Synthesis of ethyl lactate in high yields with mesoporous SnSi mixed oxide catalysts prepared by the aerosol-assisted sol-gel process

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An aerosol-assisted sol-gel method is used to prepare mesoporous tin silicate catalysts which exhibit record activity in the synthesis of ethyl lactate from dihydroxyacetone and ethanol. The method is based on the formation of an aerosol from a solution of precursors and surfactant. During the fast drying of the droplets, the surfactant self-assembles and the Sn-silica matrix is formed by polycondensation reactions. After calcination, the resulting material is composed of a true Sn-Si mixed oxide in the form of spherical microparticles with calibrated mesopores of 5-6 nm. Tin species are incorporated in the silica network, mainly in the form of single sites. The catalyst is shown to be recyclable and truly heterogeneous, as it can be reused for several cycles and as it does not leach.

1. Scope

Recently, growing efforts are being devoted to transform glycerol and its derivatives into valuable chemicals employing various catalytic processes. One attractive synthesis procedures is the synthesis of ethyl lactate from dihydroxyacetone, which can itself be easily obtained by partial oxidation of glycerol. In order to achieve high yield of ethyl lactate a catalyst displaying a combination of Lewis and mild Brønsted acid sites is required. Sn-doped silica catalysts, possessing the good combination of acid sites, have been reported as active catalysts for this reaction.[1] Also, it was observed that the reduced particle size together with the good dispersion of Sn inserted as single site in the silica architecture are key factors to improve activity.

Bottom-up preparation approaches, including sol-gel methods combined with templating strategies, are recognized as a powerful way to obtain tailored mesoporous materials with controlled composition, texture, and surface functionalities.[2] In this case, a key parameter is the homogeneity of the mixed oxide. Isolated sites of Sn oxides in silica catalyse alkyl lactate synthesis.[3] In recent years, an aerosol-assisted sol-gel process has emerged as an innovative, versatile and effective way to produce nanostructured porous catalysts exhibiting new properties and high performances.[4,5] In this synthesis process (Fig. 1), the condensation of the inorganic network occurs during a short drying time, along with the evaporation-induced self-assembly of surfactant molecules serving as sacrificial template. The method allows the formation of spherical particles with calibrated porosity and with a precise control on the composition and homogeneity of complex formulations.[6] The aerosol process can be run in a continuous mode and scaled up relatively easily to industrial scale. Here we show that the aerosol-assisted sol-gel process offers a unique opportunity for the preparation of active and efficient Sn-silicate catalysts.

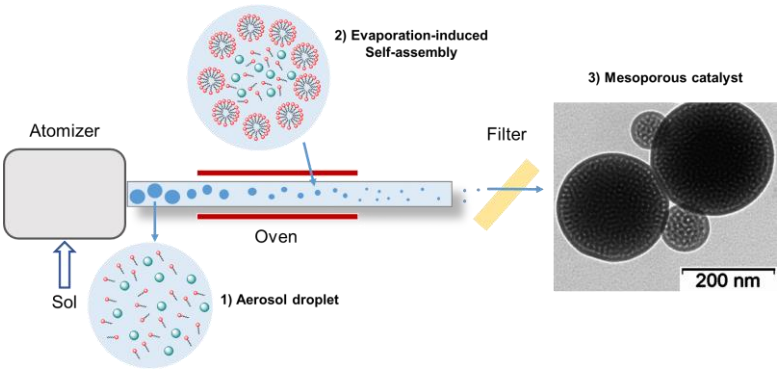

Figure 1. Schematic representation of the aerosol process

2. Results and discussion

A series of Sn-silicate nanoparticles was synthesized taking inspiration from a previously reported method.[4] An ethanolic-aqueous solution of TEOS, Pluronic 123 and tin (IV) chloride was atomized in the form of an aerosol, which was rapidly dried by passing through a quartz tube heated at 350°C. The collected powder

was aged overnight at 80°C and then calcined under static air at 550°C for 6h. Samples are denoted SnSi-X, where 'X' stands for the Si/Sn molar ratio.

