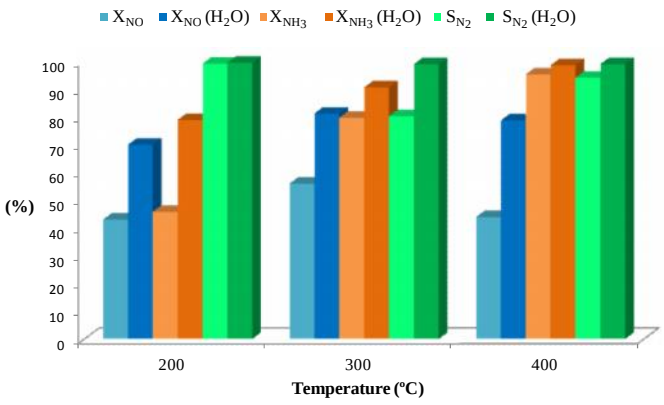

Figure 1. SCR activity values (conversion and selectivity) in dry and wet conditions.

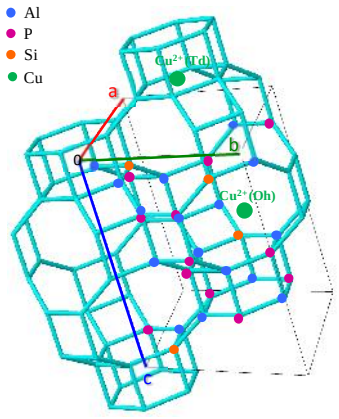

Figure 2. Location of copper species in Cu-CHA.

In the presence of water and CO_2, all the conversion values increased, pointing out that these components, in some way, improve the catalytic activity, decreasing the co-side reactions and the formation of undesired products. Different from other studies that only indicate the enhancement of these materials[3], in this contribution a depth study was carried out in order to know the intrinsic reactivity of the active species and the mechanism. In order to obtain this information, a higher number of experiments were carried out, combining *in situ* and *ex situ* analyses using mainly spectroscopy. The combination of the adsorption and co-adsorption of probe molecules with different sizes and acidity, the interaction with the reagents of the SCR reaction and the characterization of the samples provided data that allows the identification of copper species and the way in which those species interact during the reaction. XRD patterns, SEM images, X-Ray Fluorescence and Rietveld refinement indicated that the type of structure was chabazite and it was maintained with the incorporation of copper and after a hydrothermal treatment at 750ºC. The adsorption of basic molecules with different sizes allowed the confirmation of the copper incorporation inside the structure. XPS, XRD, CO adsorption at low temperatures or UV-Vis-DR corroborated the presence of a combination of Cu^{+} and Cu^{2+} species. The co-adsorption of NO, NH_3 and O_2 in both pulses and continuous flow was analyzed by FTIR in two different reaction chambers, detecting the formation of Lewis and Brönsted Acid sites and nitrate/nitrite species, together with mononitrosyl Cu^{2+} species, responsible for the SCR activity[4]. Based on all the obtained information, in Figure 2, a possible location of the species inside the chabazite structure is displayed, where Cu^{2+} species placed on the 8-rings could be the active species in the hydrated-carbonate form.

3. Conclusions

Cu-SAPO-34 with chabazite structure materials active in *quasi*-real conditions was synthesized in a reproducible way, incorporating all the copper inside the structure, with a copper percentage of up to 4%. Moreover, the active species in the SCR mechanism in dry and wet conditions were identified, being Cu^{2+} species in octahedral coordination the most active for the SCR reaction.

References

1. U. De-La-Torre, B. Pereda-Ayo, M. Moliner, J.R. González-Velasco, A. Corma, *App. Catal. B:Env.* **2016**, *187*, 419-427.
2. L. Bai, N. Chang, M. Li, Y. Wang, G. Nan, Y. Zhang, D. Hu, G. Zeng, W. Wei, *Micro. And Meso. Mat*. **2017**, *241*, 392-399.
3. T. Yu, J. Wang, M. Shen, J. Wang, W. Li, *Chem. Eng. J.* **2015**, *264*, 845-855.
4. M. Cortés-Reyes. *PhD Thesis.* **2017**.