Nopol synthesis over Sn-MCM-41
The effect of solvent and Sn precursor

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Introduction

Nopol is an unsaturated alcohol useful for the synthesis of fragrances, pesticides and household products [1]. It has been traditionally obtained by condensation of β-pinene and paraformaldehyde at high temperatures or using homogeneous Lewis acid catalysts [2]. Recently, heterogeneous catalysts: $FePO_4$, Sn-MCM-41 and Zn-Al-MCM-41, have been reported for nopol synthesis under mild conditions [3-5]. $FePO_4$ (4 h, CH_3CN) and Sn-MCM-41 (1 h, toluene) showed the highest nopol yield (>98 %). Solvent effect on nopol yield was previously reported over $FePO_4$ [3]. However, to the best of our knowledge the effect of solvent type on nopol yield over Sn-MCM-41 has not been published yet. In this regard, here we report on catalytic activities of Sn-MCM-41 to obtain nopol using solvents of different polarities. Sn-MCM-41 materials were prepared by chemical vapor deposition (CVD) using two Sn precursors, $SnCl_4$ and $SnCl_2$.

Materials and Methods

Samples of Sn-MCM-41 materials coded: $SnCl_4$-M16 and $SnCl_2$-M113 (the code number indicates μmol Sn/g catalyst as determined by atomic absorption) were employed for catalytic tests. $SnCl_4$-M16 was synthesized following the procedure previously described [3], and using 160 μmol $SnCl_4$ /g MCM-41; $SnCl_2$-M113 was synthesized by treating 0.5 g of MCM-41, packed in a tubular reactor, with 320 μmol of $SnCl_2$ at T < 450ºC in flowing N_2 (50 mL/min) and then in flowing air. Finally, the solid was pretreated the same way as $SnCl_4$-M16. Catalysts were characterized by atomic absorption, XRD and UV-vis. Reagent grade solvents without further treatment were used in catalytic tests. Reaction products were analyzed by GC and dodecane was used as internal standard.

Results and Discussion

XRD analysis of $SnCl_4$-M16 and $SnCl_2$-M113 indicate that they are mesoporous materials; after $SnCl_2$ deposition, peak intensity decreased, while the opposite was observed when $SnCl_4$ was the Sn source. It was observed that the amount of Sn deposited on $SnCl_4$-M16 was about one tenth of the initial amount. On the other hand, as can be observed in figure 1, UV-VIS spectra of $SnCl_2$-M113 showed a well defined broad band attributable to both single and polymeric Sn hexacoordinated species while $SnCl_4$-M16 exhibited a less defined band, probably due to its low Sn content.

Table 1 shows that the use of protic solvents ($47< E_T(30)< 63$) such as methanol, isopropanol, ethanol and butanol with $SnCl_4$-M16 leads to very low catalytic activities. $E_T(30)$, is an empirical solvatochromic parameter based on spectroscopic measurements that has been widely used to measure solvent polarity [6]. β-pinene conversion and nopol selectivity increased when a dipolar aprotic ($40 < E_T(30) < 47$) solvent such as tert-butanol was used.

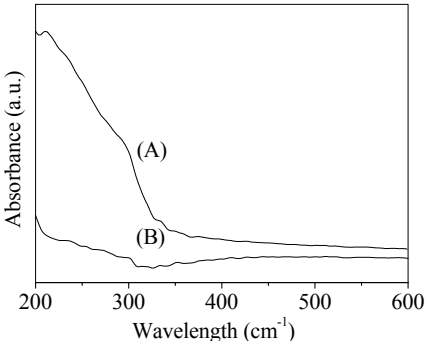

Figure 1. UV-VIS spectra of synthesized materials (A) $SnCl_2$-M113, (B) $SnCl_4$-M16

MEK and CH_3CN lead to larger selectivities, and apolar aprotic solvents ($30<E_T(30)<40$) to higher β-pinene conversions.

The effect of polarity on nopol yield may be related to reactant solubility. For example, paraformaldehyde is insoluble in alcohols and ethers. On the other hand, it is important that the solvent does not donate hydrogen bonds.

Finally, in agreement with our previous report [3], $SnCl_2$-M113 which has the highest tin loading, exhibited the lowest catalytic activity.

Table 1 Catalytic activity of $SnCl_4$-M16 ($SnCl_2$-M113)

Solvent	%Conversion	%Selectivity	$E_T(30)$, Kcal/mol	Nature
Toluene	92.8 (64.5)	84.2 (74.6)	33.9	Apolar aprotic
Ethyl acetate	86.6 (73.5)	86.5 (82.5)	38.1	Apolar aprotic
MEK	75.9	97.1	41.3	Dipolar aprotic
Tert-butanol	45.2	89.7	43.3	Dipolar aprotic
Acetonitrile	40.6 (43.1)	95.1 (92.2)	45.6	Dipolar aprotic
Methanol	5.6	0	55.4	Protic

Procedure: 0.25 mmol of β-pinene, 0.5 mmol paraformaldehyde, 12.5 mg of catalyst, 0.5 ml of solvent, 80°C, 1 h.

Significance

Dipolar aprotic solvents lead to high nopol selectivities while apolar aprotic solvents, toluene and ethyl acetate, give high β pinene conversions. $SnCl_2$ appears to be an alternative Sn source for the synthesis of Sn-MCM-41 materials with the advantage of being easier to handle compared to $SnCl_4$.

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