Nitrite reduction over platinum nanoparticles supported on tunable macroporous-mesoporous supports

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Introduction

The removal of nitrate/nitrite from ground water will be required for the foreseeable future to meet the demands in water of an expanding world population. Despite the limitation of their concentrations (nitrates: 50 $mg.L^{-1}$ and nitrites: 0.1 $mg.L^{-1}$) fixed by the World Health Organization, these pollutants are still dangerously growing up. Their removal by catalytic hydrogenation using noble metals seems one of the most promising techniques since it could directly convert nitrates/nitrites to nitrogen while offering the opportunity for continuous operation in flow reactors. Herein, by tuning the physical properties of amorphous supports derived from SBA-15 (morphology, pore sizes and pore interconnectivity), we investigate the catalytic performance of Pt-based catalysts in the catalytic hydrogenation of nitrites.

Materials and Methods

Tunable macroporous-mesoporous silica catalyst supports (called HS-X with X = bead size) were prepared on a gram-scale according to a dual-templating method adapted respectively from Oh et al.[1] This templating method involves the direct insertion of the macrotemplate (polymer spheres) in the solution following the addition of TEOS and block-copolymer for adding a mesoporous network. The prehydrolysed precursor solution subsequently impregnate the polymer spheres during one day and the in situ sol-gel transformation is obtained following hydrothermal treatment with different aging time (24h<t<96h) and temperature (80°<T<100°C), resulting in an intermediate composite nanospheres/P123-silica structure. Hybrid materials were calcined at 550°C (0.5$K.min^{-1}$) to remove the organic porogens and to generate the final siliceous solids. Pure macroporous solids have been prepared following the same method without adding the block copolymer. All siliceous materials were impregnated by hexachloroplatinic acid solutions with adjusted concentrations in order to obtain 1 wt.% Pt. The precursors thus obtained were calcined in air at 400°C and successively reduced at 350°C in H_2 overnight. Physico-chemical properties of all materials have been assessed by TGA-DSC, N_2 porosimetry, XRD, SAXS, SEM, TEM and electron tomography, H_2 chemisorption, H_2 TPR and XPS. Catalytic hydrogenation was performed at 20°C under stirring using 0.08 g of catalyst, 18.5 mg of KNO_2, 50ml of deionized water. The pH was regulated around 6 by adding CO_2 in reaction media.[2] Aliquots of 1 ml were regularly sampled and analyzed by ionic chromatography using a Methrom (844 UV/VIS Compact IC) equipped with a Metrosep A Supp 16 – 150/4.0 column.

Results and Discussion

By tuning the sol-gel synthesis parameters (Polymer:TEOS ratio, hydrothermal temperature and aging time), we succeeded in guiding the SBA-15 rod-like morphology having randomly packed macropores to a derived SBA-15 with a honeycomb macrostructure. Hence, control over the macropore sizes (ranging from 50nm to 300nm) has been successfully obtained while a non-ionic surfactant templating agent drives the formation of small mesopores. As observed table 1, all macrostructured porous silicas possess high specific surface areas and small mesopore dimensions close to the parent mesoporous silica. In addition, the mesopore window contribution is dramatically increased for Pt/HS100. Hence, the pore volume of HS-100 sample calculated from the condensation step is clearly higher (at least three times larger with respect to the parent SBA-15) while maintaining wall thickness extremely close to the mesoporous reference.

Table 1: Physical properties of selected catalysts

Catalyst	D_{Macro} /nm	D_{Wind} /nm	D_{Meso} /nm	S_{Area} /m^2g^{-1}	T.P.V. /$cm^3.g^{-1}$	$W_{thickness}$. /nm
Pt/SBA-15	-	-	5.3	784	0.83	6.2
Pt/HS200-96h	178±14	30	4.0	566	0.73	6.5
Pt/HS100-96h	78±11	38	3.9	983	2.72	6.8

Pore networks respectively generated by the hard and/or soft templates are directly visualized by TEM on the samples (figure 1A,B). It is interesting to note that the macropores are open and interconnected (figure 1.B) which suggests a better transport of the reactants to the metallic active sites with respect to SBA-15 possessing long isolated channels. Such architectures allow reaching very high dispersion of the noble metal on the support (0.70<H/Pt<0.80). We are currently undertaking tomographic analysis to study the 3D morphology of the hierarchical materials and more particularly the distribution of the platinum particles over the porous framework. Materials reactivity was subsequently evaluated towards the catalytic hydrogenation of nitrites in aqueous phase. As shown Figure 1.C, all materials are active for nitrite reduction and it is clearly observed a beneficial effect of the macroporous incorporation/organization on catalyst performance with respect to the pure mesoporous Pt/SBA-15 and the commercial Pt/Aerosil silica (figure1.C). HS-100-96h presents the best catalytic activity due to the best textural properties obtained by optimization of our synthesis procedure.

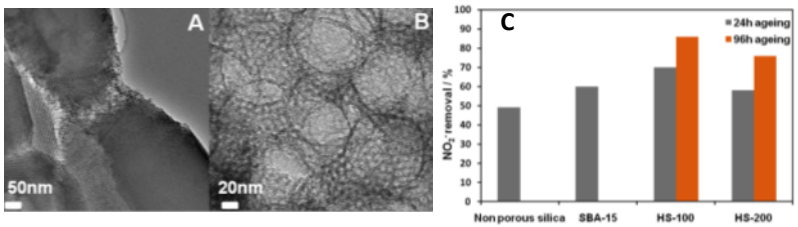

Figure1. TEM micrographs of (A) SBA-15 and (B) HS-100-96h. (C) Nitrite removal over Pt based siliceous catalysts after 6h conversion.

Significance

We demonstrated that we can easily tune the macropore entrance by a simple sol-gel method. Interconnected pore networks at the macro and meso scales confer to the derived Pt based catalysts higher catalytic performance in catalytic reduction of nitrites by alleviating the mass transport limitations encountered in liquid phase catalysis.

References

1. C.G. Oh, Y.K. Baek, S.K. Ihm, Adv. Mater. 17 (2005) 270
2. A. Garron, F. Epron, Water Res. 39 (2005) 3073-3081.