Catalysis Today 179 (2012) 159–163

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Efficient isomerization of safrole by amino-grafted MCM-41 materials as basic catalysts

Izabela Sobczak[a], Maria Ziolek[a,*], Elena Pérez-Mayoral[b], Davinia Blasco-Jiménez[a,b], Antonio J. López-Peinado[b], Rosa M. Martín-Aranda[b,**]

[a] Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznan, Poland
[b] Dpto. Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, c/Senda del Rey 9, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 11 August 2011
Received in revised form
18 September 2011
Accepted 20 September 2011
Available online 21 October 2011

Keywords:
Basicity
Mesoporous materials
MCM-41
AlMCM-41
NbMCM-41
Aminopropyl trimethoxysilanes
Isomerization
Safrole
Isosafrole

ABSTRACT

Design of base catalyst featuring large mesoporous surfaces allows performing base-catalysed reactions in the fields of production of perfumes. Post-synthesis grafting of organotrialkoxysilanes has effectively been applied to incorporate active organic functional groups onto the mesoporous silica surfaces. The novelty of our study is the use of mesoporous materials with different chemical compositions: silicate (MCM-41), aluminosilicate (AlMCM-41; Si/Al = 64) and niobosilicate (NbMCM-41; Si/Nb = 64) and consequently, different acidity, as supports for three aminopropylalkoxysilanes (APMS), [3-(2-aminoethylamino) propyl]trimethoxysilane (2APMS) and 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (3APMS). Isomerization of safrole to the corresponding thermodynamically stable isosafrole has been carried out on these amino-grafted MCM-41 materials. Maximum conversion of around 85% with a cis/trans ratio of 1/9 at 433 K in DMF as solvent was obtained. Isomerization is strongly dependent on the nature of the support and changed in the following order: APMS/AlMCM-41 > APMS/NbMCM-41 ≫ APMS/MCM-41. The nature of the amine chain is also responsible for the activity. The order of activity is APMS/AlMCM-41 > 2APMS/AlMCM-41 > 3APMS/AlMCM-41.

1. Introduction

Studies of solids with base properties and their catalytic behaviour in organic reactions have been investigated according to the environmental concerns and regulations during the last 20 years [1–3].

The bulk chemicals production is using around 95% of all industrial heterogeneous catalysts. Nevertheless, only 3–5% of such catalysts are used in the preparation of fine chemicals. Moreover, the fine chemical production accounts for approximately 20% of the profit. This fact, underlines the economic importance and the need of catalysts in the speciality production [4].

The impulse to develop new efficient and selective catalysts and the optimization of new process technology is strongly related to environmental protection, and solid acid–base catalysts play an important ecological role in the industries. The industrial processes using solid acid–base catalysts such as alkylations, isomerizations, esterifications, condensations, amination reactions, etc. among them zeolites [5], activated carbons [6], clays [7], mesoporous materials [8] and MOFs [9].

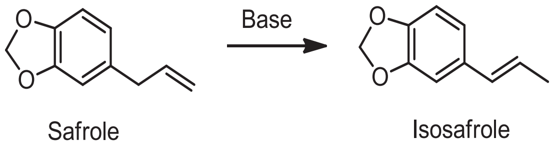
Current effort in mesoporous molecular sieves is mainly focussed on optimizing of synthesis procedures with respect to their applications in catalysis [10]. Since 1992, when mesoporous molecular sieves were synthesized by first time [11], many approaches were investigated to prepare mesoporous materials with basic properties [8], and much progress was made in the last year in the development of organo-modified mesoporous molecular sieves [12].

In our previous work, the role of chemical composition of metallosilicate mesoporous ordered supports on the catalytic activity of amino-grafted materials was investigated [13] and it was determined the influence of the nature of the amine groups (APMS, 2APMS and 3APMS) linked to MCM-41, containing various T atoms (Al–Nb); evaluation of the catalysts were assayed in the synthesis of *N*-alkylpyrazoles under ultrasound activation. Moreover, basicity of mesoporous above mentioned were also tested in the 2-propanol dehydrogenation and Knoevenagel condensation [14]. In this context, the aim of this work is to get a better insight into the role of chemical composition of amino-grafted materials based on mesoporous materials during the isomerization of safrole (Scheme 1).

---

* Corresponding author. Tel.: +48 61 829 1243.
** Corresponding author. Tel.: +34 91 398 7350.
E-mail addresses: ziolek@amu.edu.pl (M. Ziolek), rmartin@ccia.uned.es (R.M. Martín-Aranda).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.09.031



Scheme 1. Safrole isomerization catalysed by bases.

