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Sonocatalysis in solvent-free conditions: An efficient eco-friendly methodology to prepare N-alkyl imidazoles using amino-grafted NbMCM-41

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ABSTRACT

3-Aminopropyl-trimethoxysilane (APMS) was loaded by grafting on MCM-41 matrices of various chemical compositions, silicate (MCM-41) and niobosilicate (NbMCM-41 with Si/Nb = 64). The materials were characterised by N_2 adsorption/desorption, XRD, TG and test reactions: 2-propanol decomposition, acetonylacetone cyclisation and Knoevenagel condensation. The amino-grafted samples were basic and that based on NbMCM-41 exhibited much higher basicity than the APMS/MCM-41. The catalysts were studied in Michael addition between imidazole and ethyl acrylate for the production of N-alkyl imidazoles under sonic and non-sonic activation. The most important finding from this work is that the combination of amino-grafted NbMCM-41 with ultrasound conditions is a mild and effective method for the preparation of N-substituted imidazoles.

1. Introduction

Traditionally, heterogeneous catalysis has been associated with the production of bulk chemicals and petrochemicals while fine and specialty chemicals are produced mainly via homogeneous catalysts. Nowadays, heterogeneous catalysts are also used in fine-chemicals industry which needs more environmental-friendly production technology. These tendencies are assisted by the ability of novel catalytic materials and modern techniques of creating and investigating specific active sites on catalysts surface and new catalytic processes that are environmental-friendly.

In the field of chemical production, important development has been taken in the synthesis of relatively large and complex molecules include carbon–carbon bond forming reaction such as Michael additions. Bases are usually employed in reactions of organic compounds to abstract the proton and generate reaction intermediates, which are important in many organic reactions for fine-chemical syntheses. Therefore, in this work an efficient route for the preparation of N-alkyl imidazoles using a new type of amino-grafted NbMCM-41-64 and MCM-41 as catalysts under ultrasound activation and solvent-free conditions was applied. The method provides a simple procedure for the Michael-type additions in short reaction times. In this green solvent-free procedure, the Michael addition between imidazole and ethyl acrylate was studied for the production of N-alkyl imidazoles with very high efficiency when amino-grafted NbMCM-41-64 was employed under ultrasound (US) activation. The amino-grafted silicate catalysts exhibit the catalytic activity for the Knoevenagel condensation probe reaction [1,2].

Ultrasound is an alternative activation source that offers short reaction time, which is particularly convening for the pharmaceutical industry [3]. In general, the sonication presents beneficial effects on the chemical reactivity, such as to accelerate the reaction, to reduce the induction period and to enhance the catalyst efficiency [4].

2. Experimental

2.1. Synthesis of the catalysts

Mesoporous molecular sieves of MCM-41-type were synthesized by a classical hydrothermal method [5] and modified in the preparation of NbMCM-41-64 (Si/Nb = 64) [6].

Synthesis was carried out in the presence of cetyltrimethylammonium chloride (Aldrich) as surfactant from mixtures containing niobium and silica sources. The reactant mixture consisted of sodium silicate (27% SiO_2 in 14% NaOH—Aldrich) and the appropriate amount niobium (V) ammonium oxalate complex (CBMM-Brasil). The ratio of Si/Nb in the gel was assumed as 64.

The formed gel from these components was stirred for about 30 min. The pH was adjusted to 11, after which the distilled water was added. The gel was loaded into a stoppered PP bottle and heated without stirring at 373 K for 24 h. The mixture was then cooled down to room temperature and the pH level was adjusted to

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11 with oxalic acid (for NbMCM-41) and H_2SO_4 (for silicate MCM-41) in order to control the structural arrangement of MCM-41 by shifting metallosilicate polymerisation equilibrium [6]. This reaction mixture was heated again at 373 K for 24 h to produce highly ordered samples. The resulting precipitated product was washed with distilled water, dried in the air at ambient temperature, and the template in the catalysts was removed by calcination at 823 K, 2 h in helium flow and 14 h in the air under static conditions.

The ammonium forms of mesoporous molecular sieves, NH_4MCM-41 and NH_4NbMCM-41 were obtained via cation exchange with NH_4^+ ions (from NH_4Cl solution). They were transformed to hydrogen forms by calcination at 673 K for 2 h.

