Ag_x(SR) NANOCLUSTERS SUPPORTED ON ZEOLITES AS CATALYSTS FOR ENVIRONMENTAL PROCESSES

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INTRODUCTION

Metal nanoclusters have attracted considerable attention due to their outstanding properties in comparison with the nanoparticles, tuneable at atomic scale. It open a wide range of application fields like nanoelectronics, optics, biomedicine and catalysis. In the case of catalysis, thiolate protected metal nanoclusters ($M_n(SR)_m$) open up new possibilities to create atomic precise catalytic active sites with resolved structures. A truly monodisperse catalytic surface provides ideal conditions for structure reactivity correlation studies. Extend reported studies focused on Au show that, once the cluster are supported on oxides, exhibit excellent catalytic activity in oxidation and hydrogenation reactions. It has been shown an enhancement of the catalytic properties and performance in comparison with the pair nanoparticles.

Ag and Au have contrasting physical and chemical properties despite their similarity in atomic size, structure and bulk-lattice. The difference are more accentuated going down to nanoscale and even more at nanocluster range (<100 atoms) where higher catalytic properties have been observed.(Lei, Mehmood et al. 2010) Ag clusters and nanoparticles are potentially useful catalysts in several hydrogenation and oxidation reactions. Recently,Ag_{44} nanoclusters supported on MPC show different dehydrogenation mechanism reaction with higher activity in comparison with another metals such as Pt or Pd.(Urushizaki, Kitazawa et al. 2015) This point out the opportunity for the development of novel Ag cluster catalysts.

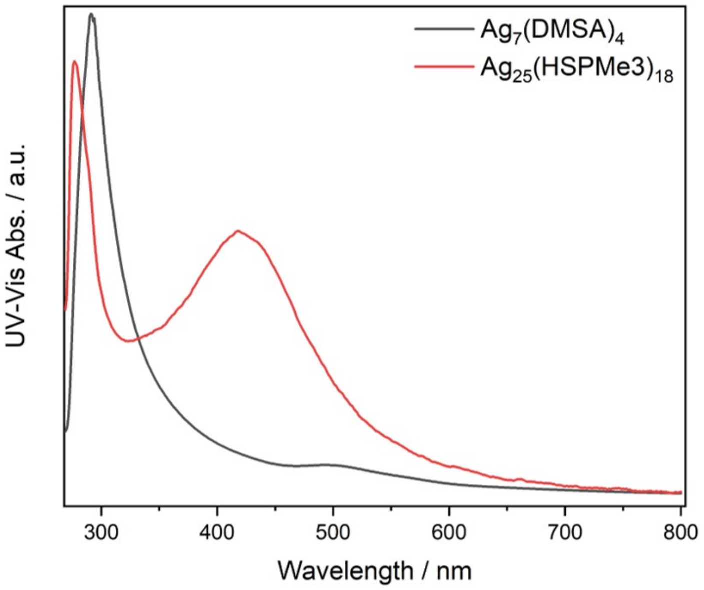
Therefore the aimof this study is the synthesis and isolation of atomically designed silver clusters, the characterization and study of their physical-chemical properties. Once the cluster are obtained, the effect of their immobilization on different kind of zeolites will be studied follow by their catalytic activity in environmental processes.

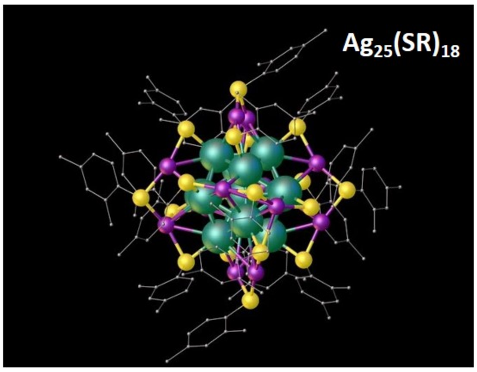
EXPERIMENTS

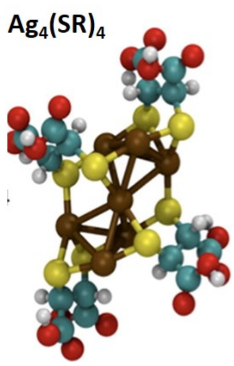
The synthesis of two different silver cluster have been performed based onBrust method [1] and previous reported works. The prepared clusters can be purified by PAGE and SEC (size exclusion chromatography). The pure Agx(SR)m clusters arecharacterized in order to know their physical-chemical properties by MALDI, UV-vis, NMR, FTIR and PL. Once the clusters are synthesized and characterized, they were immobilized in different kind of zeolites (ITQ1 and ITQ2) as supporting materials. The surface properties and his interaction with the metal will be studied by TG, FTIR-CO, XPS and TEM.

RESULTS AND DISCUSSION

The sizes of the clusters are related with the kind of thiolated ligands and the conditions of the synthesis. The first cluster synthesized was the $Ag_7(DMSA)_4$ using silver salt as precursor, DMSA as ligand and ethanol as solvent, based on reported method[2] did not lead to the expected clusters. Therefore, optimization of the synthesis protocol has been performed. The molar ratio between the precursors was adjusted as well as the times between each step. In the case of $Ag_{25}SR_{18}$, silver nitrate salt was employed as precursor, $HSPMe_3$as ligand instead of $HSPMe_2$[4] and the solvent in this case was dicloromethane (DCM). UV-vis spectra of the clusters confirm the presence of the species in the samples, showing specific bands, which are characteristics for cluster Ag_7 and Ag_{25}.







CONCLUSION

To conclude several silver clusters were made with different methods of synthesis and ligands, all based on the Brust method. Optimization of the reported synthesis protocols have been made in order to obtain the desired clusters sizes. These clusters were supported in different zeolites, and their interaction and their properties are in the process of study by several techniques. Next step represents the catalytic properties study, for this the catalyst will be tested in different reactions mainly NH_3 and propane oxidation, also further studies will be performed by XAFS at synchrotron facilities (ALBA)

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