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Hybrid Nanoreactors

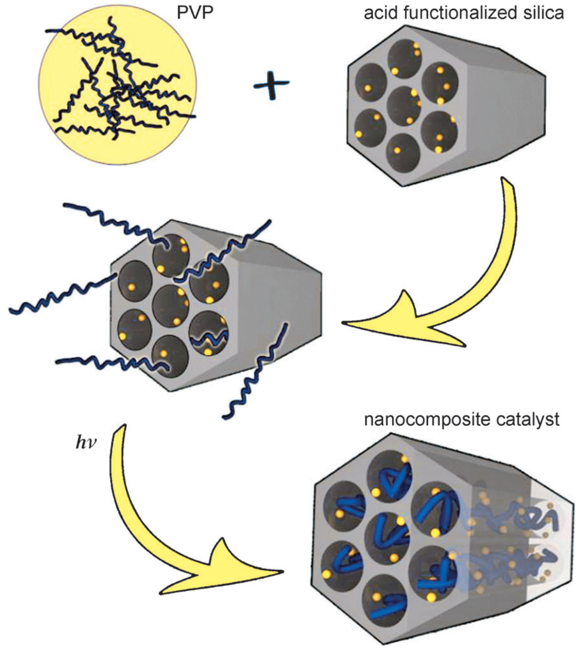
A Tailored Microenvironment for Catalytic Biomass Conversion in Inorganic–Organic Nanoreactors**

Ricardo Alamillo, Anthony J. Crisci, Jean Marcel R. Gallo, Susannah L. Scott, and James A. Dumesic**

The efficient and selective conversion of biomass-derived renewable feedstocks into chemicals and fuels remains a major techno-economic challenge.[1] Fructose, a simple carbohydrate that can be obtained from cellulose, can be dehydrated to a potential platform chemical, 5-hydroxymethylfurfural (HMF).[2] The selectivity for HMF is a function of the fructose tautomer distribution, which varies with solvent polarity and temperature.[3] Near-quantitative conversion of fructose into HMF has only been obtained in non-aqueous, polar aprotic solvents (such as, DMSO or NMP), or in ionic liquids.[4] However, HMF separation from such high-boiling and/or costly solvents is energy-intensive and lowers the yield, even when combined with immiscible, low-boiling solvents.[5] Herein, we describe an organic–inorganic nanocomposite catalyst that converts fructose selectively (> 80 %) into HMF in a flow reactor, while eliminating separation issues and the need for environmentally unfriendly solvents. We obtain the highest reported HMF yields to date in a monophasic, readily separable solvent, avoiding the undesirable use of salts.

Our previous studies of fructose dehydration to HMF employed silicas and organosilicas with pore-directed alkylsulfonic acid groups as heterogeneous catalysts.[6] Ordered mesoporous silica-based catalysts were found to be more selective and robust than catalysts with similar chemical compositions but non-ordered pores. Upon incorporating bifunctional organosilanes containing both alkylsulfonic acid groups and thioether/sulfone groups to promote fructose tautomerization to the desired furanose tautomers, we observed further, modest selectivity improvements relative to propylsulfonic acid-functionalized silicas. We hypothesized that in order to achieve HMF selectivities comparable to those reported with homogeneous systems, the microenvironment throughout the pore channels (rather than just localized near the active sites) should promote fructose tautomerization. Soluble organic polymers have been reported to act as pseudo-solvents, encapsulating reactants in a local microenvironment that can be favorably tailored for catalysis.[7] Furthermore, the pores of acid-functionalized ordered mesoporous materials (both silicas and organosilicas) are large enough to accommodate such macromolecules.[8]

Poly(vinylpyrrolidone) (PVP), a polar aprotic polymer, was intercalated by incipient wetness impregnation into the pores of unmodified SBA-15 silica (Scheme 1), as well as into three propylsulfonic acid-functionalized silica catalysts (pSO_3H-SBA-15, pSO_3H-MCM-41, and a non-ordered mesoporous silica, pSO_3H-SS). Polymer intercalation is promoted by the dissolution and disentanglement of the PVP globules in water, and results in an extended hydrogen-bonded network between the pyrrolidone carbonyl groups and the surface



Scheme 1. Intercalation of PVP into the ordered mesopores of acid-functionalized silica by incipient wetness impregnation.

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[*] R. Alamillo,[+] Dr. A. J. Crisci,[+] Dr. J. M. R. Gallo, Prof. J. A. Dumesic
Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI 53706 (USA)
E-mail: dumesic@engr.wisc.edu
Dr. A. J. Crisci,[+] Prof. S. L. Scott
Department of Chemistry & Biochemistry, University of California Santa Barbara, CA 93106-9510 (USA)
Prof. S. L. Scott
Department of Chemical Engineering, University of California Santa Barbara, CA 93106-5080 (USA)

[+] These authors contributed equally to this work.

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silanols of the silica.[9] To suppress leaching, the intercalated PVP was then cross-linked[10] using benzoyl peroxide and irradiation. Residual soluble polymer was removed from the support by Soxhlet extraction with water.

