

Titanium-modified MCM-41 Prepared by Ultrasound and by Hydrothermal Treatment, Catalysts for Acetylation Reactions

Deyanira Angeles-Beltrán,¹ Guillermo Negrón-Silva,^{*1} Leticia Lomas-Romero,² Martín A. Iglesias-Arteaga,³ Francisco J. Cadete Santos-Aires⁴

¹ Departamento de Ciencias Básicas y ²Departamento de Química, Universidad Autónoma Metropolitana, Av. San Pablo No 180, C. P. 02200, México D. F., México.

³ Facultad de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México, D.F. ⁴Institut de Recherches sur la Catalyse, Villerurbanne, France.

Recibido el 3 octubre de 2007; aceptado el 12 marzo de 2008

Abstract. Mesoporous materials type Ti-MCM-41 prepared by hydrothermal and ultrasound-assisted techniques were characterized by XRD, SEM, TEM, nitrogen physisorption, ammonia TPD, UV-vis and FT-IR. Both showed the MCM-41 characteristic structure. Hydrothermal treatment allowed obtaining a well ordered material and ultrasound procedure gave a better titanium distribution. Electronic microscopy images revealed Ti dispersion zones as well as the quantity of metal in the structure. The catalytic activity of these materials were tested by acetylation of aromatic and steroidal alcohols to afford the corresponding esters in good yields.

Key words: Ti-MCM-41, ultrasound technique, hydrothermal technique, mesoporous materials, acetylation.

Resumen. Por tratamiento hidrotérmico y por ultrasonido, se prepararon materiales tipo Ti-MCM-41 que fueron caracterizados por DRX, MEB, MET, fisisorción de nitrógeno, TDP de amoníaco y espectroscopías de IR y UV-vis. Ambos materiales mostraron ordenamiento característico de los materiales MCM-41. Se demostró que mediante la técnica de tratamiento hidrotérmico se obtuvo un material más ordenado pero, por la técnica de ultrasonido se logró mejor dispersión de titanio. Las imágenes de microscopía electrónica de barrido permitieron identificar las zonas de mejor distribución del Ti así como la cuantificación del metal en la estructura del MCM-41. La actividad catalítica de los materiales se probó en la acetilación de alcoholes aromáticos y esteroidales para obtener los ésteres correspondientes en buen rendimiento.

Palabras clave: Ti-MCM-41, técnica ultrasonido, técnica hidrotérmico, materiales mesoporosos, mesoporoso, acetilación

Introduction

MCM-41 type materials member of M41S family since its discovery [1] have been studied due to their textural features like pore size and exceptionally ordered porous arrangement, which allow diffusion of big organic molecules among its cavities. MCM-41 has been useful in different applications to catalysis [2], epoxidation of unsaturated alcohols [3] and transesterifications [4]. Corma and coworkers reported Ti-MCM-41 in 1994 [5] causing great interest on its structure and catalytic features. MCM-41 is doped with titanium in order to give it some redox sites, this procedure can be performed with the use of inorganic salts [6], colloidal precursors [7], using a CVD process at high temperatures [8] by refluxing the gel mixture at atmospheric pressure under stirring [9], sol-gel, or post-synthesis treatments [10]. Those techniques involve long processes that imply prolonged thermal treatments (2-10 days) at high temperatures (100-150°C). Ultrasound-assisted processes have been used in some different chemical reactions as well as materials synthesis, since sonochemical effects are useful to the preparation and modification of MCM-41 structure [11]. Ultrasound radiation procedures have been introduced in several chemistry processes including a variety of material synthesis [12]. The chemical effects of ultrasound derive primarily from acoustic cavitation, a phenomenon explained as continuous formation, growth and implosive collapse of bubbles formed within a liquid [13]. The high local temperatures and

pressures, combined with extraordinary rapid cooling, provide a unique means for driving chemical reactions under extreme conditions. Ultrasonic radiation used as materials synthesis procedure, allowed to shorten the times and favored good dispersion of metals. High quality silicon-MCM-41 was synthesized in three hours and its characteristics were reported [14]. Using that procedure titanium oxide was incorporated into MCM-41 pores [15], and then a variety of mesoporous materials had been obtained by ultrasonic deposition of catalyst into mesoporous [16, 17]. High-Resolution Electron Microscopy has revealed details of the mesoporous framework structures and their modifications [18].

