Nopol production over Sn-MCM-41 synthesized by different procedures – Solvent effects

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ABSTRACT

Nopol production over impregnated Sn-MCM-41 under several reaction conditions was examined and compared with Sn-MCM-41 materials previously synthesized by CVD or hydrothermal procedures. The effect of solvent on catalytic activity of Sn-MCM-41 materials and leaching tests of impregnated samples were also assessed. Selected materials were characterized by BET, XPS and H_2-TPR. The effect of solvent was explained in terms of polarity by the solvatochromic parameter, $E_T(30)$, and paraformaldehyde solubility by the Hansen solubility parameter (HSP). Nopol selectivity was enhanced at intermediate values of $E_T(30)$, and the highest β-pinene conversion was obtained when the HSP was close to 18.2 MPa$^{0.5}$. Leaching experiments confirmed that the reaction was truly heterogeneous. Catalysts characterization suggested that tin was deposited as tin oxide nanoparticles, when MCM-41 was modified by CVD and impregnation with stannic and stannous chloride, respectively. Conversely, most of the tin hydrothermally incorporated is presumably present as aggregates in the inner walls of MCM-41 and a small fraction of tin isomorphously substituted silicon atoms.

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1. 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] (Fig. 1). Heterogeneous catalysts such as FePO$_4$, Sn-MCM-41, Zn-MCM-41 and Zn-Al-MCM-41 have been reported for nopol synthesis under mild reaction conditions [3–7]. We have explored the synthesis conditions of tin and zinc supported on MCM-41 for nopol production. Several Sn and Zn loadings on MCM-41 have been obtained by: (i) chemical vapor deposition (CVD) using SnCl$_4$, SnCl$_2$·2H$_2$O, and ZnCl$_2$ as metal precursors in batch and continuous processes [6,8,9]; (ii) wetness impregnation of stannic chloride in aqueous solution [8]; (iii) incipient wetness impregnation of stannous chloride in ethyl acetate solution [10]; (iv) direct hydrothermal synthesis at room temperature, either adding the metal precursor (SnCl$_4$, SnCl$_2$·2H$_2$O, ZnCl$_2$, ZnSO$_4$ and Zn(NO$_3$)$_2$) during the gelation step as a solid or in water or ethanol solutions and with or without pH adjustment [6,9,11]. The textural and physicochemical properties of the synthesized materials depend on the synthesis procedure, i.e., pH adjustment at 11.6 by direct hydrothermal synthesis is fundamental to obtain well ordered hexagonal mesoporous arrays and specific BET surface areas above 1000 m^2 g^{-1} [11].

Usually, nopol selectivity above 80% has been obtained over 0.28–0.43 wt.% Sn-MCM-41 prepared either by CVD of stannic chloride [6,8], hydrothermal synthesis with pH control [11] or incipient wetness impregnation of stannous chloride [10]. β-Pinene conversion depends on reaction conditions; for instance, using 0.25 mmol β-pinene, 0.5 mmol HCHO, 6 mg catalyst, 0.5 mL toluene at 90 °C, the conversion is about 47 ± 5% after 30 min reaction. This conversion doubled by increasing four times the catalyst concentration under similar reaction conditions [10]. The effect of reaction conditions on β-pinene conversion and nopol selectivity has been evaluated over CVD synthesized Sn-MCM-41 samples using turpentine as β-pinene source [12] and over hydrothermally synthesized materials [13]. At temperatures lower than 90 °C, nopol selectivity is low probably owing to slow paraformaldehyde decomposition into HCHO required for this reaction [14]. Furthermore, byproducts from β-pinene and nopol were detected at temperatures above 90 °C. The best temperature reported for nopol production over Zn–Al-MCM-41 has been 90 °C [7]. Nopol selectivity and β-pinene conversion over Sn-MCM-41 synthesized by hydrothermal procedures were 90% and 56%, respectively [13]. The solvent effect on nopol production has been studied over materials synthesized by CVD [15], FePO$_4$ [4] and Sn-MCM-41 [5]. Corma and Renz tested nitriles with different carbon lengths as solvents [5]; in butyronitrile 93% β-pinene conversion and 94% nopol selectivity (T > 110 °C, 8 h) were obtained. We have found that solvents such as ethyl acetate and methyl ethyl ketone lead to higher nopol selectivity (92%) than toluene (84%) but conversion decreased to 79% compared to about 93% in toluene [15]. On the

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other hand, impregnated Sn-MCM-41 synthesized under mild conditions at room temperature and with a small amount of tin precursor is one of the most promising materials for nopol production [10]. The aim of this paper is to examine the activity of Sn-MCM-41 synthesized by impregnation and compare it with analogous materials obtained by CVD or hydrothermally assessing aspects such as the solvent effect, leaching and nature of tin active species.

2. Experimental

2.1. Catalyst synthesis

MCM-41 was synthesized following the procedure reported by Grün et al. [16]. Myristyltrimethylammonium bromide was used as template and $SnCl_4$ and $SnCl_2 \cdot 2H_2O$ as metal precursors. CVD procedures were carried out in a batch mode at 100 °C or continuously at 450 °C with stannic and stannous precursors, respectively, as previously reported [6]. Hydrothermal synthesis at room temperature was carried out either by controlling the pH at 11.6 or without pH adjustment prior to TEOS addition [6,11]. Incipient wetness impregnated materials were synthesized under inert atmosphere [10]; briefly, 3 mL of $SnCl_2 \cdot 2H_2O$ solution in ethyl acetate (28.7 μmol Sn mL^{-1}) was dropwise added to the MCM-41 support (2 g) and mixed. The wet solid was allowed to dry at room temperature for 24 h and calcined at 550 °C for 5 h. The catalysts are coded according to the precursor used ($SnCl_4$ or $SnCl_2$), the synthesis procedure: CVD ($C - x$), hydrothermal with pH control ($H1 - x$), hydrothermal without pH control ($H2 - x$) and impregnation ($I - x$), where x is the metal loading in μmol g^{-1} determined by atomic absorption, i.e., $SnCl_2$-I-24 corresponds to a material prepared using $SnCl_2$ as precursor, by incipient impregnation and contains 24 μmol of Sn g^{-1}.