The polymer content of PVP-SBA-15 was 16 wt %, as determined by thermogravimetric analysis (TGA). Signals characteristic of the polymer[11] and the anchored propylsulfonic acid sites[6a] were observed in the ^{13}C CP/MAS NMR spectrum (Supporting Information, Figure S1 a). Intercalation caused the surface area, pore diameter, and pore volume of SBA-15 to decrease by ca. 50 %, 49 %, and 65 %, respectively (Table S1), which indicates a partial obstruction (but not collapse) of the ordered pores.[12] The *p6mm* pore structure of PVP-SBA-15 remains clearly visible by SEM (Figure 1), and by XRD (Figure S2). In addition, the particle morphology and surface texture of PVP-SBA-15 are indistinguishable from those of unmodified SBA-15, and no polymer aggregates were observed by SEM. In the STEM images, the pore channels become obscured upon polymer intercalation, owing to the decrease in contrast relative to the unfilled pores (Figure S3). Similar results were obtained for pSO$_3$H-SBA-15 and pSO$_3$H-MCM-41.

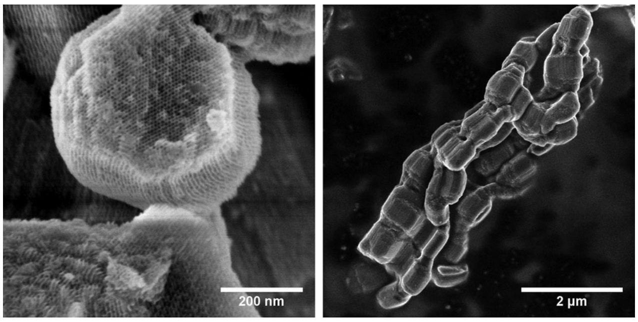

Figure 1. SEM images of the PVP-pSO$_3$H-SBA-15 catalyst at two different magnifications.

Catalytic activity in fructose dehydration was studied in batch mode at 403 K, both before and after impregnation of PVP (Table 1). Each reaction was allowed to proceed until the fructose conversion was ca. 50 %, to enable direct comparisons of selectivity. For each of the PVP-modified catalysts, the HMF selectivity was significantly higher than for the corresponding unmodified catalysts (Table 1). Both of the PVP-modified ordered mesoporous silica catalysts (MCM-41 and SBA-15) achieved HMF selectivities above 80 %. Notably, these selectivities were retained even at high conversion (ca. 85 %). In addition, PVP-pSO$_3$H-SBA-15 operated in a flow reactor (403 K and weight-hourly space velocity of 0.11 h^{-1}) at 50 % conversion achieved 78 % selectivity after 120 h on stream (versus 60 % selectivity for HMF for pSO$_3$H-SBA-15 under similar conditions at the same conversion levels).

Table 1: Batch fructose dehydration catalyzed by unmodified and PVP-modified silica-based materials.[a]

Catalyst	PVP [wt %][b]	Fructose conv. [%]	HMF [%]	Rate (×10^5)[c]
pSO$_3$H-SS	–	43	36	4.3
PVP-pSO$_3$H-SS	8	48	64	2.0
pSO$_3$H-SBA-15	–	48	68	4.0
PVP-pSO$_3$H-SBA-15	17	52	87	3.1
pSO$_3$H-MCM-41	–	45	63	1.5
PVP-pSO$_3$H-MCM-41	16	57	85	1.4

[a] Reaction conditions: unmodified catalyst (50 mg) or PVP-modified catalyst (100 mg), fructose solution (1.5 g, 2 wt %) in THF/H$_2$O (4:1 w/w) at 403 K. [b] Determined by thermogravimetric analysis (TGA). [c] Data given in units of [mol g$_{\text{cat}}^{-1}$ min^{-1}].

Despite the accompanying reduction in accessible surface area, intercalation of PVP does not dramatically impede access to the active sites, as HMF production rates decrease only modestly. We also note that HMF selectivity is unaffected by changes in acid-site accessibility and/or density: catalysts partially neutralized with NH$_4$OH achieved the same selectivity as unmodified catalysts, albeit with longer reaction times required to reach similar conversions.

Both the nature of the functional groups and their location (in relation to the acid sites) are critical to the observed increases in HMF selectivity. Thus, the increase in HMF selectivity relative to unmodified pSO$_3$H-SS was much larger for PVP-pSO$_3$H-SS (28 %) than for unmodified pSO$_3$H-SS in the presence of soluble PVP (8 wt %). Similarly, when pSO$_3$H-SS was intercalated by cross-linked poly(vinyl alcohol) (PVA) instead of PVP, HMF selectivity increased by only 8 %. We infer that the pyrrolidone functional group, which is confined within the silica pores, is responsible for the dramatic increase in HMF selectivity.