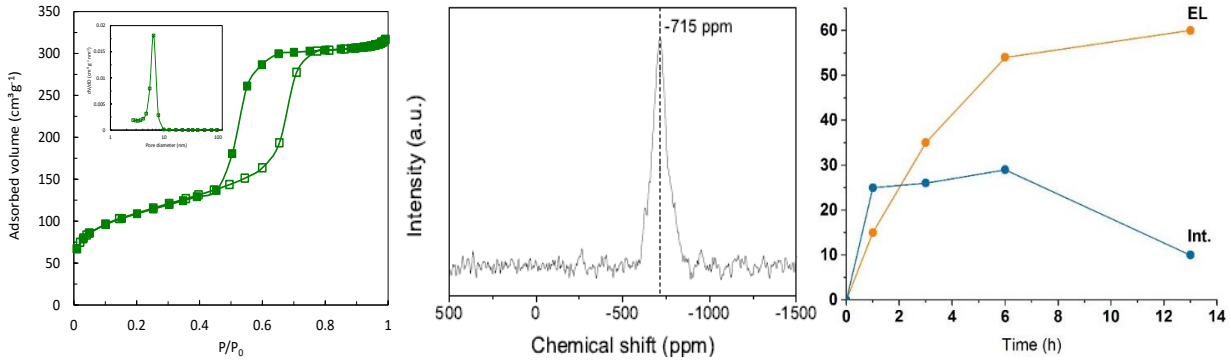

Figure 2. (left) N_2 – physisorption isotherms and pore size distribution, (center) ^{119}Sn-MAS-NMR, (right) Kinetic study on SnSi-74 (a) and SnSi-37 (b). Synthesis of ethyl lactate (50 mg of catalyst, 5 mL of 0.2 M DHA solution in EtOH at 90 °C)

SnSi samples consist of spherical particles of 20-1000 nm exhibiting size-calibrated mesopores of ~5 nm (Fig. 1 left and center). Their spherical shape is a reminiscence of the aerosol droplets and their pores correspond to P123 micelles. Specific surface area and pore volume reach 370 $m^2.g^{-1}$ and 0.48 $cm^3.g^{-1}$ respectively. Microporosity is negligible. SAXS confirms the nanoscale organization of the solid (not shown). Composition was verified with an EDX probe mounted on the SEM. Sn was homogeneously distributed throughout the sample for both catalysts. ^{119}Sn-MAS-NMR showed unambiguously that Sn was in tetrahedral coordination, thus truly incorporated into the silica network (Fig. 2 center). This was also confirmed by DRS (not shown), with a main absorption at 208 nm, indicative of dispersed SnO_x species in tetrahedral coordination, along with only minor contributions of pentahedral (245 nm) and octahedral (280 nm) species.

The new catalysts exhibited very high activity and selectivity in the conversion of dihydroxyacetone to ethyl lactate. The selectivity towards EL is related to the reaction kinetics: it increases over time as the various reaction intermediates are consumed to yield EL (Fig. 2 right). Almost full conversion of DHA to EL (~95% yield) was achieved with SnSi-37 at 90 °C after 13 h of reaction (100 mg of catalyst, 5 mL of DHA 0.2 M in ethanol). Comparison with recently reported very active catalysts[1] was done at lower conversion values: aerosol SnSi catalysts outcompeted these reference catalysts, SnSi-74 displaying the highest TON (127 after 6h). Hot filtration tests demonstrated the absence of leaching, consistently with the true incorporation of Sn in the material framework. Moreover, the catalytic activity was maintained over 3 reaction runs, attesting of the good reusability of the catalysts.

3. Conclusions

Novel mesoporous tin silicates were prepared via an easy, one-pot and continuous mode, using the aerosol-assisted sol-gel process. The new solids display interesting features for catalytic applications such as high surface area, regular mesoporosity and a successful incorporation of isolated Sn within the silica framework. These aerosol-made mesoporous Sn-silicates showed excellent catalytic performance in the conversion of dihydroxyacetone to ethyl lactate. The best catalyst displayed higher turnover number than the reference catalysts previously reported in literature. The catalysts do not leach and truly act in a heterogeneous mode. Moreover, it was successfully used in multiple catalytic cycles thus proving its stability under the selected reaction conditions. The new synthesis technique paves the way to a green and scalable preparation of highly effective heterogeneous catalysts, especially promising in biomass conversion.

References

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