The acetylation of alcohols is one of the most common methodologies for the hydroxyl group's protection. In addition to the highly contaminant standard procedure that uses the acetic anhydride/pyridine couple, some other catalytic procedures have been published. In particular, a recent report describes the fast and high yield acetylation of different alcohols using acetic anhydride and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The application of this methodology to acetylation of steroid sapogenins, results on the ring opening of the spiroketal side chain [19].

In this work we prepared and characterized Ti-MCM-41, two synthesis procedures were used: hydrothermal traditional treatment and ultrasound radiation. We describe the structural differences between both materials using several techniques: High-resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM), Fourier Transform-

Infrared (FT-IR), Ultraviolet-visible spectroscopy (UV-vis), X-Ray diffraction (XRD), Thermal Programmed Desorption of ammonia (TPD) and nitrogen physisorption (ASAP). Both Ti-MCM-41 materials were used as catalysts in the acetylation of simple aromatic alcohols (benzyl alcohol and 4-methoxybenzyl alcohol) and steroidal alcohols (diosgenin, sarsasapogenin and deoxycholic acid).

Results and discussion

Figure 1 displays the XRD pattern of Ti-MCM-41 samples prepared by hydrothermal and ultrasound treatments. Patterns correspond to hexagonal unit cell, the most intense peak corresponds to the (100) plane reflection and the others to (110) and (200) planes [20, 21]. Hydrothermal sample (DH) shows more intense principal diffraction peak than ultrasound sample (DU), indicating better order in hydrothermal material. Diffuse reflectance UV spectra of samples (fig. 2) exhibit an intense UV absorption band centered at 215 nm due to a charge transfer between oxygen atom to tetrahedral Ti (IV), as an evidence of titanium incorporation in both, but a wider band in ultrasound sample could show TiO₂ [22]. No bands of anatase were observed between 330-350 nm in hydrothermal sample spectrum. Ultrasound sample FT-IR spectra showed an intense absorption band at 960 cm⁻¹, assigned to Si-O-Ti bonds (Figure 3) and asymmetric stretching bands 1078 y 805 cm⁻¹ of bonds (Si-O-Si) [23]. Both samples showed isotherms of type IV of BET classification [24] presenting inflection around P/Po= 0.3-4.5 as a peculiar feature of mesoporous materials (Figure 4). Table 1 shows their superficial characteristics. Samples showed values close to 180 mmol NH₃/g by ammonia chemisorption in a TPD profile with two desorption peaks; the first one at almost 200 °C and the second one over 580 °C this gave us an idea of two different intensities of their acid sites. High Resolution Electron Transmission Microscopy

characterization by Fourier Transform of the sample prepared by hydrothermal treatment showed a highly ordered material with well formed channels in plane (010) or (100) and hexagonal pores that correspond to (100) plane (Figs. 5 and 6, respectively). Interplanar distances are same than calculated by XRD which are 38.65 Å. Interplanar distances could be calculated for both arrangements zones (Fig. 7) and two Ti dispersion regions were distinguished; a disordered zone which quantity of titanium is low and ordered zones where titanium is in higher quantities (Fig. 8). TEM analysis of ultrasound prepared sample shows less order grade than hydrothermal sample. Ti-MCM-41 prepared by ultrasound assisted treatment shows Ti probably in TiO₂ particles with an average sizes of are 4±1 nm, very close to the pore size of the MCM-41 (Fig. 9). Some observed regions do not contain any Ti and is detected in association with MCM-41 structure (Fig. 10). In these regions Ti is around 2% wt (Fig. 11). Most of the regions were Ti is detected in association with the MCM-41 structure are poorly crystallized (Fig. 12). Titanium was observed in «shells» or «belts» around MCM-41 type structure (Fig. 13). An EDS study performed by SEM demonstrated that titanium percentage present in a sample corresponds to TEM quantity reported (Table 2).

Catalytic evaluation results are shown in table 3. Ti-MCM-41 catalysts prepared by both procedures were used and results were similar.

