Nopyl acetate synthesis over tin-containing mesoporous materials

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Introduction

Esters are used as precursors or additives for a variety of perfumes and flavours, pharmaceuticals, agrochemicals, and polymers [1]. Nopyl acetate is an artificial fragrance compound with a fruity odor of fresh wood which is not present in nature. It is used in the preparation of soaps, detergents, creams, lotions and perfumes. This ester is prepared by the carbonyl-ene reaction of β-pinene and paraformaldehyde with subsequent acetylation of the intermediary nopol with acetic anhydride (Figure 1) [2]. Tin modified mesoporous materials (MCM-41, SBA-15) could be attractive alternatives to homogeneous catalysts, especially with voluminous organic molecules like nopol. This work aims to discuss the synthesis and characterization of Sn-MCM-41, Sn-SBA-15 and Sn-SiO_2, as well as catalytic performance in the esterification of nopol with acetic acid (HAc) and acetic anhydride (Ac_2O).

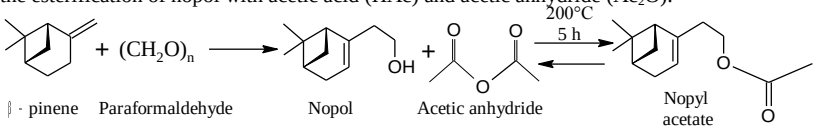

Figure 1. Nopyl acetate synthesis from β – pinene. [2]

Materials and Methods

MCM-41, SBA-15 and SiO_2 were synthesized according to Grün *et al.*, Shah *et al.* and González *et al.* respectively. Sn-containing materials were produced by incipient wetness impregnation. The esterification reaction was performed in a 25 mL three-neck round-bottom flask, coupled to a condenser. Catalyst loading was fixed at 3.7 mg/mL, 10 mL of nopol/toluene solution (0.25 M) was used with acetic acid (99.5 %) and acetic anhydride (98.5 %) at a 6:1 and 3:1 acid – anhydride: alcohol ratio. The reaction mixture was heated at 80 °C and stirred at 750 rpm. Samples were analyzed by GC.

Results and Discussion

Nopol conversion in presence of acetic acid was highest over Sn-SBA-15 (19 %), followed by 15 % using no catalyst, Sn-SiO_2 (10 %) and Sn-MCM-41 (7 %). In presence of acetic anhydride substrate conversion over Sn-SiO_2 reaches 75 % at 60 min compared to 58 % in absence of catalyst, 48 % over Sn-MCM-41 and 45 % using Sn-SBA-15. Nopyl acetate selectivity is above 98 % at 60 min through 180 min over all materials and no catalyst. Best ester selectivity in presence of acetic acid was obtained over Sn-MCM-41 and blank reaction (100 %), followed by Sn-SiO_2 (83 %) and Sn-SBA-15 (78 %). Acetic anhydride promotes a faster nopol conversion and ester formation than acetic acid. Pore volume influences catalyst performance in presence of acetic acid, as most significant substrate conversion over Sn-SBA-15 (19 %) with highest pore volume (0.243 cm^3/g), resulted at 1440 min.

Table 1. Structural properties of synthesized materials

Material	Sn (%)	BET surface area (m^2/g)	Total pore vol. (cm^3/g)
MCM-41	0	596.15	0.334
Sn-MCM-41	0.39	575.83	0.211
SBA-15	0	530.64	0.275
Sn-SBA-15	0.4	470.46	0.243
SiO_2	0	433.77	0.162
Sn-SiO_2	0.31	363.58	0.124

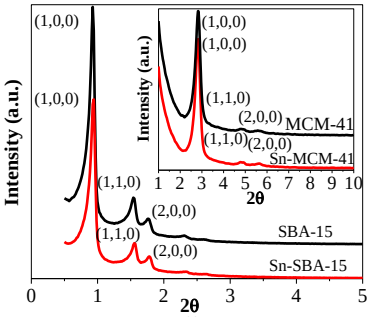

Figure 2. X-ray diffraction patterns.

Table 2. Esterification of nopol catalyzed by tin-containing materials

Entry	Catalyst	HAc (mmol)	Ac_2O (mmol)	Time (min)	X_{nopol} (%)	$S_{nopyl\ acetate}$ (%)
1	Blank	-	7.5	60	58	100
2	Blank	-	7.5	120	87	100
3	Blank	-	7.5	180	95	98
4	Blank	15	-	1440	15	100
5	Sn-MCM-41	-	7.5	60	48	100
6	Sn-MCM-41	-	7.5	120	82	100
7	Sn-MCM-41	-	7.5	180	94	100
8	Sn-MCM-41	15	-	1440	7	100
9	Sn-SBA-15	-	7.5	60	45	100
10	Sn-SBA-15	-	7.5	120	82	100
11	Sn-SBA-15	-	7.5	180	94	100
12	Sn-SBA-15	15	-	1440	19	78
13	Sn-SiO_2	-	7.5	60	75	100
14	Sn-SiO_2	-	7.5	120	88	100
15	Sn-SiO_2	-	7.5	180	98	100
16	Sn-SiO_2	15	-	1440	10	83

Reaction conditions: nopol/ toluene solution 0.25 M (10 mL), 80 °C, 750 rpm, catalyst (3.7 mg/mL).

Significance

Sn-SiO_2 exhibits best catalytic performance for nopyl acetate synthesis in presence of acetic anhydride. Sn-SBA-15 displays moderate substrate conversion (19 %) and high ester selectivity (78 %) with acetic acid. Acetic anhydride is a more effective esterifying agent than acetic acid. The economic feasibility of Sn-SiO_2 and structural properties of Sn-SBA-15 make them potential materials for replacing toxic and corrosive homogeneous catalysts.

Acknowledgments

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References

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