

Lewis acidic Sn(IV) centers—grafted onto MCM-41—as catalytic sites for the Baeyer–Villiger oxidation with hydrogen peroxide

Avelino Corma,* María Teresa Navarro, and Michael Renz

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain

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Abstract

Sn(IV) centers have been grafted onto mesoporous MCM-41 using different R_nSnX_{4-n} precursors. For a successful incorporation of the tin, one or two alkyl substituents are beneficial. The calcined samples are able to activate a carbonyl bond for nucleophilic attack as it could be shown by in situ IR spectroscopy. The resulting catalysts are active for the Baeyer–Villiger oxidation of various substrates with hydrogen peroxide and achieve good conversions and selectivities. Chemoselective oxidations toward unsaturated lactones are obtained from unsaturated ketones. The Lewis acidity and the catalytic performance of the grafted Sn(IV) centers are very similar to the directly synthesized Sn-MCM-41, but lower than those of the Sn-Beta zeolite.

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1. Introduction

Sn(IV) Lewis acid centers incorporated into a zeolite framework (zeolite Beta) have been found to be very active and highly selective catalysts for the Baeyer–Villiger (BV) oxidation of ketones with hydrogen peroxide [1,2]. The same catalyst has also been applied successfully to the Meerwein–Ponndorf–Verley reduction of ketones to the corresponding alcohols [3]. Although the Sn does not go through a formal redox cycle during the process, the catalyst can be included into the list of redox molecular sieves which are commonly referred to as redox metal-containing zeolites or zeotypes [4]. In the case of the tin Beta, the catalyst has been proposed to act as Lewis acid [1,2], and the activation of the carbonyl group through its coordination to the metal center was proposed to be the origin of the catalytic activity in both cases.

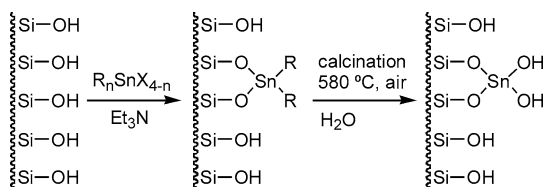
Pore-diffusion limitations in Sn-Beta were diminished when the Sn(IV) centers were incorporated successfully into the walls of an ordered mesoporous MCM-41 molecular sieve and the resulting material was active as catalyst for the BV reaction with hydrogen peroxide [5]. However, it

should be taken into account that in the case of Sn-MCM-41 catalysts the access of the reactants to the active centers may be somewhat limited as the latter can be buried within the inner walls of the solids. Additionally, the turnover numbers (TONs, mole substrate converted per mole of catalytic sites) observed with the directly synthesized Sn-MCM-41 are lower than the ones obtained with Sn-Beta for molecules that can freely diffuse in both systems. This observation can be interpreted by assuming that in the case of Sn-MCM-41 not all Sn centers were equally active and/or accessible to the reactants, and also by considering that the incorporation of Sn in the framework of MCM-41 is not as effective as in the case of Sn-Beta.

In order to investigate and compare isolated tin(IV) centers and to diminish the impact of the above limitations on the catalytic performance of Sn-MCM-41, we have prepared here a series of Sn-MCM-41 catalysts in which the Sn has been incorporated in a postsynthesis treatment by a grafting procedure (Sn_{graft}-MCM-41), to yield isolated, active and well-accessible metal centers (Scheme 1). The Lewis acidity and the catalytic performance of these sites will be compared with the tin centers introduced during the MCM-41 synthesis. Of special interest was also the nature of the tin precursors with respect to their grafting ability and the activity of the resulting catalyst.

* Corresponding author.

E-mail address: acorma@itq.upv.es (A. Corma).



Scheme 1. Grafting of $R_n\text{SnCl}_{4-n}$ precursors onto pure silica-MCM-41 followed by oxidative elimination of the organic substituents at the metal center and subsequent hydrolysis.