The hydrogen forms, H-NbMCM-41 and H-MCM-41, were the supports for grafting of 3-aminopropyl-trimethoxysilane (APMS). The grafting procedure was carried out according to [7] and was as follows: 2.3 g of the support powders were refluxed in a dry toluene solution (200 mL) containing 10 mL of APMS at 373 K for 18 h. The catalysts were recovered by filtration followed by washing in dry toluene (200 mL), water (100 mL) and acetonitrile (20 mL). The powder was dried in an oven at 373 K and stored for the later use. The obtained catalysts are denoted as APMS/MCM-41 and APMS/NbMCM-41.

2.2. Catalysts characterization

The prepared materials were characterized using XRD, N_2 adsorption/desorption, and thermogravimetric and elemental analysis.

The XRD measurements were carried out with a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ = 0.154 nm), with a step size of 0.02° and 0.05° in the small-angle and high-angle ranges, respectively.

The N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. The samples were pre-treated in situ under vacuum at 333 K for 24 h. The surface area was calculated by the BET method. The pore size distributions (PSD) and the mesopore volumes were determined from the adsorption/desorption isotherms using DFT.

The thermogravimetric analyses of the solids were carried out with a ATA Instruments thermogravimetric system, model SDT Q600 TG-DSC.

2.3. Catalytic tests

2.3.1. 2-Propanol decomposition

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.02 g with a size fraction of $0.5 < \varnothing < 1$ mm) was first activated at 673 K for 2 h under helium flow (40 $cm^3\,min^{-1}$). The 2-propanol (Aldrich) conversion was studied at 423, 473, 523, and 573 K using 2 μl pulses of alcohol under helium flow (40 $cm^3\,min^{-1}$). The reactant and reaction products: propene, 2-propanone (acetone) and diisopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 $cm^3\,min^{-1}$) and detected by TCD.

2.3.2. Acetonylacetone cyclisation

The materials were tested in acetonylacetone (AcAc) cyclisation as a probe reaction. A tubular, down-flow reactor was used in experiments that were carried out at atmospheric pressure, using nitrogen as a carrier gas. The catalyst bed (0.05 g) was first activated for 2 h at 673 K under nitrogen flow (40 $cm^3\,min^{-1}$). Afterwards, a 0.5-cm^3 of acetonylacetone (Fluka, GC grade) was being passed continuously over the catalyst at 623 K. The substrate was delivered with a pump system and vaporized before it was passed through the catalyst bed in the presence of a flow of nitrogen carrier gas (40 $cm^3\,min^{-1}$). Reaction products were collected downstream of the reactor in the cold trap and analysed by gas chromatography with a Chrom 5 chromatograph equipped with a 3-m packed column (Silicon SE (6 wt.%) on Chromosorb G).

2.3.3. Knoevenagel probe reaction

The experimental work was carried out in a Pyrex-glass batch reactor. The equimolar mixtures of the two reactants, benzaldehyde and the active methylenic compound (ethyl cyanoacetate, ethyl acetoacetate or diethyl malonate) without any solvent were pre-heated to the reaction temperature, 393 K, under continuous stirring. Then, depending on the active methylenic compound employed, ethyl acetoacetate, ethyl cyanoacetate or diethyl malonate, 1, 2 or 10 wt.% of solid catalyst was added respectively and the reaction time started. Samples were taken periodically, and the evolution of the reaction was followed by gas chromatography, using an Agilent Technologies 6890N chromatograph.

2.4. Reaction procedures in the synthesis of N-alkyl imidazoles

Prior to the reactions (both in thermal as well as in ultrasound mode) each solid was kept in the furnace 333 K for 24 h to ensure the elimination of water.

2.4.1. Thermal induced reactions

Mixture of imidazole (5 mmol) and ethyl acrylate (5 mmol) was heated in a batch reactor and in absence of any solvent at 333 K under vigorous stirring. Then, the catalyst was added and the reaction time started. The reaction mixture was analysed by gas chromatography, using an Agilent Technologies 6890N chromatograph.

2.4.2. Ultrasound induced reactions

Imidazole (5 mmol) and ethyl acrylate (5 mmol) were mixed in a flask without any solvent. The flask was suspended into the ultrasonic bath at 333 K. Then, the catalyst was added and the reaction time started. The reactions were performed in an ultrasonic bath (Selecta Ultrasound-H) with a heating system, 40 kHz of frequency and 550 W of power.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. Texture

The MCM-41 and NbMCM-41 materials, before grafting, show well-defined XRD patterns in the small-angle region typical of hexagonal mesoporous MCM-41 materials [5] (Fig. 1). They exhibit a main peak at $2\theta \sim 2^\circ$ indexed as [1 0 0] assigned to hexagonal array of parallel mesoporous tubes. The additional peaks in the range of $2\Theta = 3$–8° indicate the long-range hexagonal ordered pores.