2.2. Catalyst characterization

Selected samples were characterized by BET at −196 °C, XPS and temperature programmed reduction with hydrogen (H_2-TPR). BET analysis was carried out in a Micromeritics ASAP 2010 instrument. XPS measurements were carried out on a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromatic Al Kα source operated at 15 keV and 150 W. The pass energy was fixed at 40 eV for the detail scans. Charge neutralizer was used to compensate for the charge. All spectra were calibrated using the adventitious carbon 1s peak at 285.0 eV. A Shirley-type background was subtracted from the spectra. The XPS data were processed with the XPSPEAK 4.1 software. Transmission corrected relative sensitivity factor (RSF) values relative to F1s peak from the Kratos element library were used for elemental quantification [17,18]. H_2-TPR was performed using an Autochem 2920 instrument (Micromeritics). Typically, a 50 mg catalyst sample was loaded in a quartz reactor. Fresh samples were calcined in 50 mL min^{-1} flowing 4.6% O_2/Ar up to 500 °C. Pretreatment was continued during 1 h at 500 °C. Then, the gas mixture was switched to pure Ar and the sample cooled at room temperature. Before admitting the reducing mixture (5.1% H_2/Ar, 50 mL min^{-1}) the sample was kept in flowing Ar during 1 h. Samples were reduced by flowing 50 mL min^{-1} of 5.1% H_2/Ar and heating from 100 to 1000 °C at 5 °C min^{-1}. The H_2 uptake was monitored by a thermal conductivity detector (TCD).

2.3. Catalytic tests

Reactions were performed in 2 mL vials covered with inert silicon septa immersed in an oil bath controlled at 80 or 90 °C with an IKA fuzzy controller. The reaction products were identified by gas chromatography using either a GC Varian Star 3400 with a DB-1 capillary column [6,11] or a GC–MS Agilent 7890N with a HP-5 capillary column. Both GCs were equipped with FID detectors and autosamplers. The carrier gas was He (1 mL min^{-1}), the split ratio 100:1. The oven temperature was kept at 90 °C for 1 min and then raised to 160 °C at 10 °C min^{-1} for 7 min. Quantification of nopol and β-pinene was carried out by multi point calibration curves using dodecane as internal standard. Conversion, selectivity and yield were determined using Eqs. (1)–(3), respectively.

$$\% \text{ Conversion} = \frac{(C_{ti} - C_{tf})_{\beta\text{-pinene}}}{(C_{ti})_{\beta\text{-pinene}}} 100\% \qquad (1)$$

$$\% \text{ Selectivity} = \frac{(C_{tf})_{\text{nopol}}}{(C_{ti} - C_{tf})_{\beta\text{-pinene}}} 100\% \qquad (2)$$

$$\% \text{ Yield} = (\%\text{Conversion} * \%\text{Selectivity})/100\% \qquad (3)$$

C_{ti} and C_{tf} correspond to the initial and final concentrations, respectively.

2.4. Leaching tests

Different leaching tests were carried out [19,20]: (i) Catalyst samples were recovered after reaction, exhaustively washed either with acetone, toluene or ethyl acetate at room temperature and dried at 100 °C before being reused (leaching test L1). (ii) The reaction was carried out at conversions below 10%; then the catalyst was separated from the liquid at the reaction temperature by acrodisc® PSF syringe filters. After further addition of paraformaldehyde to the liquid fraction, it was allowed to react up to 24 h (leaching test L2). (iii) The catalyst was separated from the liquid reaction mixture after 0.5, 3 and 6 h reaction. Then, β-pinene (0.41 mmol) and paraformaldehyde (0.82 mmol) were added to the liquid fraction and allowed to react under stirring for additional 21 h (leaching test L3). (iv) Leaching test L4 was performed in order to determine whether any component of the reaction mixture favored leaching of active species. So, the reaction was carried for 2 h in toluene containing the component whose leaching effect was being analyzed (β-pinene, paraformaldehyde or nopol); after removing the catalyst, the missing components required to produce nopol (paraformaldehyde, β-pinene or both) were added to the liquid fraction and the reaction continued for 21 h. The recovered catalyst was washed with toluene, dried and tested again under regular reaction conditions.

3. Results and discussion

3.1. Effect of reaction conditions on nopol yield over SnCl_2-I-24 using toluene as solvent

Fig. 2 shows the effect of $SnCl_2$-I-24 concentration and reaction time on β-pinene conversion and nopol selectivity. When catalyst concentration increased, conversion increased but, selectivity decreased; these trends are similar to those reported for nopol pro-
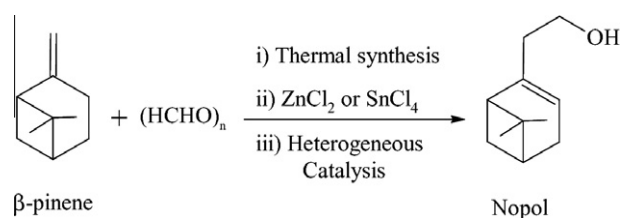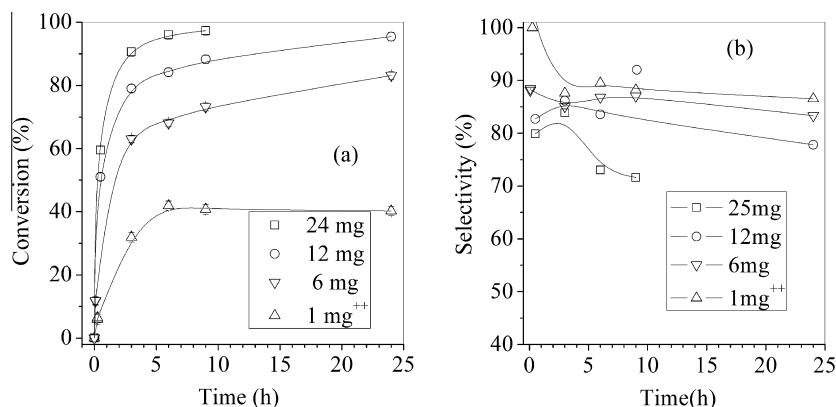

Fig. 1. Nopol production from β-pinene.

Fig. 2. Effect of the amount of SnCl$_2$-I-24 and reaction time on β-pinene conversion (a), and nopol selectivity (b). Reaction conditions: catalyst (1–24 mg), β-pinene in toluene solution 0.46 M (1 mL), paraformaldehyde:β-pinene molar ratio of 2:1, 90 °C. [++]The solution of β-pinene in toluene was 0.25 M.

duction over SnCl$_4$-C-64, using an equimolar ratio of reactants and turpentine as β-pinene source [12]. Also, a similar behavior was observed over SnCl$_2$-H1-43 using pure β-pinene under different reaction conditions [13].