2. Experimental

Sn-MCM-41 materials with different Sn/Si ratios were prepared according to the following procedure. Starting from an as-synthesized pure silica MCM-41, the template was extracted following a previous work [6] and heating the sample to 100 °C for 2 h with dynamic vacuum to eliminate the adsorbed water. The grafting of Sn ($n\text{Bu}_3\text{SnCl}$, $n\text{Bu}_2\text{SnCl}_2$, $n\text{BuSnCl}_3$, Me_2SnCl_2 , and $\text{Sn}(\text{O}t\text{Bu})_4$) onto the pretreated and activated MCM-41 material was carried out with a solution of the corresponding amount of grafting agent (Sn/Si ratio of 0.010–0.015) in anhydrous toluene at room temperature. After 1 h, triethylamine was added and the suspension stirred for an additional hour to eliminate and trap hydrochloric acid to complete the Si–O–Sn bond formation. After washing with toluene (50 mL) and drying overnight at 100 °C, the organic components were removed by calcination at 580 °C for 3 h in air stream. The X-ray diffraction patterns of the samples indicate that the mesoporous structure of the MCM-41 material is maintained after the grafting process. Two Sn_{synth} -MCM-41 samples with the tin introduced during the MCM-41 synthesis were prepared following the published procedure [5].

The activity tests were carried out as described in the following procedure: adamantanone (150 mg, 1.0 mmol) and 35% hydrogen peroxide (1.5 eq) were dissolved in dioxane (3.00 g). A sample (50 mg) of the catalyst was added, and heated to 90 °C for 7 h. The reaction was followed by gas chromatography, and the products were identified by GC-MS spectroscopy, or after purification by ^1H NMR

spectroscopy. Norcamphor (**3**) and bicyclo[3.2.0]hept-3-en-1-one (**5**) were employed under the same conditions as for adamantanone with the same molar ratios. The only exception in the case of ketone **5** was the reaction temperature which was decreased to 40 °C. The reaction with a higher substrate/catalyst ratio was carried out with adamantanone (250 mg), 50% aqueous hydrogen peroxide (150 mg), and Sn-3 in 3.0 g of dioxane. Dihydrocarvone (150 mg) was converted with 73 mg of 50% aqueous hydrogen peroxide with 75 mg of Sn-3.

GC analyses were carried out on a HP 5890 gas chromatograph equipped with a 25 m HP-5 column. A Fisons 8035 gas chromatograph coupled with a Fisons MD 800 mass spectrometer was used for GC-MS analyses to identify products. ^1H NMR spectra were recorded with a Varian Gemini at a frequency of 300 MHz. Tin contents were determined with a Varian SpectrAA 10 Plus atomic absorption spectrometer. The in situ IR spectra were recorded with a Nicolet 710 FT-IR spectrometer.

3. Results and discussion

The degree of incorporation of tin during the grafting process, as determined by atomic absorption, was found to be related to the number of chloro or *t*-butoxy substituents in the tin precursors and therewith with the number of easily hydrolyzable bonds and of potential Si–O–Sn bonds for a tin center (Table 1). With $n\text{Bu}_3\text{SnCl}$ only 42% of the tin was grafted onto the MCM-41 material (Sn-1, entry 1) whereas with $n\text{Bu}_2\text{SnCl}_2$ (Sn-2, entry 2) and with $n\text{BuSnCl}_3$ (Sn-3, entry 3) 49 and 81% of the Sn were fixed, respectively. With different alkyl substituents, i.e., methyl groups (Me_2SnCl_2) instead of *n*-butyl ($n\text{Bu}_2\text{SnCl}_2$), the incorporation could be improved from 49 to 75% (entries 2 and 5) but this was still lower than the one achieved when using $n\text{BuSnCl}_3$ as precursor. Finally, quantitative incorporation was achieved with $\text{Sn}(t\text{Bu})_4$ (Sn-6, entry 8).

The Lewis acidity of the grafted and calcined catalysts and their ability to activate the carbonyl group of the re-

Table 1
Synthesis conditions of various Sn-MCM-41 catalysts and their performance in the Baeyer–Villiger oxidation of adamantanone after 7-h reaction time