Isomerization of other olefins, such as eugenol, using Nb-containing MCM-41 mesoporous materials modified with alkaline cations was investigated by our group [15]. Traditionally, the reaction of isomerization of eugenol and safrole is catalysed by KOH in alcoholic solutions at high temperatures [16]. Other basic solids such as hydrotalcites [17], complexes of group VII elements [18], anhydrous $RhCl_3$ [19] or alkali metals supported on alumina [20] were studied for isomerization of safrole.

This contribution focuses on the isomerization of safrole over amino-grafted mesoporous materials. The effects of the chemical compositions and the type of amine-grafted group on the matrices were studied.

2. Experimental

2.1. Catalysts preparation

Classical hydrothermal method [11] modified in the synthesis of Al-MCM-41 and Nb-MCM-41-64 were followed to prepare MCM-41 matrices [21,22]. The ammonium forms of MCM-41 (NH_4MCM-41, NH_4AlMCM-41 and NH_4NbMCM-41) were obtained via cation exchange with NH_4^+ ions from NH_4Cl solution, and transformed to hydrogen forms by calcination at 673 K for 2 h.

The hydrogen forms, H-AlMCM-41, H-NbMCM-41 and H-MCM-41, were the supports for grafting of 3-aminopropyl-trimethoxysilane (APMS), [3-(2-aminoethylamino) propyl] trimethoxysilane (2APMS) and 3-[2-(2-aminoethylamino)ethylamino] propyl-trimethoxysilane (3APMS) (Aldrich). The grafting process was carried out as follows: 2.3 g of the support powders were refluxed in a dry toluene solution (200 mL) with10 mL of APMS at 373 K for 18 h. After filtration and washing in dry toluene, water (100 mL) and acetonitrile (20 mL), the catalysts were recovered. Lately, the powder was dried in an oven at 373 K [14]. The catalysts so obtained were labelled as APMS/TMCM-41, 2APMS/TMCM-41, 3APMS/TMCM-41 (where T atom is Si, Al, Nb).

2.2. Catalysts characterization

The grafted materials were characterized using N_2 adsorption/desorption, XRD, thermogravimetric analysis, FT-IR spectroscopy and elemental analysis.

The N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. Amino-grafted mesoporous materials 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.

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

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

Infrared spectra were recorded with the Vector 22 (Bruker) spectrometer (resolution 4 cm^{-1}, number of scans = 64). The pressed wafers of the materials ($\sim$5 mg cm^{-1}) were placed in the vacuum cell and evacuated in the range of RT −673 K for 1 h.

Table 1
Amount of nitrogen and texture parameters of the catalysts in the amino-grafted MCM-41 materials.

Catalyst	Surface area BET (m^2/g)	Average pore diameter (nm)	Mesopore volume (cm^3/g)	N loading (mmol/g)
MCM-41	604	2.8	0.41	0.03
APMS/MCM-41	580	2.7	0.11	3.1
AlMCM-41	909	3.9	0.76	0.2
APMS/AlMCM-41	637	3.3	0.37	1.8
NbMCM-41	1049	3.8	0.96	0.1
APMS/NbMCM-41	707	3.2	0.44	2.0

2.3. Safrole isomerization

Isomeriztion of safrole was carried out in a batch reactor. Safrole (0.4 g) in 15 mL of DMF as solvent was heated while stirring in a two-neck glass reactor at atmospheric pressure in air, fitted with a condenser. The reaction was followed by GC–MS. An Agilent Technologies 6890N chromatograph using a 60 m-long phenyl–silicone capillary column and a flame ionization detector was used. Mass spectra were obtained in a Hewlett-Packard HP5971 A. Previously, it was confirmed that there is no control of the reaction rate by external or internal diffusion.

2.4. Recyclability of the catalyst

Recyclability of the materials was investigated in the isomerization of Safrole, in DMF at 453 K using the best catalyst, APMS/AlMCM-41. For the first reaction it was used the experimental protocol described above in Section 2.3. Subsequently, the catalyst was filtered and washed with dichloromethane and dried at 333 K in an oven before using for following cycle.

3. Results and discussion

3.1. Catalysts characterization

The textural data calculated from N_2 adsorption/desorption isotherms and XRD patterns are listed in Table 1. A decrease in the surface area of amino-grafted AlMCM-41 (about 30%) and ca. 33% drop in NbMCM-41 was observed. The volume of mesopore also decreases in the amino-grafted metallosilicate materials. The decrease in the mesopore volume after grafting of amines when compared with the pristine support suggests a blockage or collapse of some mesopores.