After a 3 h reaction, isomerization products were observed. Also a white solid formed in the upper part of the reactor. Preliminary analysis and simulation of the amount of polymerized formaldehyde at the upper part of the reactor zone was carried out. A first order depolymerization rate reported for an analogue of paraformaldehyde, poly(oxymethylene)diol was assumed [21]. Also the rate of formaldehyde polymerization on glass was taken from Boyles and Toby [22]. As shown in Fig. 3, experimental and simulated paraformaldehyde formation follows a similar trend. Therefore, it is likely that the observed decrease on selectivity is due to formaldehyde vaporization from the reaction mixture which further condenses on the glass wall. β-Pinene conversions and nopol selectivities were similar over SnCl$_2$-I-24 and SnCl$_2$-H2-94 under the same reaction conditions (Fig. 4) [6]. Both, SnCl$_2$-I-24 and SnCl$_2$-H2-94 give better yields than materials prepared by CVD (i.e., SnCl$_4$-C-25 and SnCl$_2$-C-68) likely due to the presence of higher amounts of medium strength acid sites [6,10], which have been associated to selective nopol production [11].

3.2. Solvent effects

Table 1 shows nopol production over SnCl$_4$-C-16 in the presence of solvents having different polarities according to the empir-
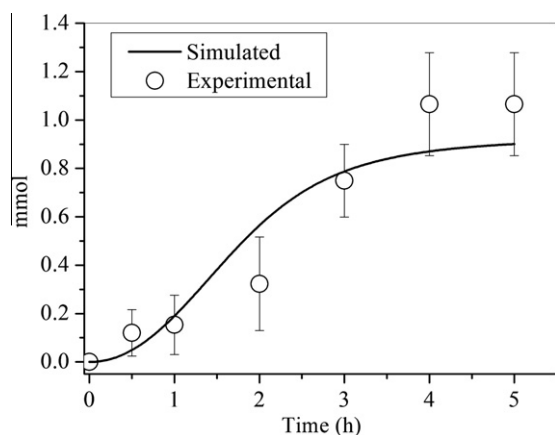

Fig. 3. Estimated profile of vaporized formaldehyde polymerization to paraformaldehyde. Reaction conditions: β-pinene in toluene solution 0.46 M (1 mL), paraformaldehyde:β-pinene molar ratio of 2:1, 90 °C. The estimated amount of polymerized HCHO was determined by weight.
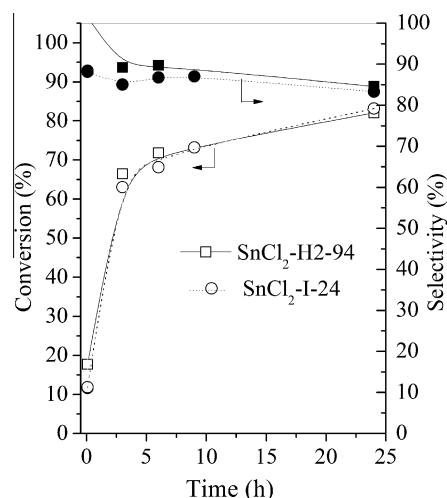

Fig. 4. Comparison of the effect of time on β-pinene conversion (unfilled symbols) and nopol selectivity (filled symbols) over SnCl$_2$-H2–94 (□, ■) and SnCl$_2$-I-24 (○, ●). Reaction conditions: catalyst (6 mg), β-pinene in toluene solution 0.46 M (1 mL), paraformaldehyde:β-pinene molar ratio of 2:1, 90 °C.

ical solvatochromic parameter $E_T(30)$. The first noticeable finding in Table 1 is that almost no activity for nopol production is detected in protic solvents. This is in agreement with previous reports for both uncatalyzed and catalyzed reactions by heterogeneous FePO$_4$; in the absence of solvent a 95% yield was obtained after 4 h by the autoclave procedure [23]. However, in the presence of ethanol as solvent, about half of the typical nopol yield was obtained after 12 h reaction. Using methanol as solvent 2% nopol yield has been reported over mesoporous FePO$_4$ [4]. Therefore, it could be stated that alcohols with protic nature are inactive in nopol production. Conversely, as listed in Table 1, β-pinene conversion over SnCl$_4$-C-16 in the presence of tert-butanol (dipolar aprotic) was seven times larger than in methanol. On the other hand, we have observed better yields in toluene than in acetonitrile, in agreement with previous reports on Sn-MCM-41 [5] and SBA-15 [24] but, contrary to the observations on mesoporous FePO$_4$ [4]. In a similar way, 100% nopol selectivity and 82% β-pinene conversion were reported over FePO$_4$ in acetonitrile as solvent (5 mmol β-pinene, 10 mmol paraformaldehyde, 10 mL acetonitrile, 0.5 g FePO$_4$, 80 °C, 6 h). This selectivity has not been reached under similar conditions over Sn-MCM-41 materials but, it increased (83%) with respect to toluene (73%). Corma and Renz [5] have attributed this effect to the neutralization of non-selective

Table 1
Effect of solvent on β-pinene conversion (X), nopol selectivity (S) and yield (Y) over SnCl$_4$-C-16.[a]

Solvent	X (%)	S (%)	Y (%)	$E_T(30)$ (kcal/mol)[b]	Nature	HSP (MPa$^{0.5}$)[c]
Hexane	68	73	50	31.0	Apolar aprotic	14.8
Toluene	93	84	78	33.9	Apolar aprotic	18.2
Ethyl acetate	87	87	76	38.1	Apolar aprotic	18.2
MEK	76	97	74	41.3	Dipolar aprotic	19.0
Tert-butanol	45	90	41	43.3	Dipolar aprotic	23.2
Acetonitrile	41	95	39	45.6	Dipolar aprotic	24.3
Isopropanol	1	t.a.	t.a.	48.6	Protic	23.6
1-Butanol	7	t.a.	t.a.	49.7	Protic	23.1
Ethanol	0	0	0	51.9	Protic	26.5
Methanol	6	t.a.	t.a.	55.4	Protic	29.5