Entry	Catalyst	Grafting agent	SnO_2 (wt%)	Incorporation ^a (%)	TON ^b	Conversion (%)	Selectivity (%)
1	Sn-1	$n\text{Bu}_3\text{SnCl}$	1.41	42	163	76	> 99
2	Sn-2	$n\text{Bu}_2\text{SnCl}_2$	1.54	49	173	89	> 99
3	Sn-2 ^c	$n\text{Bu}_2\text{SnCl}_2$	1.54	49	16	8	82
4	Sn-3	$n\text{BuSnCl}_3$	2.91	81	103	96	> 99
5	Sn-4	Me_2SnCl_2	1.84	75	153	93	> 99
6	Sn-4 ^c	Me_2SnCl_2	1.84	75	16	10	86
7	Sn-5	Me_2SnCl_2	2.16	66	131	94	> 99
8	Sn-6	$\text{Sn}(\text{O}t\text{Bu})_4$	2.41	95	36	36	> 99
9	Sn-7	Synthesis	1.30		219	95	> 99
10	Sn-8	Synthesis	2.89		104	> 99	> 99

^a Incorporation of the tin determined by atomic absorption spectroscopy with respect to the amount employed in the synthesis.

^b Moles of substrate converted per moles of tin centers.

^c Catalyst employed after grafting step without calcination.

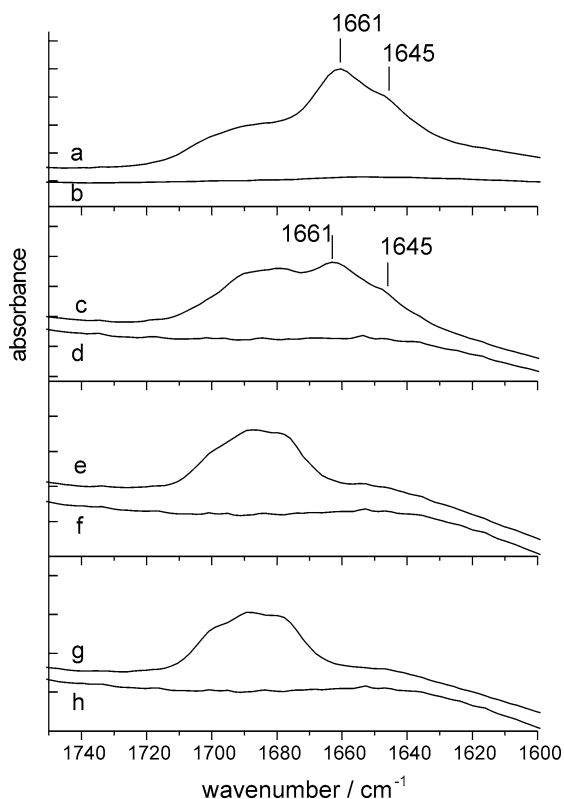


Fig. 1. IR spectra of MCM-41 samples before adsorption of cyclohexanone (b, d, f, and h), after adsorption at 25 °C and desorption at 50 °C (a, c, e, and g). Spectra a and b were done with Sn-MCM-41, spectra c and d with Sn grafted on MCM-41 after subsequent calcination, spectra e and f with pure silica-MCM-41, and spectra g and h with Sn grafted on MCM-41 before calcination.

actants were studied by in situ IR spectroscopy and with cyclohexanone as probe molecule. The ketone was adsorbed at 25 °C after previous activation of the catalyst by calcination at 400 °C in vacuum and then desorbed successively at 50 and 100 °C in a dynamic vacuum. Cyclohexanone coordinates via the carbonyl oxygen to the Lewis acid center, and the carbonyl signals of the IR spectrum (1685–1690 cm^{-1}), are shifted toward lower wavenumbers. A larger shift indicates a higher Lewis acid strength. From the results presented in Fig. 1 it can be seen that the typical IR spectra after adsorption of cyclohexanone on calcined Sn_{graft} -MCM-41 and pure silica-MCM-41 and desorption at 50 °C (spectrum c and e in Fig. 1) were different. In the presence of Sn(IV), besides the typical carbonyl bands at 1685–1690 cm^{-1} , additional bands at 1661 and 1645 cm^{-1} can be detected that correspond to a shift of 25–45 cm^{-1} in the carbonyl group band. A very similar spectrum was obtained with the directly synthesized Sn-MCM-41 (Fig. 1, spectrum a). Furthermore, a value of this range has also been observed for Sn-Beta [2,3] (48 cm^{-1}). This let us conclude that Sn centers grafted on MCM-41 possess Lewis acidity and carbonyl polarizing activity. Interestingly, when the grafted Sn-MCM-41 sample was submitted to the adsorption/desorption procedure before calcination, no shift in the original carbonyl band was

observed (1685–1690 cm^{-1} , Fig. 1, spectrum g), being the resulting IR spectrum identical to cyclohexanone adsorbed in an all-silica-MCM-41. The fact that grafted complexes which still contain alkyl substituents do not polarize the carbonyl bond of the ketone can be due either to a lower Lewis acidity or to a lack of accessibility of the ketone to the metal owing to the presence of the surface plus the still attached alkyl substituents. Since no shift in the carbonyl band was observed in this case by IR we believe that the presence of alkyl groups that are still attached to the grafted Sn before calcination do not allow the carbonyl group of the ketone to approach to the Sn center. Thus, no activation of the C=O group can be expected in this case.