XRD patterns [14] of silicate and niobosilicate MCM-41 indicate that grafting of APMS on these materials leads to the lost of the hexagonal arrangement of mesopores in the long range, which is deduced from the drop of intensity of the XRD peaks at 2θ 3–5° (Supplementary data). It can be seen after normalisation of (1 0 0) peak to the same intensity value. Nevertheless, the disordering is less pronounced in amino-grafted AlMCM-41, which preserves the ordering of mesopores after APMS immobilization. Table 1 shows that the amount of nitrogen in the APMS-grafted materials differs depending on the chemical composition of the supports: APMS/MCM-41 > APMS/NbMCM-41 > APMS/AlMCM-41. The grafting of 2APMS and 3APMS on aluminosilicate support giving rise to a higher amount of nitrogen only slightly decreases the intensity of XRD reflexes indicating that even these amines do not change significantly the ordering of the material.

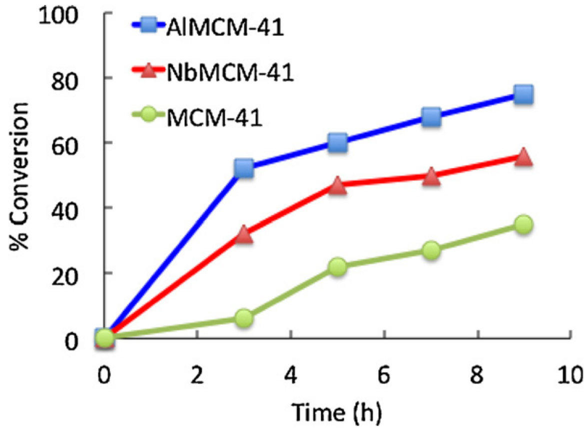


Fig. 1. Isomerization of safrole over amino-grafted MCM-41 materials with different T atoms. Safrole: 0.4 g, solvent: DMF (15 mL), catalyst: 0.25 g. Reaction temperature: 433 K.

The thermal stability of all APMS in MCM-41 type supports was estimated on the basis of infrared spectroscopy (FTIR) measurements after evacuation of the material at various temperatures and the thermogravimetric measurements. The full characterization of these samples was previously published by our group in Ref. [14].

The reaction of 2-propanol decomposition has been used as a test for basic-acidic properties of the samples and allows estimation of the nature of acidic and basic centres and the strength of the basic centres from the products formed [14]. The sequence of basicity of APMS-grafted MCM-41 materials when using this probe reaction is:

APMS/AlMCM-41 > APMS/NbMCM-41 > APMS/MCM-41

Knoevenagel test reactions for Lewis basicity of various strengths were applied for characterization of the materials prepared [14]. It is clearly evidenced that for the amino-grafting materials the order of activity is as follows:

APMS/AlMCM-41 > APMS/NbMCM-41 ≫ APMS/MCM-41

And the activity changes in the following order:

APMS/AlMCM-41 > 2APMS/AlMCM-41 > 3APMS/AlMCM-41

3.2. Isomerization of safrole

Isomerization of safrole to prepare isosafrole was used in this study to evaluate the activity of various amino-grafted MCM-41. Fig. 1 summarizes the safrole isomerization activity of various MCM-41. No isomerization products were observed in blank runs. All the amino-grafted catalysts showed considerable conversions, which vary with the T atom present in the structure of the pristine material. Then, safrole isomerization catalysed by APMS/MCM-41, in DMF at 433 K, afforded mixtures of safrole/isosafrole (cis/trans isomers) in 15:85 ratio with 35% of conversion after 9 h of reaction time. Trans isomer was predominantly obtained due to its higher thermodynamic stability as expected. APMS/NbMCM-41 and APMS/AlMCM-41 lead to higher conversions for the reactions as well as slight increase of trans isomer distribution as shown in Table 2. Among the assayed catalysts APMS/AlMCM-41 showed the maximum conversion at around 85% with a cis:trans ratio of 10:90. The reaction curves for APMS-grafted MCM-41 materials are presented in Fig. 1. It is clearly evidenced that the order of activity is:

APMS/AlMCM-41 > APMS/NbMCM-41 ≫ APMS/MCM-41

Table 2
Safrole isomerization to isosafrole over APMS-TMCM-41 catalysts.