Conclusions

Ultrasound technique demonstrated to be useful and shorter in Ti-MCM-41 synthesis. Titanium was incorporated in both cases nevertheless, high resolution transmission microscopy showed better dispersion in ultrasound assisted sample though this was meaning loss of order in its structure. Both Ti-MCM-41 samples showed zones of preferential deposit of

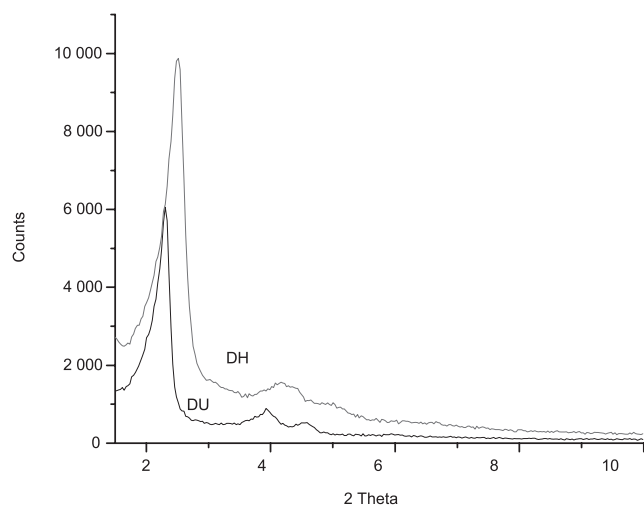


Fig. 1. XRD pattern of Ti-MCM-41 samples DU ultrasound assisted and DH hydrothermal treatments.

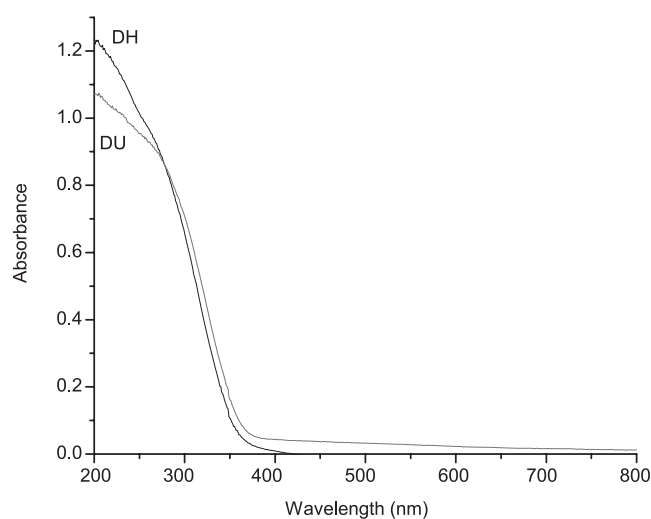


Fig. 2. UV-vis spectrum of Ti-MCM-41 samples.

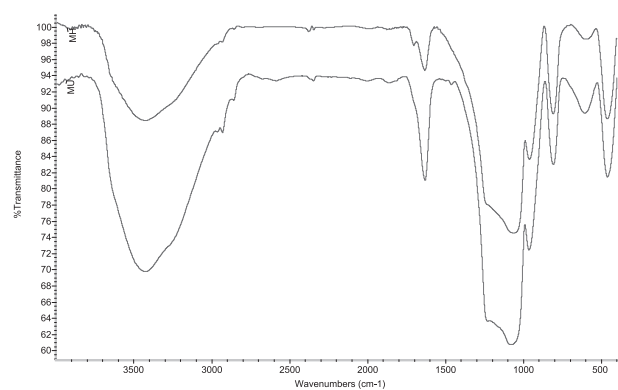


Fig. 3. FT-IR spectrum of Ti-MCM-41 samples.

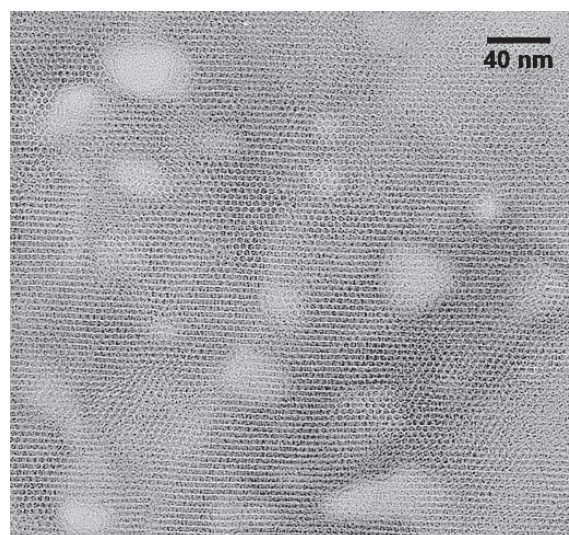


Fig. 6. TEM image for pores in DH sample.