In order to see the implications of catalyst Lewis acidity on the Baeyer–Villiger oxidation reactions, adamantanone (**1**) was chosen as test substrate for the oxidation with hydrogen peroxide. All catalysts prepared with a tin precursor with one or two alkyl substituent were quite active after grafting plus calcination, giving conversions between 89 and 95% (Table 1, entries 2–5), with selectivities above 99%. In this series there was no difference detectable between methyl and *n*-butyl substituents at the tin precursor (cf. entries 2, 5, and 7). This could be expected since the alkyl substituents are removed during calcination. The best result with respect to conversion was achieved with the catalyst prepared starting with $n\text{BuSnCl}_3$, probably due to the higher amount of tin incorporated during a very effective grafting. However, due to the fact that complete conversion is almost reached the TON was the smallest in this series. The catalyst prepared with the $n\text{Bu}_3\text{SnCl}$ precursor (Sn-1) did also result in a quite efficient catalyst. Apart from the described problem with the amount of tin incorporation and the resulting low tin content, the catalyst gave a conversion of 76% which corresponds to a TON of 163. Only catalyst Sn-6 prepared with the $\text{Sn}(\text{O}t\text{Bu})_4$ precursor gave a bad catalytic performance, with a low TON and low conversion (entry 8). Similar to that of SnCl_4 , during the grafting process oligomeric tin-oxo species can be formed easily since all bonds can be hydrolyzed. A carbon–tin bond, in contrast, is supposed to be broken oxidatively during the calcination process. This fact probably guarantees a better distribution during the grafting process, giving more isolated tin sites with higher catalytic activity. For two samples with good catalytic activity (Sn-2 and Sn-4), the catalyst precursor, i.e., the grafted complex before being calcined, was used for the BV oxidation. With both catalysts, the conversion was $\leq 10\%$ (Table 1, entries 3 and 6) versus conversions in the order of 90% for the corresponding calcined samples (entries 2 and 5). This result could be expected since the grafted Sn centers showed no activation of the carbonyl bond in the in situ IR experiment of cyclohexanone adsorption/desorption before calcination (Fig. 1).

In order to check the possible leaching and, if so, the contribution of the homogeneous reaction, an experiment was carried out in which the catalyst Sn-4 was separated by filtration after 30 min of reaction time and 17% conversion.

The solution was further heated for 6 h and the conversion did not proceed further, confirming that the active species were the metal centers grafted onto the mesoporous material. With catalyst Sn-1 the influence of the amount of hydrogen peroxide employed in the reaction was tested. It was found that after 7 h with a deficit of oxidant (0.57 eq) full conversion of the hydrogen peroxide (within the experimental error limit of 5%) and a 57% conversion of ketone **1** was obtained, which corresponded to a selectivity of 100% with respect to the oxidant. An increase to 1.06 eq of hydrogen peroxide raised the conversion to 74%. Almost identical conversions (77 and 75%) were obtained with 1.42 and 2.03 eq, respectively. This indicated that the conversion of adamantanone could not be increased over 75% by adding more hydrogen peroxide in this case. If a higher yield in gram of product per gram of catalyst is desired the 3:1 ratio (g/g) can be raised to 5:1 when the 35% aqueous hydrogen peroxide is replaced by 50%. In this case catalyst Sn-3 still gives 93% of the adamantanone conversion with 100% lactone selectivity.