Catalysts	Conversion[a] (%)	Isosafrole distribution (%)	
		Cis	Trans
APMS/MCM-41	35	15	85
APMS/NbMCM-41	56	10	90
APMS/AlMCM-41	85	10	90
Blank	–	–	–

[a] Safrole: 0.4 g; solvent: DMF (15 mL); catalyst: 0.25 g. Reaction temperature: 433 K. Reaction time: 9 h.

Table 3
Effect of solvent for the isosafrole preparation over APMS/AlMCM-41.

Solvent	Dielectric constant (ε)	Conversion[a] (%)	Isosafrole selectivity (%)	
			Cis	Trans
DMF	38.2	85	10	90
Acetonitrile	36.6	83	10	90
THF	7.5	65	15	85

[a] Safrole: 0.4 g; solvent: 15 mL; catalyst: 0.25 g. Reaction temperature: 433 K. Reaction time: 10 h.

This trend is in the line of activity sequence observed for Knoevenagel probe reaction and for 2-propanol decomposition [14]. When T atom in APMS/TMCM-41 was Al, amine groups in this APMS material resulted in the most basic centre, therefore, APMS/AlMCM-41 was the most efficient catalyst giving the highest conversions for isosafrole.

From the results mentioned above, AlMCM-41 was selected for further studies. The influence of the solvents was investigated. Table 3 shows the activity of this catalyst for safrole isomerization. DMF, acetonitrile and THF were employed. It was demonstrated that DMF and acetonitrile afforded the maximum activity around 85% with a isomer cis:trans ratio of 10:90.

From the results, it is evidenced that the conversion increases with an increase in the polarity of the selected solvents, which is in accordance with their dielectric constants. This trend is similar to those obtained by Tichit et al. [23] and Kishore and Kannan [24].

As expected, conversion of safrole increases with an increase in the reaction temperature (Fig. 2). The reaction was conducted at 413, 433 and 453 K, respectively and after 10 h of reaction time, it was observed a maximum conversion of safrole at 453 K with a value of 95%.

The role of the amino chain grafted to the mesoporous materials was also investigated. Table 4 shows conversions obtained after 10 h of reaction time when using as catalysts APMS-AlMCM-41, 2APMS-AlMCM-4 and 3APMS-AlMCM-41. Isomerization reaction

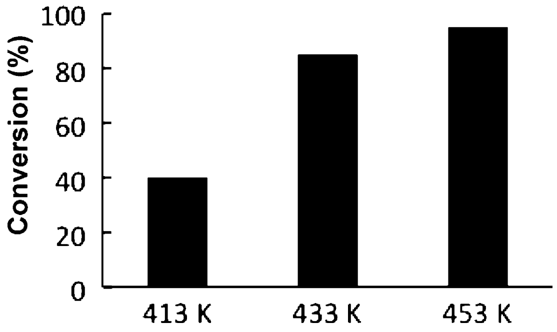
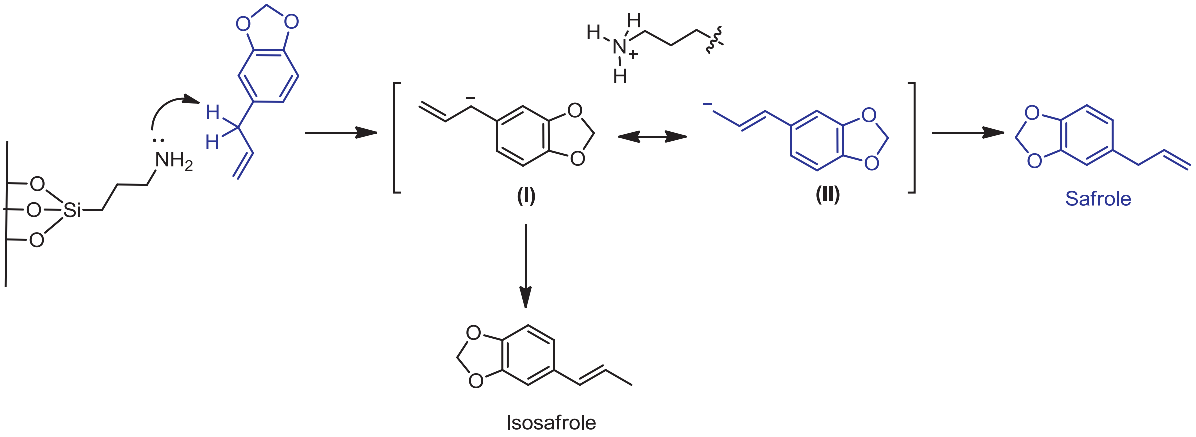


Fig. 2. Effect of the reaction temperature on the safrole isomerization. Safrole: 0.4 g, solvent: DMF (15 mL), catalyst: 0.25 g. Reaction temperatures: 413, 433 and 453 K. Reaction time: 10 h.



