Characterization of the surface properties of SILP catalyst

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Introduction

The possible use of ionic liquids (ILs) for a number of applidations is currently and increasingly reported in the international literature. Although the ability of biphasic hydroformylation catalysis in ionic liquid media systems generally has successfully been demonstrated, the chemical industry still prefers heterogeneous catalyst systems because of some its own limitation. The biphasic system requires a large amount of ionic liquid. In addition, the high viscosity of ionic liquids can induce **mass transfer limitations** if the chemical reaction is fast, causing a minor part of the ionic liquid and the precious transition metal catalyst dissolved therein to take part in the catalyzed reaction.

These drawbacks have been circumvented by R.Ferhmann's group and other groups using **supported ionic liquid phase (SILP)**system.[1,2] in which a thin film of ionic liquid containing the metal complex is confined on the surface of a highly porous solid.The SILP catalyst enables the application of **fixed-bed** technology for simple continuous processing and the usage of significantly reduced amounts of the ionic liquid.

This report would focus on characterization of the surface properties of SILP catalyst by using popular techniques such as: SEM-TEM, FT-IR, Raman spectra, physiscal adsorption as well as chemical adsorption, in oder to give more useful and interesting information about SILP system.

Materials and Methods

Synthesis of SILP catalyst: Synthesis of SILP: SILPs were synthesized by the Schlenk technique.(Ionic liquid is [BMIM][*n*-$C_8H_{17}O$-SO_3] (pH) 8.3, H_2O < 500 ppm, Cl^- < 100 ppm, Solvent-Innovation, $Rh(CO)_2(acac)$ from Aldrich, sulfoxantphos ligand were impreganated onto calcinated SiO_2)

***Characterization*:** The SILPs are characterized by FT-IR, Raman, N_2 adsorption/desorption, SEM, TEM, TGA-DSC, TPD C_3H_6, TPD CO.

Results and Discussion

SILP catalyst (*0.2%wt*Rh/SiO_2, *10%wt* IL/SiO_2) showed good activity, selectivity and stability in hydroformylation of propylene *(100 °C, 10 bar total pressure (H2:CO:C_3H_6=1: 1:1), $n_{rhodium}$= 3.88x10^{-6} mol, τ =0.057 s)* (TOF (h^{-1}):**170**, selectivity n/iso butanal **95%**, stable in long time (**36h**) is in good agreement with the previous publication.[2]

From TGA-DSC profiles and N_2 adsorption/desorption isotherms, it could be concluded that SILP is stable at temperature lower than 200°C. The result from table 2 show that the amount of physisorbed nitrogen decreased with IL loading, causing a reduction in the surface area, total pore volume and mean pore size. A decrease of the mean pore diameter from 77.6 (SiO_2)to 77.4 Å(SILP) is attributed to a thin film of IL on the surface.

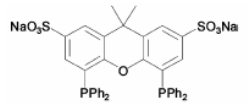
Table 1. The textural property and pore structure of the SILP and relevant sample

Catalyst	IL loading %		S_{BET}(m2/g)[b]	Vp tot(cm3/g)[c]	d_{BJH}(Å)[d]
	%wt	α[a]			
Calcinated SiO2	0	0	417	0.9	77.6
SILP	10	0.11	238	0.6	77.4

a Pore filling degrees of ionic liquid in SiO2 support as volume IL/proe volume support
b.BET specific surface area
c. Total pore volume d. Mean pore diameter determinded by BJH method

Significance

Surface properties such as surface specific area, porous system or adsoptive properties are generally supposed to be the main specific characteristics of hetergeneous catalyst. SILP could be considered as a kind of hetergeneous catalyst. So a careful study about SILP's surface properties is useful for evaluation catalytic activity of SILP in hydroformylation reaction.



(1) sulfoxantphos

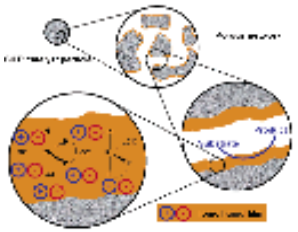


Fig 1:Schemantic princible of SILP

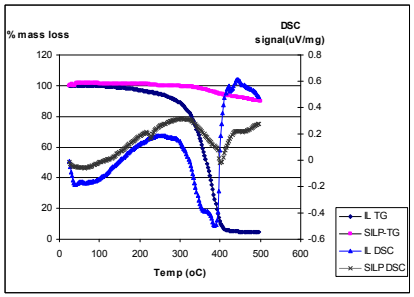


Fig 2: TG-DSC profiles of ionicl liquid and SILP catalyst

References

[1] Riisager, A.; Fehrmann, R.; Haumann, M.; Wassersheid, P. *Topics in Catalysis* 2006, *40*, 91.
2. Riisager, A.; Fehrmann, R.; Haumann, M.; Gorle, B.S.K.; Wassersheid, P. *Ind. Eng. Chem. Res*. **2005**, *44*, 9853.3.