When the catalysts Sn_{graft}-MCM-41 prepared by grafting are compared with Sn_{synth}-MCM-41 it can be seen that the conversions after 7 h are very close with the two catalytic systems, but the directly synthesized samples seem to give higher conversion and TON. Indeed, with the catalyst Sn_{synth}-MCM-41 Sn-7 containing 1.30 wt% of SnO₂ 95% of conversion was observed whereas the grafted ones, e.g., Sn-1 (1.41 wt% SnO₂) and Sn-2 (1.51 wt% SnO₂) gave 76 and

89%, respectively. However, it is not appropriate kinetically to compare catalyst activity at such high levels of conversion, and therefore a new series of experiments was performed and conversion was determined after 15 min of reaction time. Then, when conversion and turnover frequency (TOF, defined as TON per hour) are compared at these reaction conditions (Table 2), we see that MCM-41 samples with similar level of Sn, either grafted or introduced by direct synthesis, result in similar activity. However, it should be pointed out that the directly synthesized Sn-MCM-41 samples give better results. This may indicate that, if all the Sn grafted on the most efficient catalyst is accessible and active, then very little, if any, of the Sn introduced by direct synthesis in MCM-41 is buried in the internal tetrahedra of the wall, but on the contrary they should be accessible to the reactant since similar TON numbers are obtained.

3.1. Oxidation of other ketones

Norcamphor (**3**) and bicyclo[3.2.0]hept-3-en-1-one (**5**) were oxidized under similar reaction conditions as above on different MCM-41 samples with Sn grafted or Sn introduced by direct synthesis (the results are given in Table 3). For norcamphor (**3**) 70% of conversion was achieved with Sn-3 and Sn-8. However, with Sn-3 (grafting) 10 h of reaction time were necessary whereas with Sn-8 (synthesis) this value was reached after 7 h. With bicyclo[3.2.0]hept-3-en-1-one (reaction temperature 40 °C) and the grafted Sn catalyst Sn-3


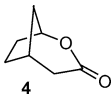



Table 2

Turnover frequencies (TOFs, moles of substrate converted per moles of tin centers per hour) and the corresponding conversions after 15 min for various Sn-MCM-41 catalysts in the Baeyer–Villiger oxidation of adamantanone

Entry	Catalyst	Grafting agent	SnO ₂ (wt%)	TOF	Conversion (%)	Selectivity (%)
1	Sn-1	<i>n</i> Bu ₃ SnCl	1.41	100	12	> 99
2	Sn-2	<i>n</i> Bu ₂ SnCl ₂	1.54	200	26	> 99
3	Sn-3	<i>n</i> BuSnCl ₃	2.91	112	27	> 99
4	Sn-4	Me ₂ SnCl ₂	1.84	136	21	> 99
5	Sn-5	Me ₂ SnCl ₂	2.16	132	24	> 99
6	Sn-6	Sn(<i>Or</i> Bu) ₄	2.41	48	10	> 99
7	Sn-7	Synthesis	1.30	208	23	> 99
8	Sn-8	Synthesis	2.89	100	25	> 99

Table 3

Comparison of conversions and selectivities observed in the Baeyer–Villiger oxidation of norcamphor (**3**) and bicyclo[3.2.0]hept-3-en-1-one (**5**) catalyzed by Sn_{graft}-MCM-41 Sn-3 and Sn_{synth}-MCM-41 Sn-8

Entry	Substrate	Catalyst	Time (h)	Conversion (%)	Selectivities ^a (%)	Selectivities ^b 6a:6b	Products
1		Sn-3	10	71	> 98		
2	3	Sn-8	7	71	> 98		4
3		Sn-3	7	62	> 98	67:33	
4	5	Sn-8	7	67	> 98	71:29	

^a Selectivity for lactone **4** in the case of substrate **3** and for the regioisomeric lactones **6a** and **6b** for substrate **5**.

^b For identification and assignment, see Ref. [2].

62% conversion was obtained whereas with catalyst Sn-8 a slightly higher conversion of 67% was observed for the same reaction time (7 h). It is clear that, independently of the reactant ketone, the differences in activity observed always indicate that the directly synthesized Sn-MCM-41 samples are somewhat more active.

In the case of bicyclo[3.2.0]hept-3-en-1-one with both type of catalysts the desired lactones were the only products in the usual 2:1 ratio [2], and no epoxidation reaction could be detected. In other words, also Sn(VI) centers grafted onto the mesoporous material exhibit an extraordinary chemoselectivity with unsaturated ketones [1,2]. This was confirmed once more with dihydrocarvone which has been tested before with directly synthesized Sn-MCM-41. A 68% lactone selectivity was observed in that case whereas mCPBA resulted in 71% epoxidation products and only 11% of the unsaturated lactone [5]. With Sn-3 a conversion of 40% was achieved with 90% selectivity toward the lactone product.