Scheme 2. Mechanism of safrol isomerization over APMS/AlMCM-41 catalysts.

was carried out in the presence of the best solvent, DMF, at 433 K, conversion values were in a range of 69–95%. Remarkably, safrole/isosafrole ratio was 1:9 in all the cases. The order of activity observed is:

APMS/AlMCM-41 > 2APMS/AlMCM-41 > 3APMS/AlMCM-41

Das and Sayari [25], and by Blasco-Jiménez et al. [14] obtained similar results for the amino-grafted silicate mesoporous materials. From this trend, it can be deduced that there is an optimum number of amines grafted groups to enhance the basicity of these mesoporous materials during the catalytic process. The presence of acidic sites located on the support (T atom = Al or Nb) produces a decrease of basicity on amine groups because of the possible chemical interaction as previously reported by us [14]; this acid–base interaction is increased when the aminohydrocarbon chain is longer even blocking the accessibility of the reagents and products. In this sense, too high concentration of amines decreases the activity due to its lower accessibility to the safrole. These results are in accordance with those reports by Sharma et al. [26].

Considering the possible mechanism presented in Scheme 2 in a first step, the amino group anchored to the mesoporous matrix may act as Brönsted basic site, abstracting the proton of the active methylene group of the allylic chain of safrole structure. This form is stabilized by resonance as a carbanion (structures I and II). In a second step, the carbanion is combined with a proton, affording the thermodynamically more stable isomer, isosafrole restoring the catalyst.

Recyclability of the mesoporous catalysts was tried on the isomerization of safrole in DMF at 453 K using the best catalyst, APMS/AlMCM-41; thus, the used material was filtered, washed and dried before using for the isomerization of safrole. No significant differences were observed for the second and third cycles, probably because of the absence of by-products as shown in Fig. 3. A small decrease in the conversion was noted in the fourth cycle (around 6%).

Table 4
Effect of the amino chains grafted to the Al-MCM-41 in the safrole isomerization.

Catalyst	Conversion[a] (%)	Isosafrole selectivity (%)	
		Cis	Trans
APMS/AlMCM-41	95	10	90
2APMS/AlMCM-41	81	10	90
3APMS/AlMCM-41	69	10	90

[a] Safrole: 0.4 g; solvent: DMF (15 mL); catalyst: 0.25 g. Reaction temperature: 453 K. Reaction time: 10 h.

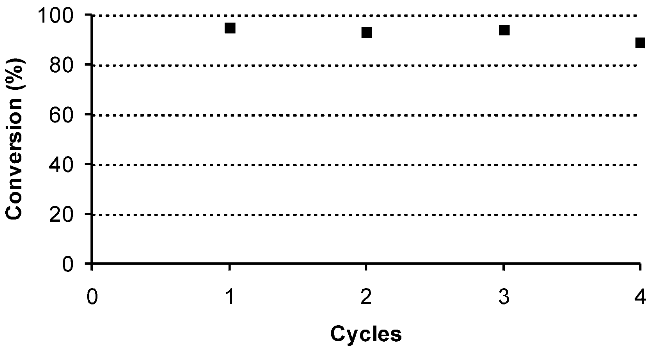


Fig. 3. Reusability of the APMS/AlMCM-41 on the safrole isomerization. Safrole: 0.4 g, solvent: DMF (15 mL), catalyst: 0.25 g. Reaction temperature: 453 K. Reaction time: 10 h.

4. Conclusions

Amino-grafted mesoporous materials T-MCM-41 where T = Al, Nb and Si were prepared by anchoring three different amino functionalized chains (with primary, secondary and tertiary amine groups; APMS, 2APMS and 3APMS, respectively). Isomerization of safrole was conducted over theses materials. Among the studied catalysts, APMS-AlMCM-41 showed conversions around 85% after 9 h, using DMF as solvent at 433 K. The conversion of safrole significantly depends on the nature of the support for grafted amine chains (APMS/AlMCM-41 > APMS/NbMCM-41 ≫ APMS/MCM-41). The polarity of the solvent is an important factor to enhance the formation of isosafrole, being DMF the optimum solvent to carry out the isomerization. The nature of the amine chain is also responsible of the achieved conversion of safrole to isosafrole. The order of activity is APMS/AlMCM-41 > 2APMS/AlMCM-41 > 3APMS/AlMCM-41. Basic amino groups attached to the mesoporous materials are probably the active sites involved in the isomerization reaction; incorporation of acidic sites on the support supposed an enhancement of the basicity of the amine groups in APMS/TMCM-41 when T = Al or Nb.