[a] Adapted and complemented from our previous contribution, Ref. [15]. Procedure: 0.25 mmol of β-pinene, 0.5 mmol of paraformaldehyde, 12.5 mg of catalyst, 0.5 mL of solvent, 80 °C, 1 h. t.a., trace amounts of nopol were observed.
[b] $E_T(30)$, empirical solvatochromic parameter based on spectroscopic measurements.
[c] HSP, Hansen solubility parameter [26]. All parameters were taken from Ref. [27] excepting the value for tert-butanol [28].

catalyst acid sites by the weak basic acetonitrile molecules. However, under homogeneous conditions improved nopol selectivity (93%) was reported for a β-pinene to ZnCl$_2$ molar ratio of 5 in acetonitrile as solvent [25]. This suggests that in the presence of Lewis acid catalysts acetonitrile is a suitable solvent and supports the idea that solvent polarity is crucial for nopol production from β-pinene. Dipolar aprotic solvents such as MEK, tert-butanol and acetonitrile are preferred to synthesize nopol over Sn-MCM-41 obtaining selectivities above 90% (Table 1). Using a less polar solvent such as hexane, conversion is unexpectedly low. At this point, we believe that besides the effect of solvent on catalyst acidity and surface stabilization of reaction intermediates, the solubility of paraformaldehyde should not be ignored. For example, paraformaldehyde is insoluble in alcohols and ethers and nopol yield was too low in polar solvents. A parameter that relates polymer solubility and polarity is the Hansen's solubility parameter (HSP) [26] listed in Table 1 for tested solvents. When a solvent and a polymer show similarities in this parameter (Table 1), a favorable solubility of the polymer on that solvent is expected. Moreover, solvents with similar HSP parameters have similar behavior when a polymer is dissolved. To the best of our knowledge, the HSP of formaldehyde polymer or paraformaldehyde (poly(oxymethylene) glycol, HO(CH$_2$O)$_n$H, with n between 8 and 100) has not been reported, but polyoxymethylene, POM, (more than 100 units of poly(oxymethylene) glycol) which is analogous to paraformaldehyde has a HSP around 20.5 MPa$^{0.5}$ [26]. The similarity of the HSP parameter of toluene, ethyl acetate, MEK, butyronitrile and POM, may be one reason to explain conversion enhancements obtained with these solvents. Also, in agreement with HSP of hexane, β-pinene conversion was lower in hexane than in toluene. Therefore, both parameters, the polarity and the solubility of paraformaldehyde, are needed to explain the effect of solvent on nopol synthesis.

β-Pinene conversion and nopol selectivity on SnCl$_2$-I-24 showed in Table 1 are almost similar to those recently reported on Sn-SBA-15 [24]. Table 2 lists the properties related to polarity and solubility of paraformaldehyde in other solvents different to those listed in Table 1, which have been reported for the heterogeneous catalytic synthesis of nopol. One interesting solvent is butyronitrile since it has a higher boiling point than acetonitrile. Although it is dipolar aprotic, its HSP is close to that observed for toluene and ethyl acetate. A higher conversion is favored with respect to acetonitrile, but selectivity is similar on hydrothermally synthesized Sn-MCM-41 and Sn-SBA-15 [5,24]. On the other hand, when the reaction was carried out over SnCl$_4$-C-64 in the presence of α-pinene instead of toluene [12], β-pinene conversion did not vary (80 ± 2%) in comparison to the reaction carried out with further amounts of toluene (10 mL/mmol β-pinene). This appears to be in agreement with the similarity of HSP to toluene and ethyl ace-

tate (Tables 1 and 2). Taking the polarity and HSP of halogenated solvents, i.e., chloroform and dichloromethane, it appears reasonable that they are used for the acid catalyzed Prins reaction to produce unsaturated alcohols [29]. Depending on the solvent, nopol yield on FePO$_4$ decreases in the following order: dichloromethane ≈1,4-dioxane > cyclohexane [4]. These results may be related to the less expected conversion and selectivity in cyclohexane according to its polarity and lower affinity to paraformaldehyde.

Thus, both solvent polarity and affinity with paraformaldehyde are important to achieve nopol production at comparable rates. Moreover, 90 °C is the preferred temperature to enhance selectivity to nopol. Fig. 5 compares ethyl acetate and toluene as solvents under different conditions. At the initial stage higher conversions and lower selectivities were obtained over SnCl$_2$-I-24 when toluene was used instead of ethyl acetate (Fig. 5) but conversion was higher in ethyl acetate after 6 h. Nopol yield was maintained in the first catalyst reusing (R1), Fig. 6, but, it decreased in the second one (R2).

Table 2
Properties of other solvents reported for nopol synthesis.

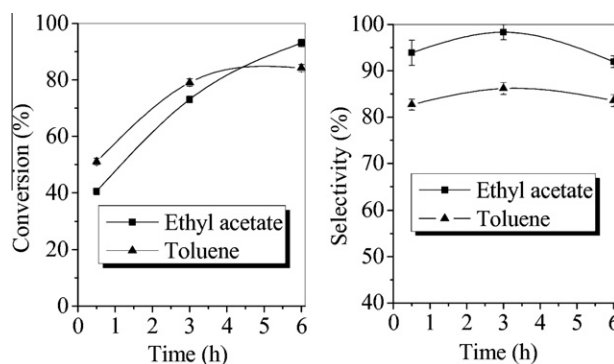| Compound	$E_T(30)$ (kcal/mol)	Nature	HSP (MPa$^{0.5}$)
α-Pinene	n.a.	Apolar aprotic	17.3
Cyclohexane	30.9	Apolar aprotic	16.7
1,4-Dioxane	36.0	Apolar aprotic	19.5
Chloroform	39.1	Apolar aprotic	18.3
Dichloromethane	40.7	Dipolar aprotic	20.8
Butyronitrile	42.5	Dipolar aprotic	20.4

n.a., not available.