3.2. Catalyst deactivation and recycling

With respect to catalyst life, we have observed for Sn_{graft}-MCM-41 (Sn-5) that some loss in activity occurs during the reaction when the same catalyst is reused four times, i.e., when the catalyst is repeatedly filtered out and submitted to a new reaction batch without any further treatment (Fig. 2). The activity is lowered to 64% of the original one after 4 cycles. In comparison with Sn_{synth}-MCM-41, it can be seen that the activity loss is slightly smaller in every recycling

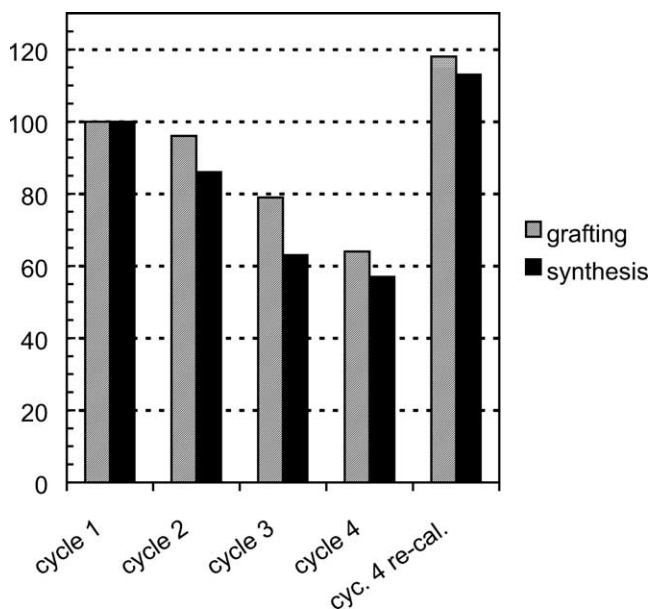


Fig. 2. Relative activity of Sn-5 (grafting) and Sn-8 (synthesis) in four cycles without regeneration and after subsequent calcination (selectivities were in all cases > 98%). In the first four cycles 150 mg of adamantanone, 1.5 eq H₂O₂, and 3.00 g of dioxane were employed and 50 mg (cycle 1) of the catalyst or the total recovered amount (cycles 2–4) were added. In the fifth cycle 25 mg of the recalculated catalyst was added to a mixture of 75 mg of adamantanone, 1.5 eq H₂O₂ and 1.50 g of dioxane.

step (Fig. 2). The loss of activity could be due to lactone remaining adsorbed on the catalyst after the reaction. Indeed, lactone **2** has been identified after extraction of the catalyst with methanol for 14 h, and the catalyst activity is almost completely recovered after the extraction procedure. When the used catalyst (4 times) was recalculated the initial activity was recovered and even improved by more than 10% in both cases. This increase in activity upon the second calcination may indicate that not all the organic was removed during the activation of the catalyst during the calcination step after the catalyst synthesis. In order to check this the carbon content was analyzed after grafting and calcination, and indeed 0.1 wt% carbon was detected. This sample was calcined a second time and its catalytic activity for the adamantanone oxidation increased by 10%. A third calcination did not have any further effect on conversion.

4. Conclusions

It could be shown that grafting of Sn(IV) onto mesoporous MCM-41 material resulted in active catalysts for the Baeyer–Villiger oxidation with good conversions, high TONs, and excellent selectivity, including high chemoselectivity toward unsaturated lactones when reacting unsaturated ketones. For an effective grafting, precursors with two or three chloro substituents and two or one alkyl substituents, respectively, guarantee best incorporation and avoid inactive polymeric tin-oxo species. After the grafting the alkyl substituents must be removed oxidatively by calcination since these catalyst precursors were found to be inactive for the Baeyer–Villiger oxidation. Grafted Sn(IV) sites (after calcination) have similar Lewis acidity as Sn(IV) incorporated during the MCM-41 synthesis. The catalytic activity is similar for the two sets of Sn-MCM-41 samples, but the ones prepared by direct synthesis give some higher activity.

Acknowledgments

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