The XRD patterns of MCM-41 samples modified by grafting with 3-aminopropyl-trimethoxysilane indicate only one well-distinguished peak at $2\theta \sim 2^\circ$. Moreover, the intensity of this [1 0 0] peak decreases after the modification with APMS. This can suggests a transformation from MCM-41 with the hexagonal structure into a lower-symmetry one [8] or a partial collapse and lower regularity of the arrangement of pores after grafting.

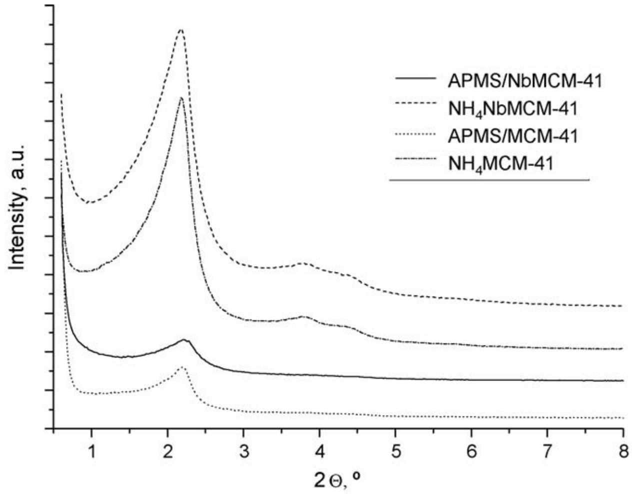

Fig. 1. XRD patterns of the MCM-41 catalysts in the small-angle range.

Table 1
The results of nitrogen adsorption.

Catalyst	BET surface area (m^2/g)	Average pore diameter (nm)	Mesopore volume (cm^3/g)
H-MCM-41	604	2.8	0.41
APMS/MCM-41	58.4	2.7	0.11
H-Nb-MCM-41	1049	3.8	0.96
APMS/Nb-MCM-41	681	3.2	0.44

3.1.2. Nitrogen adsorption

The texture changing after grafting with APMS was confirmed by nitrogen adsorption isotherms. All of them, excluding that of APMS/MCM-41, are of type IV, characteristic for mesoporous materials according to the UPAC classification [9]. However, the surface area significantly decreased after APMS modification from 604 to ~58 m^2/g for H-MCM-41 and from 1049 to 681 m^2/g for H-NbMCM-41 (Table 1). APMS/MCM-41 material exhibits the type II of isotherm, so the introduction of the amino groups leads to loss of mesoporosity. After APMS modification the mesopore volume decreases significantly.

Table 2
The results of elemental analysis.

Catalyst	% C	% H	% N
H-MCM-41	0.19	1.80	0.05
APMS/MCM-41	11.2	3.25	4.40
H-NbMCM-41	0.30	1.64	0.12
APMS/NbMCM-41	6.64	2.37	2.78

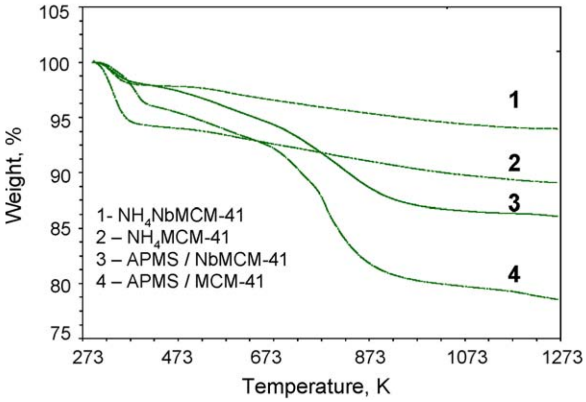

Fig. 2. TG curves of MCM-41 catalysts.

3.1.3. Thermogravimetric analysis

Thermal stability of the samples was estimated by thermogravimetric (TG) analyses. TG curves of amino-grafted samples, shown in Fig. 2, indicate two well distinguished weight losses, one at the temperature at about 373 K and the second above 673 K. The first is related to desorption of water, whereas the second is assigned to APMS removal. The pristine supports exhibit only one loss of weight from water desorption.

3.1.4. Elemental analysis

The increase of the percentage of nitrogen in the grafted materials (Table 2) shows that the grafting processes are successful. The amount of nitrogen in APMS/MCM-41 is about 1–6 times higher than the amount of nitrogen in APMS/NbMCM-41. This fact demonstrates that the anchoring process is more efficient if the support is MCM-41 than if the original support is NbMCM-41.

