Direct Hydrothermal Synthesis of Mesoporous Sn-SBA-15 and Catalytic Application for the Synthesis of Nopol by Prins Condensation

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Introduction

Incorporation of tin within the silica framework of many micro- and mesoporous molecular sieves that are reported so far is to impart in these materials interesting properties that make them useful as sensors, electrodes and catalysts [1-3]. Highly acidic conditions of preparation of Si-SBA-15 normally prohibit the incorporation of Sn due to the high solubility of their precursors. It is still a challenge to find a one-step route of metal incorporation into SBA-15 in order to increase the acidity without changing its structural order or increasing the complexity of the synthesis. We report here an optimized procedure for the synthesis of Sn-SBA-15 materials in which Sn^{4+} ions are probably part of the mesoporous structure of silica. A direct synthetic route for the preparation of Sn-SBA-15 materials with Si/Sn ratios ranging from 100 to 10 under milder acidic conditions were made through an adjusting the molar H_2O/HCl ratio which indicate the formation of Si-O-Sn linkages that lead to isomorphous substitution of Si^{4+} by some Sn^{4+} ions. By adjusting the H_2O/HCl molar ratio to 796, Sn gets incorporated into the lattice of SBA-15 at a low Sn concentration, which is evidenced by XRD, TEM, UV and ^{29}Si MAS NMR spectroscopic data. The method of preparation, H_2O/HCl ratio, and the Si/Sn ratio influence the type of Sn species formed in these samples. The Sn^{4+} ions could assume a tetrahedral coordination and be part of the hexagonal structure of silica, although at a low concentrations in Sn-SBA-15 [4]. The resulting material was used for the synthesis of nopol by the Prins condensation of β-pinene and paraformaldehyde. Nopol is an optically active bicyclic primary alcohol used in the agrochemical industry to produce pesticides and also in the manufacture of soaps, detergents, polishes and other household products.

Materials and Methods

An optimized procedure for the synthesis of Sn-SBA-15 molecular sieves is worked out by changing the H_2O/HCl ratio. The first set of Sn-SBA-15 samples was prepared by using a ratio of 276 (70 mL of 0.29 M HCl), as reported by Vinu et al. [5] with the initial Si/Sn ratios of 100, 80, 60, 40 and 10. The second set of samples was prepared by using H_2O/HCl molar ratio of 796 (70 mL of 0.07 M HCl) with similar initial Si/Sn ratios. The molar gel composition was 1TEOS: 0.01–0.1 SnO_2: 0.016 P123: 0.16–0.46 HCl: 127 H_2O. The resultant solid was filtered, washed, dried at room temperature and calcined at 823 K. The Sn-SBA-15 samples were designated as Sn-A-X, Sn-B-X where A and B refer to the two procedures with different n_{H2O}/n_{HCl} ratios and X denotes the input n_{Si}/n_{Sn} ratio. The samples are characterized by powder XRD, N_2 adsorption, TEM, UV-visible and ^{29}Si MAS NMR spectroscopic techniques.
The reactions were carried out in the temperature range of 323-383 K in a batch mode in a two-necked round-bottomed flask using β-pinene (5 mmol) and para formaldehyde (10 mmol) with 0.05 g of freshly prepared catalyst. The reaction mixture was analyzed by GC. The catalyst can be reused after washing with acetone and drying at 373 K. We here report our preliminary results on the synthesis of nopol from β-pinene and paraformaldehyde over Sn-SBA-15 and was compared with the SBA-15 and MCM-41. The influence of various reaction parameters such as temperature, time and catalyst amount was studied in detail over Sn-SBA-15 catalysts.

Results and Discussion

Incorporation of Sn in SBA-15 framework is successfully achieved by adjusting the molar ratio of n_{H2O}/n_{HCl} to 796 of the gel. Adjusting the molar n_{H2O}/n_{HCl} ratio without affecting the structural ordering of SBA-15 materials can control the amount of Sn incorporation. An expansion of the lattice (powder XRD), absence of a separate tin oxide-like phase and an increase in mesopore area (low temperature N_2 adsorption) clearly indicate incorporation of Sn in the SBA-15 matrix. The UV–vis DR spectra of calcined Sn–SBA-15 samples show a characteristic absorbance centered around 211 nm, which can be assigned to $O^{2-}\rightarrow Sn^{4+}$ transition, when Sn is in tetrahedral coordination in the framework. Sn–SBA-15 samples prepared by methods A show presence of Sn^{4+} essentially in octahedral coordination. The TEM images of Sn–SBA-15 samples show a well-ordered hexagonal array of mesopores with no individual tin oxide particles are observed at low Sn concentrations. By using a H_2O/HCl molar ratio of 276, SnO_2 agglomerates are formed in the channels or on the external surface. ^{29}Si MAS NMR spectra show the presence of Si in (2Si, 2Sn) *i.e.,* Q2 environment may point to incorporation of considerable Sn^{4+} ions in tetrahedral positions. SBA-15 and Sn-SBA-15 samples were used to catalyze the Prins condensation of β-pinene and para formaldehyde at 363 K in the presence of toluene as solvent. There was no conversion of nopol below 323 K. Above 343 K, the rate multiplies to reach a very high conversion of nopol (>95%) at 383 K. Conversion and yield to nopol increase with the reaction temperature from 323 to 383 K. The reaction is much faster over Sn-SBA-15 that on SBA-15 and MCM-41. The kinetic studies shows that the Nopol conversion increases with increase in reaction time. We verified that the reaction does not occur in the absence of catalyst and it is not the result of homogeneous catalysis by leached elements. The nopol conversion increases with an increase in catalyst amount, which may be due to increase in Sn content of the SBA-15 samples. No loss of activity was observed after 3 runs and the catalyst activity is restored. The samples prepared under method B leads to a strong acidic character than by methods A, which is supported by TPD. There is, thus a good catalytic effect of Sn on the reaction, presumably due to the presence of acid sites of medium strength. The appearance of strong acidic property is attributed to a high dispersion of Sn atoms at the atomic level in the SiO_2 lattice.

References

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