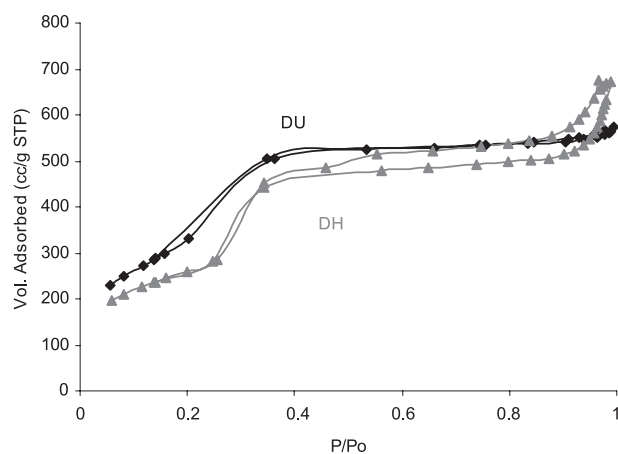


Fig. 4. Nitrogen Adsorption-desorption isotherm of Ti-MCM-41 samples.

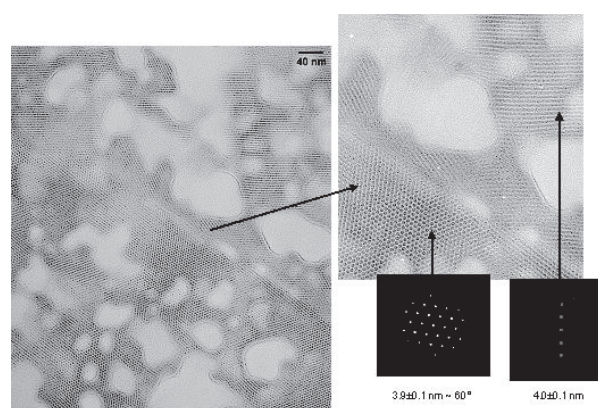


Fig. 7. High resolution TEM of DH.



Fig. 5. TEM image for channels in DH sample

Table 1. Surface properties of Ti-MCM-41 samples.

Sample	BET Area (m ² g ⁻¹)	Pore Volume (cc g ⁻¹)	Pore size (Å)
DH	950.03	0.94	39.82
DU	1233.10	0.87	28.21

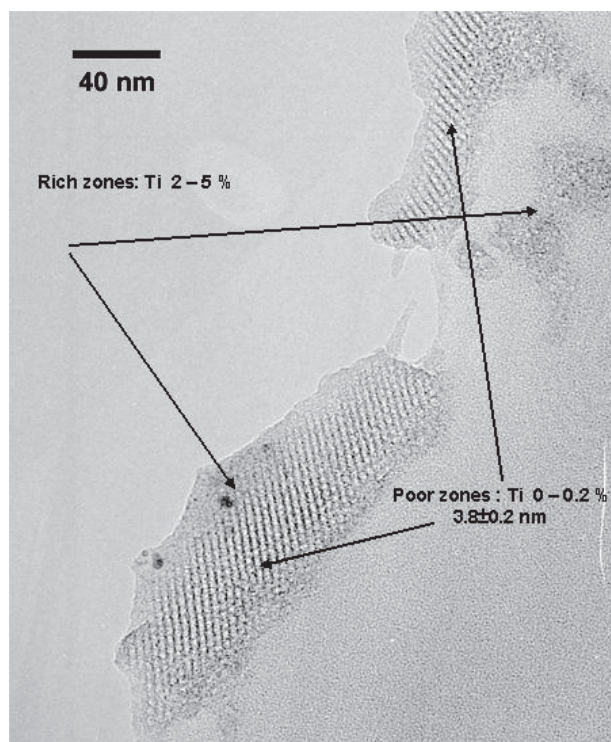


Fig. 8. Ti dispersion analysis of DH.

