Ionic liquid in SCILL: a key in selectivity and stability of catalyst

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Abstract: OMS-2, the cryptomelane form of manganese oxide, has been investigated as well or after the deposition of 5wt% Pt for the oxidation of benzyl alcohol and oxidative coupling of 1-butanethiol and thiophenol. Subsequently, a thin layer of [Bmim][NTf_2] or [Bmpyr][NTf_2] has been used to prepare SCILL catalysts. The deposition of platinum led to a partial degradation of OMS-2 to Mn_3O_4 during the alcohol oxidation. However, the presence of IL determined a significant increase in the catalyst's stability. Further, changes in the selectivity were determined after the combination of O_2 with an inert (N_2, He, Ar) gas.

Keywords: OMS-2, SCILL, oxidation.

1. Introduction

Solid **C**atalyst with **I**onic **L**iquid **L**ayer (SCILL)[1] belongs to the heterogeneous catalyst class. Obviously, covering the solid surface with a thin layer of IL provides an increase of the stability and an improvement of the selectivity. OMS-2 is a porous mixed-valent oxide ($KMn^{4+}{}_7Mn^{3+}O_{16}\cdot nH_2O$) with a 2 × 2 tunnel architecture and a large surface area[2]. Changing of K with protons[3] generates acid properties. On the other side, the oxidation of benzyl alcohol is an important process because benzaldehyde is a valuable chemical for perfumery, pharmaceutical and also as an industrial solvent[4]. In addition, disulfide bonds produced through the oxidation of thiols play an important role in the folding and stability of many proteins[5]. Therefore the challenge is the oxidation with O_2 under mild reaction conditions. The aim of this research was to establish the impact of the SCILL catalysts in benzyl alcohol and oxidative coupling of 1-butanethiol / thiophenol as well as the influence of some mixtures of O_2/inert or reactive gas on the reaction selectivity.

2. Experimental

All the organic reagents were of analytical purity and were used without any further purification. OMS-2 was synthesized using the sol-gel method, 5wt% Pt/OMS-2[6] was prepared by incipient wetness impregnation using a platinum nitrate solution and SCILL catalysts[7] were obtained by mixing a solution of the ionic liquid in dichloromethane followed by the solvent removal and drying under vacuum. NMR, XRD, DRIFT, Raman, BET, Dynamic Light Scattering, XPS, TEM, SEM were used to check the modifications generated by platinum in OMS-2 and by the ionic liquid deposition onto the 5wt% Pt/OMS-2 surface. The benzyl alcohol oxidation was performed under a vigorous magnetic stirring in an autoclave and in presence of deionized water at 100 °C for 4 h. The oxidation of thiols to disulfides, was performed in a glass batch reactor where thiols (1-butanethiol or thiophenol) were stirred in the presence of catalysts and cyclohexane at the reflux temperature.

3. Results and discussion

The XRD patterns of OMS-2 and 5wt% Pt/OMS-2 presented only the lines assigned to the support with a chemical composition of KMn_8O_{16}. No significant changes in the structure of the support had occurred after the deposition of the ILs as confirmed by DRIFT, RAMAN and XPS. SEM images of OMS-2 and 5%wt Pt/OMS-2 showed the characteristic nano-rod like morphology of OMS-2 (Figure 1 (a,b)). The TEM image of 5wt% Pt/OMS-2 (Figure 1 (d)) showed uniform distribution of spherical Pt nanoparticles of mean diameter ~1.2 nm on the surface of OMS-2 molecular sieve. The aggregation of the catalysts particles in water was different as a function of the type of the IL producing the SCILLs. 5wt% Pt/OMS-2 aggregated in larger particles than the two SCILL catalysts showing a protecting effect of the IL shell (80.27 μm versus 43.15 μm and 49.48 μm). Both SCILL catalysts displayed the ionic liquid loading ε, pore filling degree α and the layer thickness s_{IL} approximately identical. The pores were not fully filled with the ionic liquid.

The catalytic tests indicated a low activity of OMS-2 in the oxidation of benzyl alcohol in the presence of air or molecular oxygen, while the deposition of 5wt % Pt led to a total conversion of benzyl alcohol. Using SCILL catalysts, the increase of the oxygen pressure led to an increase in the conversion in the detriment of selectivity. The presence of platinum on the surface resulted in changes of OMS-2 with the formation of Mn_3O_4. The presence of the IL on the surface of SCILL reduced the degradation of the support structure. Also, different N_2, He, Ar, CO_2 / O_2 mixture led to significant changes in selectivity and conversion indicating that the oxygen solubility in the IL may be controlled by the diluent gas and has an important effect on the oxidation of benzyl alcohol (Figure 2).

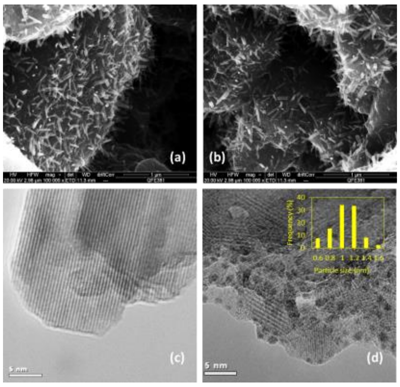

Figure 1. SEM image of OMS-2 (a), SEM image 5%wt Pt/OMS-2 (b), TEM image of OMS-2 (c), TEM image of 5%wt Pt/OMS-2 (d).

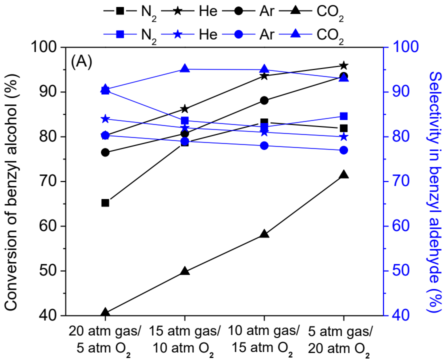

Figure 2. The variation of the conversion and selectivity in benzyl alcohol oxidation as a function of the gas mixture composition for 5wt% Pt/OMS-2/[Bmim][NTf$_2$].

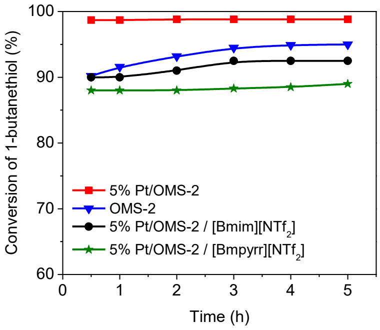

Figure 3. The activity of the catalysts in the conversion of 1-butanethiol.

For the oxidation of thiol 5wt% Pt/OMS-2 also exhibited a high catalytic activity that has been associated with an increased basicity as a result of a synergistic effect of K, octahedral MnO_6 and Pt. The SCILL catalysts resulted in slightly lower conversions that have been compensated by a total selectivity in disulphide.

4. Conclusions

SCILL catalysts were easily prepared via the deposition of IL without any modification in the support structure. The presence of ILs on the surface of SCILL reduced the degradation of the support structure during the oxidation reactions. The selectivity for the benzyl alcohol oxidation was tuned by using N_2, He, Ar, and CO_2/O_2 mixtures with different compositions. For thiols the catalytic performances of SCILL were comparable for aromatic and aliphatic compounds.

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