Acknowledgements

Authors thank Spanish MICINN (Projects CTQ2009-10478 and CTQ2010-18652) and Polish Ministery (Grant No. N N204 032536) for financial assistance. D.B.J. thanks the ERASMUS Program of EU for the possibility of doing research work at the A. Mickiewicz University (Poznan), and Universidad Nacional de Educación a Distancia (UNED) for a PhD Fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.09.031.

References

[1] Y. Ono, Catal. Today 38 (1997) 321.
[2] H. Hattori, Appl. Catal. A: Gen. 222 (2001) 247.
[3] R.A. Sheldon, I. Arends, U. Hanefeld, Green Chemistry and Catalysis, Wiley-VCH Verlag GmbH and Co. KgaA, Weiheim, Germany, 2007.
[4] W. Hölderich, Catal.Today 62 (2000) 115.
[5] A. Corma, Chem. Rev. 95 (1995) 559.
[6] V. Calvino-Casilda, A.J. López-Peinado, C.J. Durán-Valle, R.M. Martín-Aranda, Catal. Rev. 52 (2011) 82.
[7] J. Weitkamp, M. Hunger, U. Rymsa, Micropor. Mesopor. Mater. 48 (2001) 255.
[8] (a) R.M. Martín-Aranda, J. Cejka, Top. Catal. 53 (2010) 141;
(b) F. Domínguez-Fernández, J. López-Sanz, E. Pérez-Mayoral, D. Bek, R.M. Martín-Aranda, A.J. López-Peinado, J. Čejka, ChemCatChem 1 (2009) 241;
(c) I. Matos, E. Pérez-Mayoral, E. Soriano, A. Zukal, R.M. Martín-Aranda, A.J. López-Peinado, I. Fonseca, J. Cejka, Chem. Eng. J. 161 (2010) 377.
[9] (a) V. Calvino-Casilda, R.M. Martín-Aranda, Rec. Pat. Chem. Eng. 4 (2011) 1;
(b) E. Pérez-Mayoral, J. Čejka, ChemCatChem 3 (2011) 157.
[10] A. Taguchi, F. Schüth, Micropor. Mesopor. Mater. 77 (2005) 1.
[11] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, D.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[12] E. Sujandi, A. Prasetyanto, S.-E. Park, Appl. Catal. A: Gen. 350 (2008) 244.
[13] D. Blasco-Jiménez, I. Sobczak, M. Ziolek, A.J. López-Peinado, R.M. Martín-Aranda, Catal. Today 142 (2009) 283.
[14] D. Blasco-Jiménez, I. Sobczak, M. Ziolek, A.J. López-Peinado, R.M. Martín-Aranda, Catal. Today 152 (2010) 119.
[15] V. Calvino-Casilda, E. Pérez-Mayoral, R.M. Martín-Aranda, Z. Zienkiewicz, I. Sobczak, M. Ziolek, Top. Catal. 53 (2010) 179.
[16] G.V. Salmoria, E.C. Dall'Oglio, C. Zucco, Synth. Commun. 27 (1997) 4335.
[17] D. Kishore, S. Kannan, J. Mol. Catal. A: Chem. 223 (2004) 225.
[18] T. Carlen, A. Ludi, Helv. Chim. Acta 75 (1982) 1604.
[19] L. Cerveni, A. Krejeiknova, A. Marhoul, V. Ruzicka, React. Kinet. Catal. Lett. 33 (1987) 471.
[20] L.N. Thach, D-L. Hanh, N. Hiep Ba, A.S. Radhakrishana, B.B. Sing, A. Loupy, Synth. Commun. 23 (1993) 1379.
[21] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[22] M. Ziolek, I. Nowak, Zeolites 18 (1997) 356.
[23] D. Tichit, D. Lutic, B. Coq, R. Durand, R. Teissier, J. Catal. 291 (2003) 167.
[24] D. Kishore, S. Kannan, J. Mol. Catal. A: Gen. 244 (2006) 83.
[25] D.D. Das, A. Sayari, Stud. Surf. Sci. Catal. 170 (2007) 1197.
[26] K.K. Sharma, R.P. Buckley, T. Asefa, Langmuir 10 (2008) 14306.