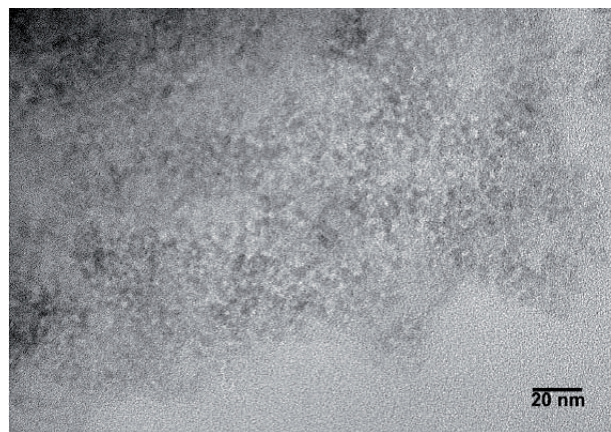


Fig. 9. TEM image for pores in DU sample.

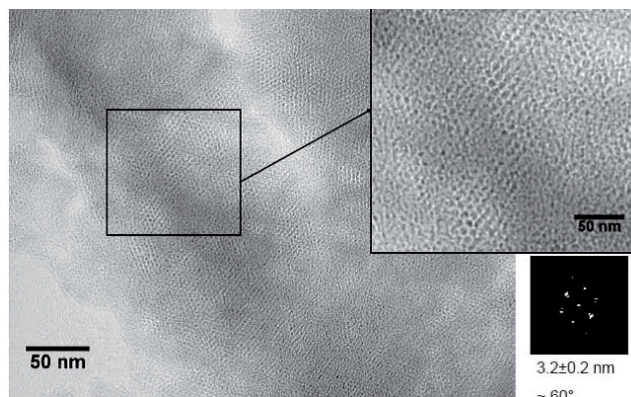


Fig. 10. High resolution TEM of DU.

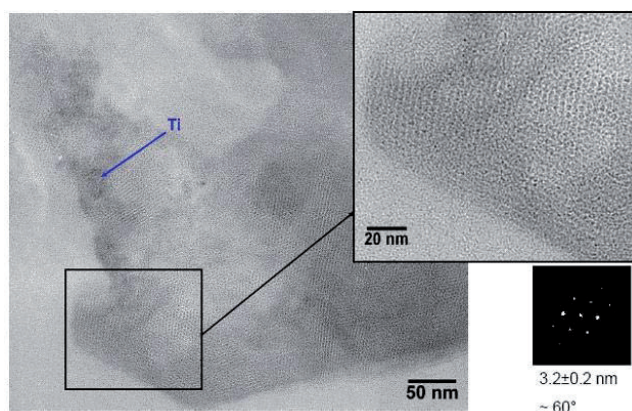


Fig. 11. Ti dispersion analysis of DU.

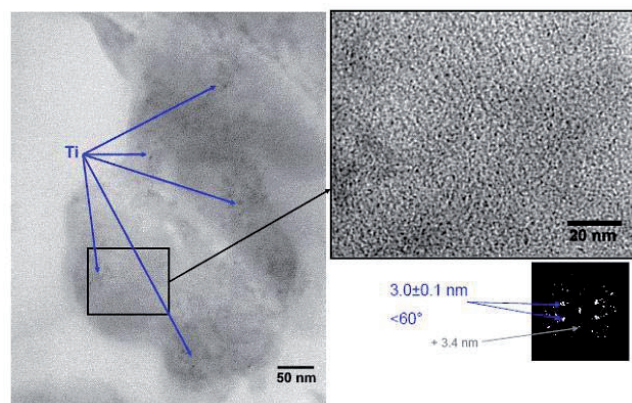


Fig. 12. Ti dispersion analysis of DU related with the pore order.

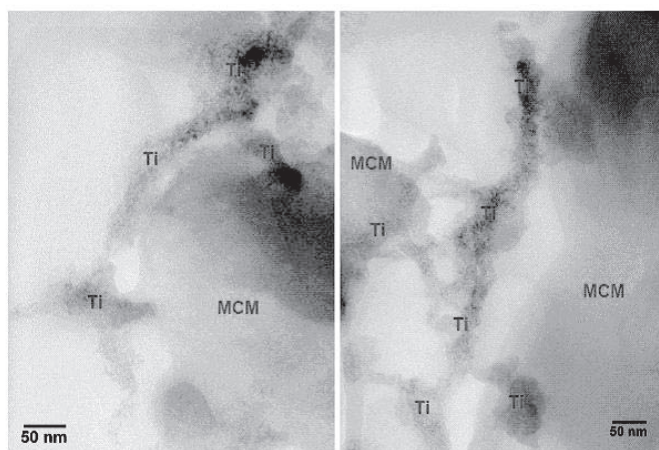
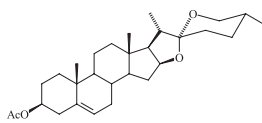
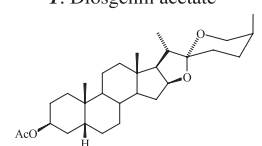
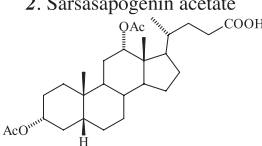
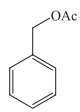
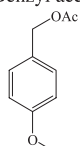