Fig. 5. Solvent effect on β-pinene conversion and nopol selectivity over SnCl$_2$-I-24. Reaction conditions: catalyst SnCl$_2$-I-24 (12 mg), β-pinene in ethyl acetate (or toluene) solution 0.46 M (1 mL), (HCHO)x:β-pinene molar ratio of 2:1, 90 °C.
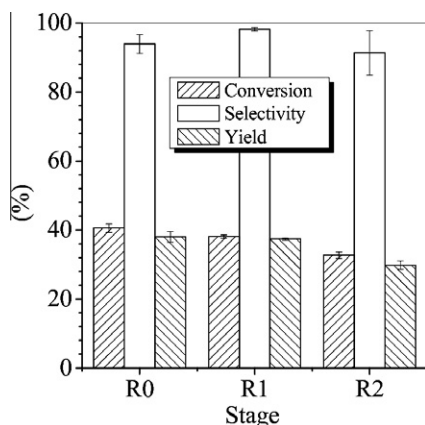
Fig. 6. Reuse of SnCl$_2$-I-24 after ethyl acetate washing. Reaction conditions: catalyst SnCl$_2$-I-24 recovered from batches in Fig. 6 (12 mg), β-pinene in ethyl acetate solution 0.46 M (1 mL), (HCHO)x:β-pinene molar ratio of 2:1, 90 °C, 0.5 h.
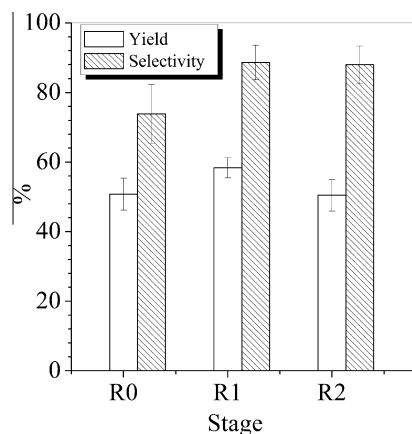

Fig. 8. Nopol yield over fresh and recovered SnCl$_2$-I-24 catalyst. Reaction conditions: catalyst SnCl$_2$-I-24 (6 mg), β-pinene in toluene solution 0.46 M (1 mL), (HCHO)x: β-pinene molar ratio of 2:1, 90 °C.

Fig. 7. Nopol selectivity and yield over fresh (R0) and recovered (R1 and R2) SnCl$_2$-I-24. Reaction conditions: catalyst SnCl$_2$-I-24 (24 mg), β-pinene in toluene solution 0.46 M (1 mL), paraformaldehyde:β-pinene molar ratio of 2:1, 90 °C, 0.5 h. The catalyst was recovered after 0.5, 3, 6 and 9 h, washed with acetone at room temperature and dried before reusing tests. Bars represent the standard deviation.

Fig. 9. Leaching tests over SnCl$_2$-I-24. X: conversion, Y: yield. Regular reaction conditions: catalyst (12 mg), β-pinene in toluene solution 0.5 M (1 mL), (HCHO)x:β-pinene molar ratio of 2:1, 90 °C. After removing catalyst the paraformaldehyde (1 mmol) was added to the filtrated liquid mixture. Blank reaction was carried out without catalyst.

3.3. Leaching tests of SnCl$_2$-I-24 in toluene as solvent

In agreement with previous reusing tests of SnCl$_2$-I-24 in toluene as solvent [10], nopol yield did not vary, within experimental error, after being reused twice (Fig. 7). In contrast, an increase of nopol selectivity and a decrease of β-pinene conversion, which is recovered by calcination, have been observed over other Sn-MCM-41 materials after the first reusing test [8,10]. Calcination procedures have been also successfully used for the activation of Sn-MCM-41 synthesized by hydrothermal procedures at 135 °C after being used in nopol production [5] and in the Baeyer–Villiger oxidation reaction of ketones [30]. Then, organic deposits over Sn-MCM-41 seem to be its main deactivation route. Fig. 8 shows that when the catalyst was reused after its washing with toluene instead of acetone, nopol yield was similar to the value obtained over untreated reused samples. Fig. 9 shows the results of several leaching tests over SnCl$_2$-I-24. Without catalyst, β-pinene conversion and nopol yield were lower than 3% at a reaction time of 24 h; furthermore, results of L2 leaching tests indicate that β-pinene conversion over the catalyst after 2 min of reaction was about 12%. After 24 h reaction of the liquid fraction the conversion was around 15%. The results of leaching test L3 (Table 3) show that after adding more reagents to the reaction mixture and further stirring for 21 h,
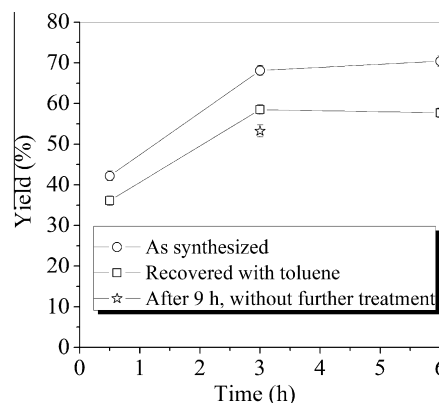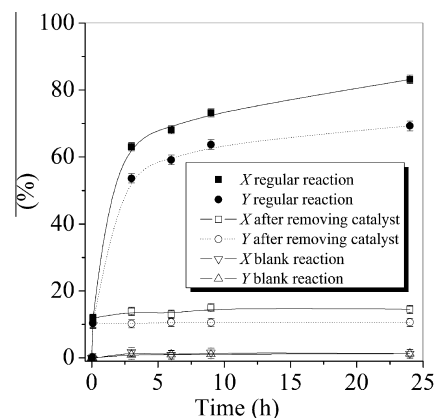
β-pinene and nopol concentrations are very similar to their initial concentrations suggesting the absence of metal leaching from the catalyst.

The results of the leaching test L4 are shown in Table 4. When the reaction was carried out without one of the reactants (runs 2 and 5), β-pinene conversion and nopol yield were insignificant or lower than under regular conditions; when the reactant was nopol (run 8) low conversion was observed. Camphene and limonene were some of the β-pinene isomerization products detected depending on the Sn-MCM-41 synthesis method and reaction conditions [6]; other compounds that may be produced are myrtenol, bornyl formate and nopyl acetate [6]. Allylic oxidation products from β-pinene such as pinocarvone, myrtenol and myrtenal have been reported over Fe–Zn double metal cyanide solid acid catalyst [31]. β-Pinene conversion and nopol yield at 21 h in runs 3, 6 and 9 were similar to the values obtained in the blank reaction test (see Fig. 8). The solids recovered from runs 4, 7 and 10 give similar yields as the fresh catalyst (run 1). These results suggest that β-pinene, paraformaldehyde and nopol do not promote leaching of tin species. Besides, either component can be removed with toluene suggesting that they are not strongly adsorbed on the catalyst. Therefore, the yield decrease under regular reaction conditions after washing with toluene (Fig. 7) could be attributed to adsorbed isomerization byproducts or even polymerization products that

Table 3
Leaching test L3 of SnCl₂-I-24.