3.2. Catalytic tests

3.2.1. 2-Propanol decomposition

The modification of the acid/base properties of the mesoporous solids were investigated by controlling the selectivity to the

Table 3
The results of 2-propanol dehydration and dehydroxylation.

Catalyst	Temperature (K)	2-Propanol conversion (%)	Propene selectivity (%)	Diisopropyl ether selectivity (%)	Acetone selectivity (%)
H-MCM-41	423	0.2	100	0	0
H-MCM-41	473	3	89	10	0
H-MCM-41	523	24	97	3	0
H-MCM-41	573	66	100	0	0
APMS/MCM-41	423	0.1	100	0	0
APMS/MCM-41	473	0.2	100	0	0
APMS/MCM-41	523	0.2	87	0	13
APMS/MCM-41	573	0.3	92	0	8
H-NbMCM-41	423	0.1	100	0	0
H-NbMCM-41	473	4	26	74	0
H-NbMCM-41	523	33	97	3	0
H-NbMCM-41	573	67	99	0.5	0
APMS/NbMCM-41	423	0.1	57	0	43
APMS/NbMCM-41	473	1	63	9	28
APMS/NbMCM-41	523	10	99	0	1
APMS/NbMCM-41	573	27	99.5	0	0.5

Table 4
The results of acetonylacetone reaction at 623 K.

Catalyst	AcAc conv. (%)	DMF-selectivity (%)	MCP-selectivity (%)	MCP/DMF
H-MCM-41	42	98	2	0.02
APMS/MCM-41	3	59	41	0.7
H-NbMCM-41	55	98	1	0.01
APMS/NbMCM-41	54	98	2	0.02

different products in the decomposition of isopropanol. The results are shown in Table 3.

In this reaction, acid sites are required to form propene by dehydration reaction, and diisopropyl ether by an intermolecular coupling reaction. The latter requires the presence of pairs, Lewis acid–base centers. On basic sites acetone is formed by oxidative dehydrogenation [10].

In the two cases of APMS modified mesoporous molecular sieves, the activity decreases in relation to that of pristine supports. However, the selectivity to acetone is observed only in the reaction carried out on the amino-grafted catalysts. It clearly evidences the basicity of the APMS modified materials. One can note that the selectivity to acetone decreases when temperature rises because 2-propanol conversion increases.

3.2.2. *Acetonylacetone cyclisation/dehydration*

The acid and base characteristics of the prepared materials were also evaluated using the probe reaction reported by Dessau [11], i.e. acetonylacetone cyclisation and dehydration. In this reaction, dimethylfuran (DMF) is produced on Brønsted acid centers, whereas Brønsted basic centers are involved in the formation of methylcyclopentenone (MCP). It has been established that the selectivities MCP/DMF $\gg 1$ characterize basic properties of the catalyst, whereas MCP/DMF $\ll 1$ indicates acidic character of the material. If this ratio is 1, then the acid–basic character of the catalyst can be concluded [12].

In this study, we observed that the activity of APMS/MCM-41 decreases significantly with regard to the pristine support (Table 4). It is not a case of the catalyst based on NbMCM-41 support. All the materials studied indicate the domination of Brønsted acidity over Brønsted basicity as concluded from MCP/DMF ratio below 1. It is worthy to stress that acetone is formed from 2-propanol on Lewis basic centers whereas methylcyclopentenone formation from AcAc requires Brønsted basic centers.

3.2.3. *Knoevenagel probe reaction*

Corma et al. [13] proposed the condensation of benzaldehyde with active methylenic compounds of different p*K*a values to measure the total amount of basic sites and the basic strength distribution in base solid catalysts.

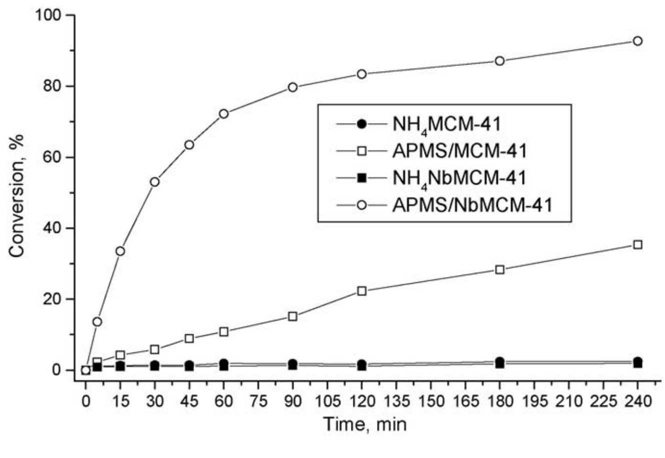

Fig. 3. Condensation of benzaldehyde and ethyl cyanoacetate at 393 K using MCM-41 and NbMCM-41 catalysts (before and after APMS modification).