Fig. 13. Two Ti dispersion zones analysis of DU.

Table 2. EDS analysis results of Ti-MCM-41 samples.

Sample	% Si	% Ti	% O	% C
DH	28.54	1.21	46.50	8.29
DU	15.15	0.892	50.49	40.81

Table 3. Catalytic evaluation results.

Entry	Yield %
 1. Diosgenin acetate	70
 2. Sarsasapogenin acetate	91
 3. 3α,12α-diacetoxy-5β-cholanic acid	70
 4. Benzyl acetate	99
 5. 4-Methoxybenzyl acetate	99

the titanium; shells or belts but well ordered zones have not big quantities of the metal. We demonstrated that Ti-MCM-41 prepared by hydrothermic or ultrasound assisted treatments were efficient catalysts for acetylation reactions of alcohols. For acetylation of steroidal sapogenins this method was soft and convenient, because acetylation occurred on hydroxylic function in C-3 without the ring opening of the spiroketal side chain. We managed to replace other catalysts used frequently reactions acetylation reactions and to shorten reactions time.

Experimental

Ti-MCM-41 was prepared as follows; a gel molar composition TEOS:0.2CTMABr:0.02Ti:0.6EA:0.20TMAOH:150H₂O was treated via two procedures; the hydrothermal according to procedure described before [25], in a Parr Teflon-lined vessel during 69 h at 140 °C and the ultrasound assisted, in a sealed glass bottle for 3.5 h under ultrasound radiation at room temperature (Ultrasonic Cleaner Branson 5210). After treatment, solids were recovered and washed with deionized water. Ti-MCM-41 samples were calcinated at 600 °C for 7 h in air. Powder X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert instrument using Cu K-Alpha radiation (45kV, 40 mA). Nitrogen adsorption/desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2000 equipment. UV-vis diffuse reflectance spectra were performed with a Varian CARY 16 spectrometer using a quartz cell. Thermal Programmed Desorption of ammonia (TPD) measurements were recorded on a Micromeritics TPD/TPR 2900 instrument (samples were activated at 370 °C for 10 min in He flow (10 ml/min) and then saturation of ammonia at 100 °C (20% NH₃ in He) and desorption at 10 °C/min to 600 °C. High resolution transmission electron microscopy (TEM) analysis was made using a JEOL JEM 2010 200kV equipped with a LaB₆ electron gun, a high-resolution pole piece and a Pentafet Link ISIS EDS-X spectrum instrument. Scanning Electron Microscopy observations were done with a Leica-Zeiss LEO 440 Microscope. FT-IR spectra were recorded with a Nicolet Magna-IR 750 spectrometer by KBr tablet technique.

All acetylations were performed in a screw tip vial at room temperature in solvent-free conditions during 60 min. In a typical experimental were placed 0.25 mmol of diosgenin, 1 mL of acetic anhydride and 0.05 g of Ti-MCM-41. After reaction, catalytic material was recovered by filtration and washed several times with methylene chloride. The filtrated was washed twice with water and then with an aqueous solution of NaHCO₃ 10%, finally, organic extract was dried over sodium sulfate anhydrous and evaporated under reduced pressure, providing acetylated diosgenin. Acetylated products were identified GC-FID, mass spectra analyzed by GC-MS (Agilent 6890, Detector 5973) in methane chemical ionization and by comparison with authentic samples, which were obtained by the classic procedures [26] with the aid of FT-IR and NMR analysis (Varian Unity INOVA 300 MHz spectrometer using TMS for ¹H or the solvent signal CDCl₃).

