Meso/macroporous ceramics for catalytic conversion of lignocellulosic biomass into chemicals of industrial interest

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Abstract: The present work aims at development of supported heterogeneous catalysts to promote the conversion of lignocellulosic biomass into chemicals of industrial interest. The central idea is to prepare hybrid meso/macroporous glasses that are sufficiently stable in the corrosive environments of biomass hydrolysis and additionally possess the intrinsic mesoporous nanostructure with highly active surfaces, required for the catalytic conversion processes involved. Sol-gel derived mesoporous materials were explored as support for vanadium and niobium oxides (V_2O_5 and Nb_2O_5): pure (SiO_2) and phenyl-modified silica ($Ph_{0.17}SiO_{1.9}$) xerogels were synthesized using an ionic liquid and triblock copolymer (Pluronic P123) as soft-templating.

Keywords: Biomass, Porous ceramics, Hydroxymethylfurfural

1. Introduction

The heterogeneously catalyzed conversion of biomass into fuel and fine chemicals is a new research field of particular attraction and relevance to the Brazilian national economy. While a wide range of suitable catalysts (as zeolites, mesoporous zeolites and mesoporous materials) have been studied in laboratory scale [1], at the present time no large-scale industrial plant utilizing such catalysts are in operation in Brazil. The transport of heavy biomass molecules into the catalyst pores is very cumbersome and impaired by severe mass transfer limitations. To transform, the biomass requires a dispersant as a reaction medium and hydrolytically stable catalyst materials endowed with a large system of interconnected macropores. We aim to achieve this goal using macroporous ceramic scaffolds based on silicate prepared via sol-gel chemistry. Dual templating strategies are pursued to generate hierarchically ordered single phase materials combining both meso- and macroporosity. The properties of the resulting materials are designed to catalyze the reaction of cellulose into hydroxymethylfurfural (HMF) [2], a high value chemical.

2. Experimental

SiO_2 and phenyl-modified silica xerogel with bulk composition $Ph_{0.17}SiO_{1.9}$ were synthesized by the sol-gel method, based on experimental procedure adapted from the syntheses of de Queiroz et al. [3]. Mesoporous glass-supported vanadia and niobium catalysts (transition metal loadings from 1.0 to 9.0 wt%) were prepared by alcoholic impregnation method [4]. For characterization of the materials, N_2 adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 volumetric adsorption analyzers at -196 ºC. The samples were outgassed at 110 ºC for 2 hours under vacuum prior to each measurement. The specific surface area (S_{BET}), the total pore volume (V_t) and the pore size distribution (PSD) were calculated using the adsorption branches of isotherms. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure P/P_0 range of 0.05–0.2. The total pore volumes (V_t) were estimated from the amount adsorbed at the relative pressure of 0.98. The pore size distributions were calculated from adsorption branches of nitrogen adsorption isotherms using the improved KJS method [5].

3. Results and discussion

Fig. 1(A) and (B) illustrate the N_2 adsorption–desorption isotherms and the PSD curves for the pure and phenyl-modified silica materials. All the samples possess hysteresis loops characteristic for mesoporous materials. The textural and structural properties of the studied materials are summarized in Table 1. Afterwards, the local and structural organization of the matrices and the catalytically active species will be examined in detail using advanced single and double nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) spectroscopies and transmission electron microscopy (TEM).

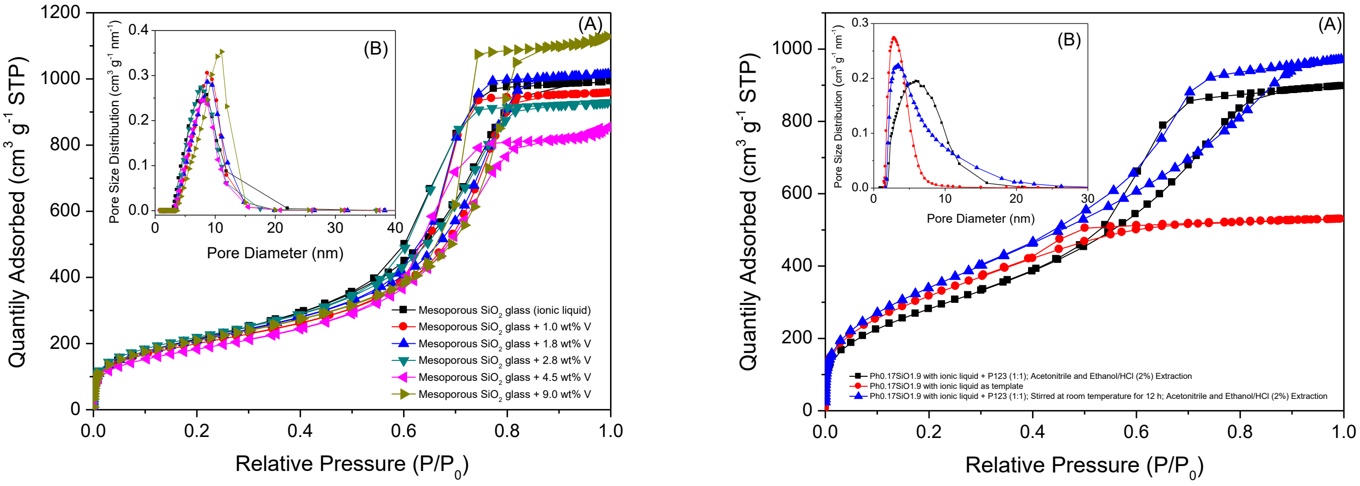

Figure 1. (A) N_2 adsorption–desorption isotherms and the corresponding pore size distributions (B; inset) for the reference materials and the supported vanadia catalysts obtained via sol-gel synthesis.

Table 1. Textural properties of samples studied

Sample	V_t Pore volume (cc/g)	S_{BET} (m^2/g)	WKJS Pore size at PSD max (nm)
Mesoporous SiO_2 glass (ionic liquid)	1.53	794	7.62
Mesoporous SiO_2 glass + 1.0 wt% V (NH_4VO_3)	1.48	732	8.72
Mesoporous SiO_2 glass + 1.8 wt% V (NH_4VO_3)	1.56	772	8.70
Mesoporous SiO_2 glass + 2.8 wt% V (NH_4VO_3)	1.43	797	7.66
Mesoporous SiO_2 glass + 4.5 wt% V (NH_4VO_3)	1.31	671	7.65
Mesoporous SiO_2 glass + 9.0 wt% V (NH_4VO_3)	1.73	763	11.0
$Ph_{0.17}SiO_{1.9}$ with ionic liquid	0.82	1199	2.87
$Ph_{0.17}SiO_{1.9}$ with ionic liquid + P123 (1:1 mixture of ionic liquid and P123); Acetonitrile and Ethanol/HCl (2%) Extraction	1.38	1067	5.96
$Ph_{0.17}SiO_{1.9}$ with ionic liquid + P123 (1:1 mixture of ionic liquid and P123); Stirred at room temperature for 12 h; Acetonitrile and Ethanol/HCl (2%) Extraction	1.50	1299	3.43

4. Conclusions

In this study, porous glasses were synthesized using organic template and sol-gel method. Mesopores were created by using ionic liquid 1-butyl-3methyl-imidazolium-tetrafluoroborate and triblock copolymer (Pluronic P123) as the template. The physicochemical characterization of the materials by N_2 adsorption–desorption showed promising results for the novel synthesized mesoporous glasses.

References

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The project is being financed by the São Paulo Research Foundation (FAPESP) Grants # 2013/07199-6 and # 2016/14165-0.