Run	Conditions	Time in reaction (h)	$C_{\beta\text{-pinene}} \pm$ 0.0050 (M)	$C_{nopol} \pm$ 0.0020 (M)
1	RR[*]	0.5	0.2285	0.1970
1a	Filtrate of run 1 + Reactants[a]	0	0.6333	0.1837
1b		21	0.6415	0.1923
2	RR[*]	3	0.0977	0.3180
2a	Filtrate of run 2 + Reactants[a]	0	0.5901	0.2951
2b		21	0.5806	0.2953
3	RR[*]	6	0.0737	0.3284
3a	Filtrate of run 3 + Reactants[a]	0	0.5544	0.3042
3b		21	0.5483	0.3027

[*] Regular reaction conditions (RR): catalyst (6 mg), β-pinene in toluene solution 0.46 M (1 mL), paraformaldehyde: β-pinene molar ratio of 2:1, 90 °C. Reaction conditions: for runs 1, 2 and 3 after 0.5, 3 and 6 h of the reaction, respectively.

[a] The liquid was separated from the catalyst and mixed with more β-pinene (0.41 mmol) and paraformaldehyde (0.82 mmol) and stirred 21 h at 90 °C.

might be produced from β-pinene in toluene in the presence of Lewis acid catalysts [32]. Thermogravimetric analysis (TGA) of a re-used SnCl₂-I-24 sample (Fig. 10) shows a weight loss of 12% below 150 °C and an additional 12% weight loss up to 600 °C; this weight loss is about half the value previously reported for SnCl₂-H1-43 [11], which suggests a lower trend to deactivation of SnCl₂-I-24 compared to SnCl₂-H1-43.

3.4. Nature of tin active species for nopol synthesis

According to previous results [6,10,11] the most promising catalysts for nopol production are SnCl₄-C-30, SnCl₂-I-24 and SnCl₂-H1-43. Therefore, samples of these catalysts were characterized by XPS. The survey scans (Fig. 11) of SnCl₂-I-24, SnCl₂-H1-43 and MCM-41 show peaks around 26, 104, 155, 533 and 977 eV that are assigned to O2s, Si2p, Si2s, O1s and oxygen KLL Auger transition, respectively [33]. MCM-41 and SnCl₂-I-24 show a C1s peak around 285 eV that corresponds to adventitious carbon. Peaks at 488 and 496 eV, which are attributed to Sn3d₅/₂ and Sn3d₃/₂, respectively, were only observed in the profile of SnCl₂-I-24. Fig. 12 shows the high resolution spectra of several samples for the regions that correspond to Si2p, O1s and Sn3d. Fig. 12a, exhibits a main signal around 103.8 eV assigned to Si–O–Si of silica network [34] and has also been reported for Si-MCM-41 materials [35]. This signal was deconvoluted into Si2p₃/₂ and Si2p₁/₂ around 103.7 and 104.5 eV, respectively, for MCM-41. The shift of the binding energy of materials prepared by CVD is of the same order; however, the shift to higher binding energy of the SnCl₂-H1-43
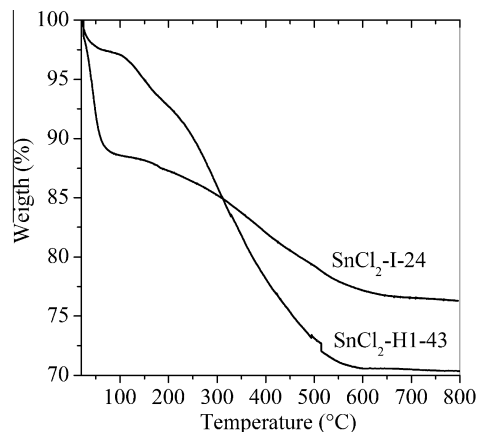

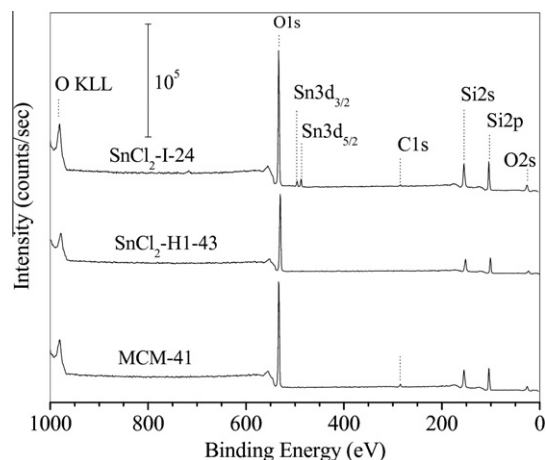**Fig. 10.** TGA analyses of SnCl₂-I-24 and SnCl₂-H1-43 after acetone treatment.

Fig. 11. Wide scan XPS spectra of selected samples.

sample might be associated to the presence of surface Si–O–Sn species, as the presence of Sn weakens the electronic density on the surface of Si because of its higher Pauling's electronegativity, which causes an increase of the binding energy of Si2p [36]. In agreement with this analysis, the T–O–T lattice vibration around 1073 cm⁻¹ in the FTIR spectra of several loaded Sn-MCM-41

Table 4
Effect of paraformaldehyde, β-pinene and nopol on leaching of Sn.[*]

Run	Conditions	Time (h)	% Net β-pinene conversion	% Nopol yield
1	Regular reaction (RR)	3	79.1	68.1
	β-pinene effect on catalyst leaching			
2	RR without HCHO	2	11.3	0
3	Filtrate of run 1 + 0.92 mmol HCHO	21	1.4	1.5
4	RR over catalyst recovered from run 2, washed with toluene and dried	3	80.1	70.5
	Paraformaldehyde effect on catalyst leaching			
5	RR without β-pinene	2	nm	nm
6	Filtrate of run 3 + 0.46 mmol β-pinene	21	2.5	1.8
7	RR over catalyst recovered from run 5, washed with toluene and dried	3	81.6	70.9
	Nopol effect on catalyst leaching			
8	RR with neither HCHO nor β-pinene but, with nopol	2	4.3[§]	nm
9	Filtrate of run 5 + 0.92 mmol HCHO + 0.46 mmol β-pinene	21	2.1	−1.0[@]
10	RR over catalyst recovered from run 8, washed with toluene and dried	3	79.7	69.3

nm, not measured/not measurable.