(25R)-Spirost-5-en-3 β -ol acetate, Diosgenin acetate (Entry 1). m.p. 196-197 °C; GC-MSD for C₂₉H₄₄O₄: [M+1]⁺: 457, [M+29]⁺: 485, [M+41]⁺: 497; IR (cm⁻¹): 2937, 2905, 2891, 2866, 2840, 1719, 1450, 1377, 1366, 1237, 1037, 1001, 982, 962.

(25S)-5 β -Spirostan-3 β -ol acetate, Sarsasapogenin acetate (Entry 2). m.p. 143-144 °C; GC-MSD for C₂₉H₄₆O₄: [M+1]⁺: 459, [M+29]⁺: 487, [M+41]⁺: 499; IR (cm⁻¹): 2937, 2919, 2862, 1737, 1467, 1448, 1364, 1375, 1249, 1239, 1227, 1172, 1067, 1047, 1025, 984, 966, 919, 851.

3 α ,12 α -Diacetoxy-5 β -cholan-24-oic acid (Entry 3). m.p. 78-80 °C; GC-MSD for C₂₈H₄₄O₆: [M+1]⁺: 477, [M+29]⁺: 505, [M+41]⁺: 517; IR (cm⁻¹): 2926, 2869, 1734, 1708, 1449, 1378, 1363, 1244, 1028, 756. ¹H NMR (300 MHz, CDCl₃): 5.09 (m, 1H, H-12 eq.); 4.71 (m, 1H, H-3 ax.), 2.11 (s, 3H, CH₃ acetyl); 2.04 (s, 3H, CH₃ acetyl), 0.97 (s, 3H, H-19); 0.82 (d, J= 6.3 Hz, 3H, H-21) 0.73 (s, 3H, H-18).

Benzyl acetate (Entry 4). GC-MSD for C₉H₁₀O₂: [M+1]⁺: 151, [M+29]⁺: 179, [M+41]⁺: 191; IR (cm⁻¹): 3033, 2930, 1740, 1497, 1454, 1380, 1362, 1227, 1025, 965, 748, 697, 610, 492.

4-Metoxybenzyl acetate (Entry 5). GC-MSD for C₁₀H₁₂O₃ (mw: 180 g/mol): [M+1]⁺ = 181, [M+29]⁺ = 209, [M+41]⁺ = 221; IR (cm⁻¹): 2937, 2905, 2890, 2839, 1722, 1612, 1514, 1451, 1377, 1363, 1302, 1235, 1175, 1034, 982, 962.

Acknowledgments

We thank to CONACyT for the scholarship granted and Dirección General de Asuntos del Personal Académico (DGAPA-UNAM) for financial support (project IN200105).

References

1. Beck, J. S.; Vartulli, J. C.; Kennedy, G. J.; Kresge, C. T.; Schramm, W. *J. Chem. Mater.* **1994**, 2, 1816-1821.
2. Corma, A. *Chem. Rev.* **1997**, 97, 2373-2419.
3. Berlini, C.; Guidotti, M.; Moretti, G.; Psaro, R.; Ravasio, N. *Catal. Today* **2000**, 60, 219-225.
4. Srinivas, D.; Srivastava, R.; Ratnasamy, P. *Catal. Today* **2004**, 96, 127-133.
5. Corma, A.; Navarro, M. T.; Pérez-Pariente, J. *J. Chem. Soc. Chem. Commun.* **1994**, 147-148.
6. Lu, Y.; Lu, G. Z.; Guo, Y. L.; Wang, Y. S. *Cat. Commun.* **2002**, 3, 129-134.

