COPPER-PLATINUM NANOPARTICLES SUPPORTED ON ACTIVE CARBON AS CATALYST FOR DENITRIFICATION OF DRINKING WATER.

N. Barrabés, A. Dafinov, F. Medina, J.E. Sueiras
Chemical Engineering Department, University Rovira i Virgili, Campus Sescelades,43007 Tarragona, Spain
noelia.barrabes@urv.net

Introduction

Metal nanoparticles are particularly interesting nanoscale systems because they can easily be synthesised and modified chemically. In this group, copper nanoparticles attracted considerable attention because of their catalytic, optical and conducting properties. Their synthesis has been achieved via various routes such as reduction in micro emulsions [1], reverse micelles [2], polyol process [3] or alcohol reduction [4]. To avoid oxidation, these methods were usually performed in non-aqueous media, at low precursor concentration and under an inert atmosphere. The use of soluble polymers or surfactants as capping agents for the preparation of copper nanoparticles is necessary [5,6]. One of the cationic surfactants used is the CTAB (cetyltrimethylammonium bromide), which have a remarkable structure-directing property in the seed-mediated growth approach. Besides, recently, A.A.Athawale et al. [7] have shown that CTAB also produces the reduction of Cu^{2+} ions under ambient conditions when the CTAB/Cu^{2+} ratio is higher than 30. However, the posterior elimination of the high amount of surfactant is an important drawback for its application in catalysis.

A comparison between different protocol synthesis such as polyol, and CTAB processes for the preparation of copper nanoparticles, with the minimum amount of surfactant, has been performed. The incorporation of platinum on the surface of copper nanoparticles during the synthesis has also been studied. Besides, the preparation of copper-platinum nanoparticles supported on activated carbon as well as their catalytic behaviour in the selective hydrogenation of nitrates in contaminated drinking water, using a continuous reactor, has been also carried out.

Experimental section

Copper nanospheres of around 350 nm were obtained using polyol process [8]. Once obtained, an ethanol solution of copper nanospheres was mixed with an aqueous solution containing the appropriate amount of platinum salt (H_2PtCl_6). The noble metal is reduced by redox reaction on the surface of the copper nanoparticles, where it is deposited. The Cu/Pt atomic ratios on the nanosphere surface were 1/4 and 1/1. On the other hand, an ethanol solution containing copper nitrate salt is reduced drop by drop with an ethanol solution containing CTAB under stirring. When the nanoparticles are formed a colour change from blue to red wine is observed. Then, an ethanol platinum solution is added to the copper nanoparticles solution. The particle size was around 7 nm and the Cu/Pt atomic ratios on the nanoparticles surface were 6/1 and 60/1. The active carbon was impregnated with the obtained suspension of copper-platinum nanoparticles. Finally, the materials were dried and then reduced under hydrogen flow at 350 ºC for 3 hours. Samples were characterised by XRD, TEM, SEM, UV; BET, XPS, and hydrogen chemisorption.

The catalytic reduction of nitrates (60 mg/l) was performed in a fixed bed reactor and analytical methods were previously described [8].

Result

Using CTAB method, the Cu-Pt nanoparticle size obtained is in the range of 50 times lower than for the Polyol process. However, a very well Pt dispersion on the surface of copper nanoparticles is observed in both cases. The Cu-Pt nanoparticles catalysts showed higher activity converting all the nitrates to nitrogen avoiding the formation of more harmful products such as nitrite and ammonium. The catalytic activity increases when the Pt amount in the sample increases. When compare the catalytic activity of the samples in terms of amount of nitrate converted to nitrogen per gram of noble metal an per hour and compare it with the polyol and CTAB methods to prepare the Cu-Pt nanoparticles, we observe that catalysts obtained by CTAB method are more efficient in the nitrate reduction reaction with respect to the polyol method.

References:

[1] P.Barnickel, A.Wokaun, W.Sagerand, H.F.Eicke; *Journal of Colloid Interf. Sci.*,148 (1992) 80.
[2] C. Petit, P. Lixon, M. P. Pileni; *Journal of Phys. Chem.*, 97 (1993) 12974.
[3] L.K. Kurihara, G.M. Chow, P.E. Schoen; *Nanostruct. Mater*, 5 (1999) 607.
[4] H. Huang, X. P. Ni, G.L. Loy et al.; *Lagmuir*, 12 (1996) 909.
[5] S.S.Joshi, S.F.Patil, V.Iyer, S.Mahumuni; *Nanostruct. Mater.*, 10 (1998) 1135.
[6] I. Lisiecki, F.Billoudet, M.P. Pileni; *J. Phys. Chem.*, 100 (1996) 4160.
[7] A.A.Athawale, P.P.Katre, M.Kumar, M.B.Majumbar; , 91 (2005) 507-512.
[8] N.Barrabés, J.Just, A.Dafinov, F. Medina, et al., *Applied Catalysis B: Enviromental*, 62 (2006) 77-85.

Figures:

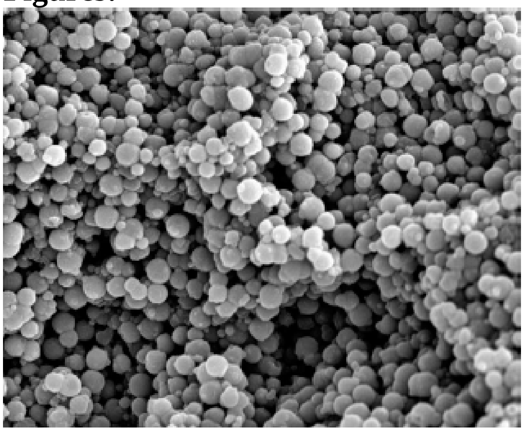

Figure 1. SEM image of Copper Nanospheres synthesized by polyol method (350nm)

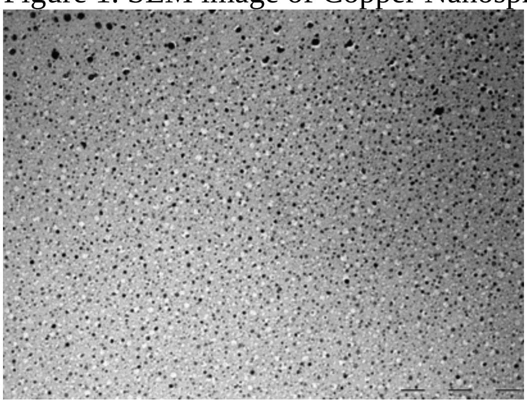

Figure 2. TEM image of Copper Nanoparticles synthesized by direct synthesis (7 nm)