[*] General reaction conditions: 12 mg of SnCl₂-I-24, 1 mL of 0.46 M β-pinene (or nopol) in toluene solution, (HCHO)x: β-pinene molar ratio of 2:1, 90 °C.

[§] % nopol conversion.

[@] Nopol transformed to some byproducts with a conversion of 1.4%. Deviation in both conversion and yield are estimated up to 1.5%.
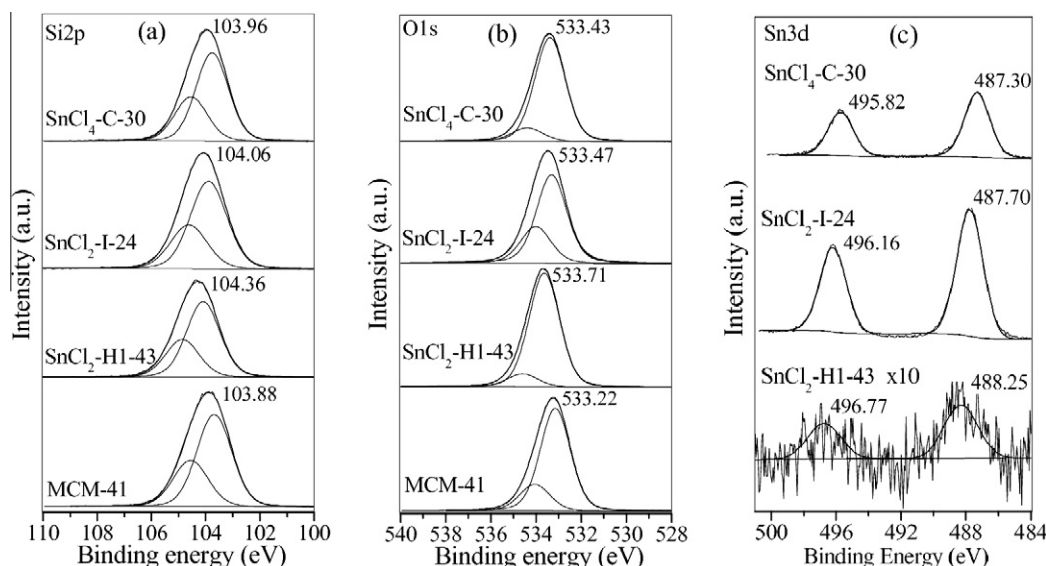
Fig. 12. High resolution XPS and deconvoluted signals of Si2p (a), O1s (b) and Sn3d (c) regions for selected samples.

materials synthesized by CVD did not shift to lower binding energies [8].

It is generally accepted that silanol groups, commonly present in MCM-41 materials are anchoring and grafting sites of several metal precursors as tin halides [37]. The O1s region in Fig. 12b shows a signal and a shoulder around 533.2 and 534.0 eV, respectively, which are assigned to oxygen from silica framework and surface silanol groups, respectively, in MCM-41 materials [35]. Therefore, MCM-41 is an appropriate carrier for metal loading by both CVD and impregnation procedures. As the tin loading of the synthesized materials is low, the binding energy signal for oxygen associated to Sn–O around 530 eV is not observed [38,39]. However, as aforementioned for Si2p the presence of Sn–O–Si is also related to the shift to higher binding energy of O1s signal for Sn supported materials which is pronounced in $SnCl_2$-H1-43 [40]. Fig. 12c, displays a doublet that corresponds to the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ transitions at low and high binding energies, respectively [41]. The reported binding energies of SnO and SnO_2 are 486.5 and 487.5 eV, respectively [42]. The values reported for Sn $3d_{5/2}$ and Sn $3d_{3/2}$ transitions for tin hydroxide, $Sn_6O_4(OH)_4$ with Sn(II) species, are 486.7 and 495.1 eV, respectively [43]. For SnO_x nanoparticles, signals at 487 and 495.5 eV have been observed [44]. By XPS and Auger spectroscopy, Jiménez et al. found positive binding energy shifts of around 1 eV in the Sn3d transitions of very low SnO and SnO_2 coverage over silica [45]. Electron energy loss spectroscopy, EELS, showed that this shift was probably due to interaction effects among SnO_x species and the SiO_2 support, since excitation energy of Sn–O–Si tends to be higher than Sn–O–Sn species [45]. This can also explain the shift observed in the spectra of $SnCl_2$-H1-43 with respect to post-synthesized materials ($SnCl_4$-C-30, $SnCl_2$-I-24). Sn $3d_{5/2}$ and Sn $3d_{3/2}$ transitions around 488.0 and 496.3 eV, respectively, were reported for Sn-HMS materials prepared by hydrothermal synthesis with hydrated stannic chloride precursor [46]. The Sn $3d_{5/2}$ and Sn $3d_{3/2}$ transitions obtained for $SnCl_2$-H1-43 samples (Fig. 12c) are closer to those observed for Sn-HMS and attributed to tin centers due to isomorphous substitution of Si by Sn.

Table 5 lists the surface and bulk composition of selected materials. The nominal values were calculated assuming MCM-41 as SiO_2 and tin species as SnO_2. The O/Si ratio is higher than 2 owing to the presence of –OH groups in MCM-41 identified in the deconvoluted O1s signals (534.0 eV). The higher O/Si ratio in $SnCl_4$-C-30,

$SnCl_2$-I-24 samples could be ascribed to the decrease of Si atoms because of the presence of surface tin also associated to oxygen (Table 5). The similarity of surface and bulk Sn/Si ratios of $SnCl_2$-H1-43 samples suggests that tin may be distributed in the bulk and not on the surface as in the case of $SnCl_4$-C-30, $SnCl_2$-I-24 materials. This is confirmed by the poor XPS signal in spite of their higher tin content. Then, the tin concentration in the amorphous silica walls of $SnCl_2$-H1-43 samples is high. In contrast, materials obtained by CVD and impregnation showed a surface tin loading up to 6 and 15 times higher than in the bulk, respectively.