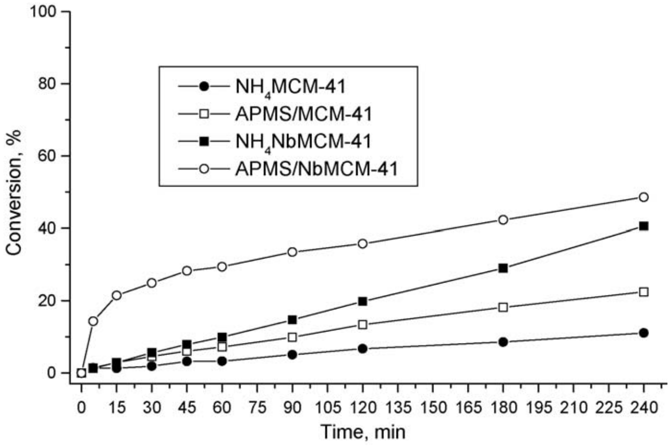

Fig. 4. Condensation of benzaldehyde and ethyl acetoacetate at 393 K using MCM-41 and NbMCM-41 catalysts (before and after APMS modification).

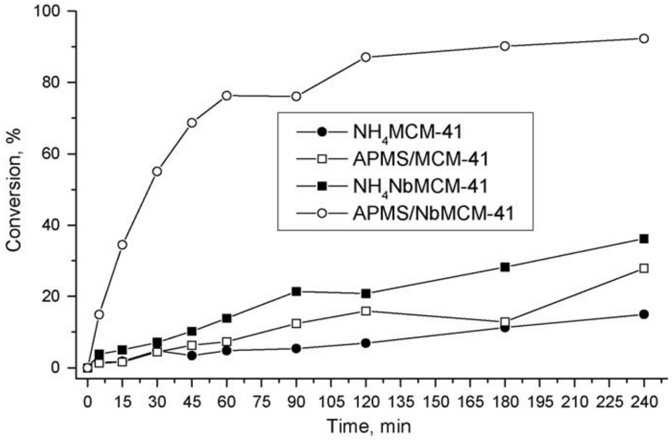

Fig. 5. Condensation of benzaldehyde and diethyl malonate at 393 K using MCM-41 and NbMCM-41 catalysts (before and after APMS modification).

Previous probe reactions required the activation of the catalyst at 673 K. Such a treatment could partially decompose grafted 3-aminopropyl-trimethoxysilane. That is why Knoevenagel probe reactions were also chosen to test the basicity of the prepared catalysts under mild conditions.

Figs. 3–5 summarise the results of Knoevenagel probe reactions. In the reaction between benzaldehyde and ethyl cyanoacetoacetate, the pristine supports show very low conversion, whereas the modified catalysts exhibit much higher activity. During the whole reaction time APMS/NbMCM-41 catalyst shows the best conversion reaching 93% after 240 min, whereas the conversion obtained using APMS/MCM-41 is 35%. In all the cases the selectivity to Knoevenagel product is 100%.

In the reaction between benzaldehyde and ethyl acetoacetate, NH_4-MCM-41 and APMS/MCM-41 show lower conversion than the NbMCM-41 based catalysts (Fig. 4). In both types of catalysts, silicate and niobosilicate, the amino-grafted materials show higher conversion than the pure supports. For this reaction also APMS/NbMCM-41 exhibits the highest activity during the whole reaction time, like in the previous described one. The final conversion after 240 min is 39%, whereas the conversion obtained on NH_4-NbMCM-41, NH_4-MCM-41 and APMS/MCM-41 is 35%, 11% and 23%, respectively. In all the cases the selectivity to Knoevenagel product is 100%.

