Tunable catalysts for solvent-free biphasic systems – Pickering Interfacial Catalysts over amphiphilic silica nanoparticles

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Introduction

Clean and efficient conversion of biobased raw materials into fine chemicals and transportation fuels is a key challenge in the design of biorefineries. Typical organic syntheses using fatty derivatives and polyols usually encompass the reaction of immiscible reagents. To avoid the use of surfactants and solvents, the development of amphiphilic particles providing concomitant Pickering emulsification and catalytic properties would be highly desirable.[1] Here we show one of the rare examples of such a concept using the solvent-free acid-catalyzed acetalization reaction of immiscible long-chain fatty aldehydes (n>9) with ethlylene glycol (EG) as an example, for which few literature is available. To this aim, we rationally-designed amphiphilic silica nanoparticles functionalized with propylsulfonic and alkyl groups with variable chain lengths (Figure 1A). The sulfonic acid groups served not only as active sites, but also as hydrophilic moieties for tuning the amphiphilic properties of the particles.

Materials and Methods

The amphiphilic silica nanoparticles were prepared by a co-precipitation method in three steps: (1) co-condensation of tetraethyl orthosilicate (TEOS) with organosilanes and (3-mercaptopropyl)trimethoxysilane with a molar ratio of 16:4:1 and a variable carbon length Cn (n=3, 8, 18, i.e. trimethoxy(propyl)silane, trimethoxy(octyl)silane, trimethoxy(octadecyl) silane) under alkaline conditions using ethanol and water as co-solvents; (2) oxidation of thiol (-SH) groups into sulfonate ($-SO_3X$, X= NH_4^+, Na^+) using aqueous H_2O_2; and (3) acidification to obtain sulfonic acid functionalized particles. The mean particle size was in each case 166, 153 and 310 nm with effective Cn/sulfonic molar ratios of 0.1, 5.5 and 7.9, respectively. The density of alkyl moieties was 0.2, 11.0 and 20.3 groups/nm^2 for SiNP_SO3H_C3, SiNP_SO3H_C8, and SiNP_SO3H_C18, respectively, whereas the density of SiOH groups was in each case 12.7-14.6, 14.3-23.2 and 33.5-51.2 groups/nm^2 according to complementary information from TGA and quantitative ^{29}Si solid state NMR.

Results and Discussion

The catalytic activity of the SiNPs was tested in the biphasic acetalization reaction of fatty C_{12}-aldehyde with EG at 60 °C for 1 h under low excess of EG. Benchmark catalysts were also tested, including heterogeneous HZSM-5 and a H-Resin. Remarkably higher turnover numbers (TON) to the acetal were achieved on SiNP_SO3H_C8 and SiNP_SO3H_C18, reaching values about 1602 and 1850, respectively (Figure 1). The activity of SiNPs was also assessed in comparison to *p*-toluenesulfonic acid (PTSA), a commonly used homogenous acid catalyst for biphasic reactions. PTSA was indeed more active (TON=750) than SiNP_SO3H_C3 (295), but less than SiNP_SO3H_Cn (n =8 or 18, TON > 1500) (Figure 1B). A devoted optical microscopy study revealed that a stable C_{12}-aldehyde/EG emulsion was generated under SiNP_SO3H_C8 and SiNP_SO3H_C18, while no droplets were observed under PTSA after 10 min reaction. Likewise, SiNP_SO3H_C3 was unable to form stable droplets due to its patent hydrophilic behavior, showing a fast phase separation.

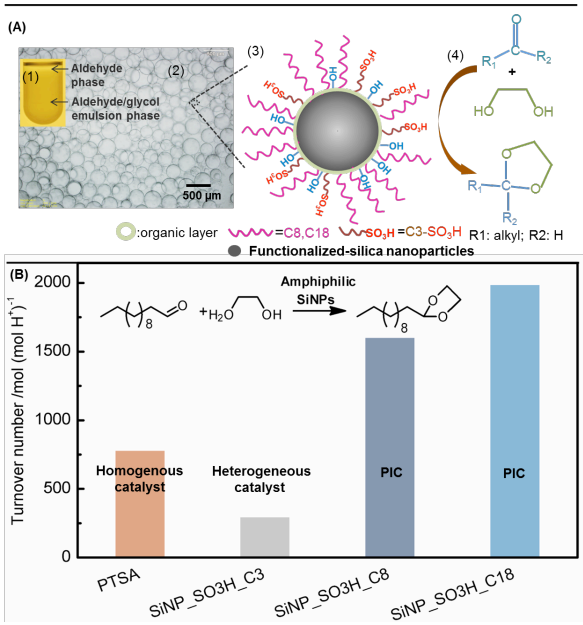

Figure 1. (A) Biphasic acetalization reaction catalyzed by amphiphilic silica nanoparticles under Pickering Interfacial Catalysis (PIC); (A1) Picture of the solution using 50 v/v.% EG and 50 v/v.% aldehyde and 1.7 wt.% SiNP_SO3H_C18 after homogenization at 60 °C for 15 min, (A2) Typical optical micrographs of the emulsions, (A3) scheme of amphiphilic silica nanoparticles located at the aldehyde/EG interface, (A4) scheme of the catalytic action of sulfonic acid sites nearby hydrophobic chain on acetalization of aldehyde by EG; (B) turnover numbers for acetalization of C_{12}-aldehyde by EG over PTSA, SiNP_SO3H_C3, SiNP_SO3H_C8, and SiNP_SO3H_C18; Reaction conditions: 60 °C, C_{12}-aldehyde (0.1 mol), EG (0.2 mol), catalyst amount adjusted to provide the same H^+ equivalents (9.5 µmol, particle loading ca. 1.7 wt.% for the solid samples).

Significance

We demonstrated that amphiphilic silica nanoparticles with a suitable balance between hydrophilic and hydrophobic properties can behave as efficient interfacial catalysts for the acetalization of fatty aldehydes with EG by stabilizing Pickering emulsions. The catalysts could be recovered by centrifugation after reaction and reused with no appreciable deactivation after several consecutive runs.

References

1. Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E. *Science* **2010**, *327*, 68.