7. A. Mohammed, A. D.; Stein, A. *Chem. Mater.* **2003**, 15, 2638-2645.
8. Li, K. T.; Lin, C. C. *Catal. Today* **2004**, 97, 257-261.
9. Laha, S. C.; Kumar, R. *Mic. Mes. Mat.* **2002**, 53, 163-177.
10. a) Anunziata, O. A.; Beltramone, A. R.; Cussa, J. *Appl. Catal. A: Gen.* **2004**, 270, 77-85. b) Ahn, W. S.; Lee, D. E.; Kim, T. H.; Seo, G.; Ryoo, R. *Appl. Catal.* **1999**, 181, 39-49.
11. S. Suslick, K. S. *Science* **1990**, 247, 1439-1445.
12. Zhu, J.; Koltypin, Y.; Gedaken, A. *Chem. Matter.* **2000**, 12, 73-78.
13. Suslik, K. *MRS Bulletin*, April **1995**, 29-34.
14. Tang, X.; Liu, S.; Wang, Y.; Huang, W.; Sominiski, E.; Palchik, O.; Koltypin, Y.; Gedanken, A. *Chem. Commun.* **2000**, 2119-2120.
15. Wang, Y.; Tang, X.; Yin, L.; Huang, W.; Rosenfeld, Y.; Gedanken, A. *Adv. Mater.* **2000**, 12, 1183-1186.
16. Gedanken, A.; Tang, X.; Wang, Y.; Perkas, N.; Koltypin, Y.; Landau, M. V.; Vradman, L.; Herskowitz, M. *Chem. Eur. J.* **2001**, 7, 4546-4552.
17. Perkas, N.; Wang, Y.; Koltypin, Y.; Gedanken, A.; Chandrasekaran, S. *Chem. Commun.* **2001**, 988-989.
18. Thomas, J. M.; Terasaki, O.; Gai, P. L.; Zhou, W.; González-Calbet, J. *Acc. Chem. Res.* **2001**, 34, 583-594.
19. a) Das, B.; Venkataiah, B.; Madhusudhan, P. *Synth. Commun.* **2002**, 32, 249-252. b) Breton, G. W. *J. Org. Chem.* **1997**, 62, 8952-8954. c) Martínez-Pascual, R.; Viñas-Bravo, O.; Meza-Reyes, S.; Iglesias-Arteaga, M. A.; Sandoval-Ramírez, J. *Synth. Commun.* **2004**, 34, 4591-4596. d) Sandoval-Ramírez, J.; Castro-Méndez, A.; Meza-Reyes, S.; Reyes-Vázquez, S.; Santillán, R. L.; Farfán, N. *Tetrahedron Lett.* **1999**, 40, 5143-5146. e) Sandoval-Ramírez, J.; Meza-Reyes, S.; Del Río, R. E.; Hernández-Linares, G.; Suárez-Rojas, A.; Rincón, S.; Farfán, N.; Santillán, R. L. *Steroids* **2003**, 68, 199-204.
20. He, J.; Ma, H.; Guo, Z.; Evans, D. G.; Duan, X. *Topics in catalysis.* **2003**, 22, 41-51.
21. Bhaumik, A.; Tatsumi, T. *J. of Catal.* **2000**, 189, 31-39.
22. Chao, M. C.; Lin, H. P.; Mou, C. Y.; Cheng, B. W.; Cheng, C. G. *Catal. Today* **2004**, 97, 81-87.
23. Alba, M. D.; Luan, A.; Klinowski, J. *J. Phys. Chem.* **1996**, 100, 2178-2182.
24. Webb, P. A.; Orr, C. *Analytical Methods in Fine Particle Technology*. Micromeritics Instruments Corp. (Ga., USA, 1997).
25. Ángeles Beltrán, D.; Maubert Franco, A. M.; Lomas Romero, L.; Lara Corona, V. H.; Cárdenas, J.; Negrón Silva, G. *J. Mex. Chem. Soc.* **2003**, 47, 155-159.
26. a) Hajipour, A. R.; Mazloumi G. *Synth. Commun.* **2002**, 32, 23-30. b) Hossein, E.; Parvaneh, S. *J. of Chem. Res.* **2004**, 12, 802-805. c) Tochtrop, G. P.; DeKoster, G. T.; Cistola, D. P.; Covey, D. F. *Bio. & Med. Chem. Lett.* **2002**, 12, 433-435. c) Tochtrop, G. P.; DeKoster, G. T.; Cistola, D. P.; Covey, D. F. *Bioorg. Med. Chem. Lett.*, **2002**, 12, 433-435. d) Kantam, M. L.; Khathija, A.; Likhar P. R. *Catal. Commun.* **2006**, 484-487. e) Khazaei, A.; Rostami, A.; Tanbakouchian, Z.; Zinati, Z. *Catal. Commun.* **2006**, 7, 214-217. f) Kamal, A.; Khan, M. N. A.; Reddy, K. S.; Srikanth, Y. V.; Krishnaji, T. *Tetrahedron Lett.* **2007**, 48, 3813-3818.