HMF is formed preferentially from the fructofuranose tautomers (α- and β-),[13] which are favored over the pyranose forms in polar aprotic solvents. For example, in water at 303 K, 29 % of the fructose exists in the furanose forms,[13] whereas in *N*-methylpyrrolidone (NMP, a molecular analog of PVP), this fraction increases to 69 %. The influence of NMP (and, presumably, by analogy, PVP) on the fructose tautomer distribution also depends upon the pyrrolidone concentration. For aqueous fructose solutions (2 wt %), the presence of either 10 wt % NMP or 10 wt % PVP had no observable effect on the tautomer distribution at RT, as judged by ^{13}C NMR spectroscopy. (We note that 10 wt % is the maximum solubility of NMP and PVP in the 4:1 THF/H$_2$O solvent mixture selected as a single-phase solvent system for use in our flow reactor).[6b]

The tautomer distribution of pore-confined fructose was assessed for PVP-SBA-15. The modified silica was saturated with a 2 wt % fructose solution in 4:1 THF/H$_2$O at 298 K, and the furanose fraction was observed by solid-state ^{13}C HR-MAS NMR spectroscopy. Relative to the 33 % furanose forms seen in solution, an increase to 44 % was observed for the PVP-SBA-15. The furanose fraction is expected to be even higher at elevated temperatures. In contrast, unmodified SBA-15 had no discernible effect on the tautomer distribution. We infer that PVP acts as a polar aprotic solvent in the confined microenvironment of the mesopores, increasing the stability of the furanose tautomers and resulting in increased HMF selectivity relative to catalysts without PVP modification.

To assess the stability of the new catalysts, cross-linked PVP-SBA-15 was exposed to batch reaction conditions, but in the absence of fructose. The solid was then recovered, washed, dried and re-exposed. After four cycles, the PVP loading remained constant, as determined by TGA (Figure S4). Conversely, PVP intercalated without cross-linking leached quickly into solution, and was lost after just one cycle. In the presence of fructose under batch reaction conditions, recycled pSO_3H-SS lost activity with each reuse, whereas PVP-pSO_3H-SS showed stable activity (Figure 2). The PVP-modified catalyst experienced only a minor decrease in selectivity after the first use (Figure S5).

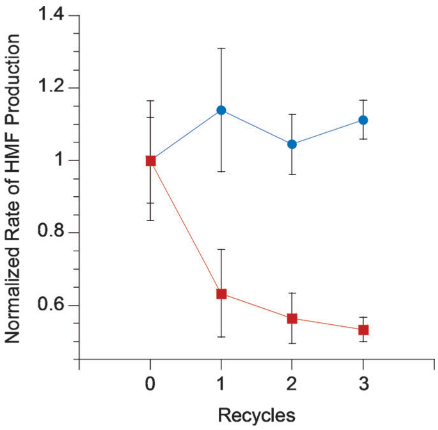

Figure 2. Effect of pSO_3H-SS (red) and PVP-pSO_3H-SS (blue) catalyst recycling on HMF production rate at 403 K in 4:1 THF/H_2O (w/w). After each reaction, the catalyst was recovered, washed, dried, and reused.

Based on our prior studies, silica-based catalysts deactivate by hydrolysis and subsequent leaching of the propylsulfonic acid sites.[6b] Deactivation rates were quantified by continuously measuring catalytic activity in a flow reactor. Pseudo-first-order deactivation rate coefficients for pSO_3H-SS and pSO_3H-SBA-15 were previously measured to be $0.152\,h^{-1}$ and $0.124\,h^{-1}$, respectively, at 403 K.[6b] Under similar conditions, the deactivation rate coefficients for PVP-pSO_3H-SS and PVP-pSO_3H-SBA-15 are $0.088\,h^{-1}$ and $0.050\,h^{-1}$, respectively. Thus, intercalation of PVP into the pores of SBA-15-based catalysts leads to significant stabilization.

In summary, although acid-functionalized ordered mesoporous silica catalysts show high selectivity for HMF in the absence of PVP,[6] incorporation of PVP causes the selectivity to approach levels previously achieved only with ionic liquids and high-boiling aprotic organic solvents. The high concentration of pyrrolidone groups in the confined space of the nanochannels favors the furanose tautomers of fructose. As HMF is derived from these tautomers, a corresponding increase in selectivity occurs. Unlike other selective methods for HMF production, the solid catalyst is easily recovered from the reaction mixture and the product is readily isolated from the low-boiling, single-phase solvent system. Thus, the reaction environment within the catalyst has been designed to favor the desired product. Modification of inexpensive solid catalysts with functional polymers may have more general applications. For example, PVP is known to stabilize nanoparticles; thus, PVP-SBA-15 may function as a support for catalytically active nanoparticles, or as a vehicle for therapeutic nanoparticles used in drug delivery.

Experimental Section

SBA-15,[14] pSO_3H-SBA-15,[6a] and pSO_3H-MCM-41[15] were synthesized according to modified reported procedures; pSO3H-SS was purchased from Silicycle Inc (Quebec). To prepare the nanocomposites, each silica was modified with PVP using an incipient wetness method. Subsequently, the intercalated polymer was cross-linked by photoinitiated homolysis of benzoyl peroxide. Catalytic performance in fructose dehydration was examined in a batch reactor. The PVP loading was optimized for the highest selectivity for HMF. Details on catalyst preparation, characterization, and activity testing can be found in the Supporting Information.

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