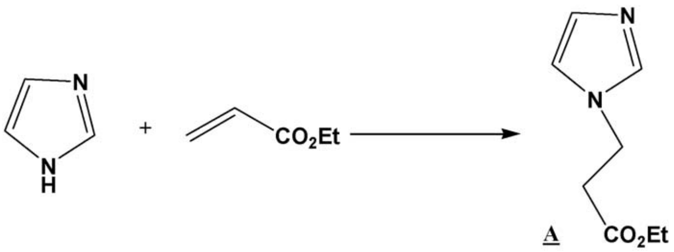

Fig. 6. Scheme of the condensation of imidazole and ethyl acrylate.

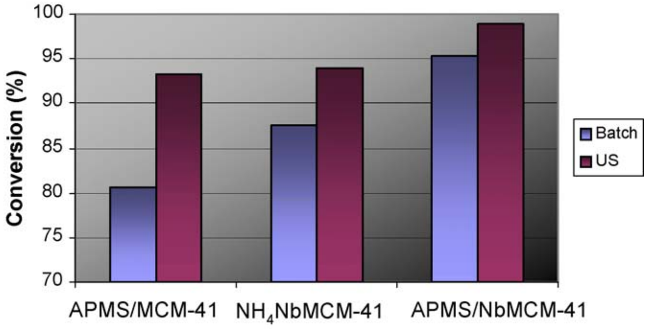

Fig. 7. Condensation of imidazole and ethyl acrylate after 180 min of the reaction in a batch reactor and in an ultrasonic reactor at 333 K.

In the reaction between benzaldehyde and diethyl malonate (Fig. 5), the APMS/NbMCM-41 solid shows the best conversion, and after 240 min the conversion is 92% whereas the conversion obtained using NH_4-NbMCM-41, NH_4-MCM-41 and APMS/MCM-41, is much lower: 36%, 15% and 28%, respectively. In this process also the amino-grafted catalysts show higher conversion than the pristine supports. The selectivity to Knoevenagel product is higher when the reaction is catalyzed by the amino-grafted solids. The highest and more stable selectivity (in the range of 90–95%) is obtained by using APMS/NbMCM-41. The supports exhibit non-stable selectivity in the range of 15–45%. The reaction catalyzed by APMS/MCM-41 provides a rather stable selectivity in the range of 60–70 during the first 120 min but it decreases in the last 2 h. This phenomenon could be explained by the auto-condensation of the products.

The three test reactions demonstrate that the introduction of APMS into the studied mesoporous structures increases the basic character of the solids. This effect is more pronounced when niobium containing support is applied. All the Knoevenagel probe reactions lead to the same conclusion: the most basic catalyst is APMS/NbMCM-41. Niobosilicate mesoporous materials enhances Lewis basicity of APMS grafted on its surface because NbMCM-41 support contains mobile electrons located on oxygen connected with framework niobium species, as was proved elsewhere [14,15]. This fact can explain the high activity obtained by using the solid APMS/NbMCM-41 as catalyst, even though its content of amine 41 is lower than in APMS/MCM-41 as thermogravimetric and elemental analysis showed.

3.3. Synthesis of N-alkyl imidazoles

In the present work the condensation of imidazole and ethyl acrylate has been carried out under mild experimental conditions and in the absence of any solvent, using temperature or the ultrasound activation to accelerate the process. Under our experimental conditions, we have found that N-substituted derivative A (Fig. 6) is selectively obtained when ethyl acrylate is added to imidazole.

Fig. 7 shows the conversion at 180 min in a batch reactor and in a ultrasonic reactor at 333 K. The more active catalyst is APMS/NbMCM-41 in both conditions: ultrasound activated reaction and batch reaction. The conversion rises when the reaction is done by ultrasound activation by using the three chosen catalysts (NH_4-NbMCM-41, APMS/NbMCM-41 and APMS/MCM-41). The selectivity was 100% in all the cases.

4. Conclusions

The basicity of the 3-aminopropyl-trimethoxysilane grafted MCM-41 and NbMCM-41 is clearly evidenced by the results of test reactions carried out within this work, especially Knoevenagel condensation processes. The chemical composition of the mesoporous supports influence the basicity of the amino-grafted catalysts giving rise to the higher basicity of the sample based on NbMCM-41 matrix. This catalyst exhibits basicity during the Michael addition under sonic and non-sonic activation. The obtained results demonstrate that the combination of this type of amino-grafted NbMCM-41 with ultrasound conditions is a mild and effective method for the preparation of N-substituted imidazoles. This method thus offers a practical alternative to conventional heating catalysis and the process itself is environmental-friendly with minimal waste.

Amino-grafted NbMCM-41 can successfully be employed to obtain imidazoles with antiviral activities. These solid catalysts can compete with the traditionally used NaOH/EtOH.

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