The presence of SnO and SnO_2 species is confirmed from XPS binding energies and valence band energy analysis. When tin is supported on Al_2O_3, SnO is characterized by two peaks of $Sn5s^2$ valence distribution around 3.5 and 9.5 eV, and an O2p derived peak between 6 and 7 eV. The O2p derived peak for SnO_2 is around 5 eV [47]. Interaction effects with the support also produce around 1 eV shifts in the corresponding signals with respect to the pure oxides [48]. Post-synthesized materials ($SnCl_4$-C-30, $SnCl_2$-I-24) exhibited signals around 10 and 7 eV (Fig. 13) suggesting the presence of SnO. $SnCl_2$-H1-43 samples exhibit a spectra similar to that of MCM-41, but with lower intensity peaks (Fig. 13); this feature has been observed in tin oxides deposited over SiO_2 at Sn/Si ratio lower than 0.06. In spite of the lower Sn/Si of the samples prepared by CVD and impregnation ($SnCl_4$-C-30, $SnCl_2$-I-24) the broad intense signals between 0 and 6 eV are ascribed to both SnO and SnO_2 [42,45]; moreover, the valence band edge shift to lower binding energy of such samples might be due to the presence of tin oxides or to interactions with the support.

The presence of surface tin oxide nanoparticles in $SnCl_2$-H1-43 samples was not detected by XPS. As can be observed in Table 5,

Table 5
Surface and bulk composition of selected materials.

Material	Surface composition by XPS			Bulk Sn/Si atomic ratio	
	O/Si	Sn/Si	Sn/(Sn + Si)	Nominal	Experimental*
MCM-41	2.393	0	0	0	0
$SnCl_4$-C-30	2.395	0.0178	0.0175	0.0096	0.0018
$SnCl_2$-I-24	2.425	0.0351	0.0339	0.0026	0.0014
$SnCl_2$-H1-43	2.273	0.0032	0.0032	0.0067	0.0022

* Tin was determined by atomic absorption (AA). MCM-41 was assumed as SiO_2.

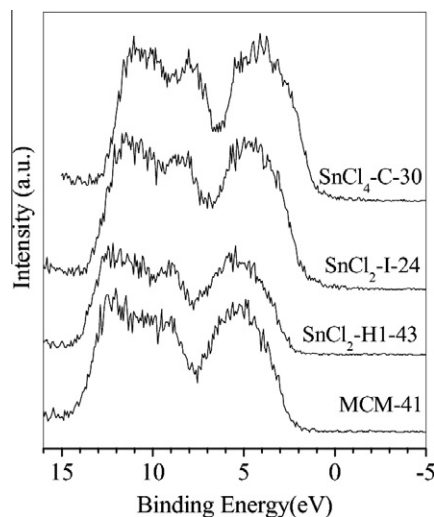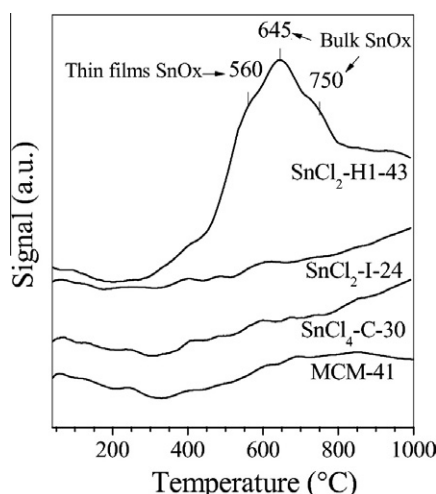**Fig. 13.** Valence band spectra of selected samples.

Fig. 14. Temperature programmed reduction with hydrogen, H_2-TPR, of selected samples.

served. Conversion increased and selectivity decreased when catalyst concentration increased from 1 to 24 mg/mL. If toluene is replaced by a more polar solvent the selectivity could be improved but, protic solvents such as linear chain alcohols are not useful to carry out nopol synthesis. For solvents with adequate polarity for nopol production, the affinity between paraformaldehyde and the solvent in terms of the Hansen's parameter is required to better explain solvent effects. Solvents having HSP values close to 18.2 $MPa^{0.5}$ give higher β-pinene conversion. Nopol selectivity increased from 83% to 95% over $SnCl_2$-I-24 when ethyl acetate that has a higher polarity than toluene was used. Leaching tests over $SnCl_2$-I-24 showed that β-pinene, paraformaldehyde or nopol are not directly related to the deactivation of the catalyst when toluene was used as solvent. In the latter case, the used catalyst was regenerated by washing it with acetone. However, when the reaction was carried out in ethyl acetate, catalyst samples should be washed with this solvent, instead of toluene, to recover their initial activity. Regarding tin active sites, the characterization analysis suggests that grafted species by impregnation and chemical vapor deposition using both stannic and stannous chlorides produce tin oxide nanoparticles supported on MCM-41. Whereas, tin isolated centers presumably surrounded by four –O–Si– groups, $Sn(OSi)_4$, or hydroxylated groups in which one of these Si atoms is replaced by –OH, $(HO)Sn(OSi)_3$ appear to be present in hydrothermally synthesized materials.

Acknowledgements

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the composition of the surface and the bulk are similar for $SnCl_2$-H1-43. Previous UV–VIS analyses indicate the presence of bulk tin oxide species [10]. The reduction peaks of TPR above 600 °C in $SnCl_2$-H1-43 samples are attributed to bulk tin oxide species (Fig. 14) [11]. Therefore, Sn species are most likely present as aggregates in the inner walls of MCM-41, and the active sites are probably $Sn(OSi)_4$ or $(HO)Sn(OSi)_3$ entities as claimed by Corma and Renz in their Sn-MCM-41 obtained by hydrothermal method [5]. On the other hand, $SnCl_2$-H1-43 exhibits quite different properties from $SnCl_2$-I-24 and $SnCl_4$-C-30 associated mainly to the state of tin centers. Conversely, textural properties did not show significant differences, for instance, typical pore size diameters around 2.1 nm were obtained by BET of MCM-41, $SnCl_2$-I-24 and $SnCl_2$-H1-43. Moreover, CVD materials usually have exhibited pore sizes around that value [3].

4. Conclusions

Tin impregnated MCM-41 ($SnCl_2$-I-24) exhibited nopol yields similar or higher than those previously reported over $SnCl_2$-H1-43 and $SnCl_4$-C-30. However, some similarities have been ob-

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