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Nanosized MCM-22 zeolite using simple non-surfactant organic growth modifiers: synthesis and catalytic application.

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1.- Experimental Methods

1.1.- Zeolite synthesis

1.1.1.- Synthesis of the N-butyl-N-methylhexamethyleneiminium (BMH)

The synthesis of the BMH is a modification of the synthetic protocol described by Pomelli et al. (C. Chiappe, C. S. Pomelli and S. Rajamani, *J. Phys. Chem. B*, 2011, **115**, 9653-9661)

Step 1: Synthesis of N-butylhexamethyleneiminium bromide

The reaction was carried under argon atmosphere. 60.88 g of 1-bromobutane (0.445 moles) was added during 1 hour, dropwise under stirring, to a dry-DMF hexamethyleneimine solution (44.14 g; 0.4436 moles, 250 ml). Then, the resulting mixture was heated up to 70°C and reacted overnight. A white crystalline solid was formed under the course of the reaction. When the reaction was concluded, the crude was cooled in an ice-bath to complete crystallization of the solid. The product was then separated by filtration and the crystals were washed with an ethyl acetate-hexane solution to remove traces of dimethylformamide. Finally, the product was dried at reduced pressure.

Elemental Analysis ($C_{10}H_{22}BrN$). %N: 5.969; %C: 50.717; %H: 9.903 (Exp.). %N: 5.93; %C: 50.85; %H: 9.39; %Br: 33.83 (Calc.)

Step 2: Synthesis of N-butylhexamethyleneimine

The bromide salt obtained in the previous step (50.39 g; 0.2133 moles) was dissolved in 400 ml of distilled water. Then, 22.61 g of anhydrous Na_2CO_3 (0.2133 moles) was added and the solution was left to react under strong stirring at room temperature over 1 hour. The free amine was formed in the upper part of the biphasic solution. Then, the solution was decanted and the organic phase was reserved. The organic phase was washed with NaCl saturated solution (100 ml) and dried with anhydrous $MgSO_4$. Finally, *N*-butylhexamethyleneimine was isolated as a dense transparent liquid after filtration.

^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 0.90 (t, CH_3, 3*H*); 1.30 (m, CH_2, 2*H*); 1.44 (m, CH_2, 2*H*); 1.62-1.65 (m, CH_2; 8*H*); 2.4 (m, CH_2, 2*H*); 2.61 (m, CH_2, 4*H*).

^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 14.06 (CH_3); 20.79 (CH_2); 26.99 (CH_2, 2); 27.97 (CH_2); 29.76 (CH_2); 55.57 (CH_2, 2); 58.11 (CH_2).

Step 3: Synthesis of N-butyl-N-methylhexamethyleneiminium (BMH)

Caution: highly exothermic reaction. A solution of N-butylhexametilenimine (21.84 g; 0.141 moles) in 200 ml of chloroform was added to a two-neck round flask, provided with stirring and a glass condenser. The mixture was cooled in an ice-bath (0°C) and then, 39.91 g of iodomethane was added dropwise (0.281 moles) over 1 hour time. When the solution was stabilized at room temperature, the mixture was left to react 72 h. Once the reaction was finished, the solvent was removed under reduced pressure and the product was isolated after crystallization with ethyl acetate. *N*-butyl-*N*-methylhexamethyleneiminium iodide was achieved as a white solid (40.01 g; 0.1346 moles).

The resultant iodide salt was used directly in the synthesis gel.

Elemental Analysis ($C_{11}H_{24}IN$). %N: 4.654; %C: 44.386; %H: 8.489 (Exp.). %N: 4.71; %C: 44.45; %H: 8.14; %I: 42.70 (Calc.).

^{1}H-NMR (300 MHz, D_2O), δ (ppm): 0.89 (t, CH_3, 3*H*); 1.32 (m, CH_2, 2*H*); 1.63 - 1.70 (m, CH_2; 6*H*); 1.82 (m, CH_2; 2*H*); 2.94 (s, CH_3, 3*H*); 3.23 (m, CH_2, 2*H*); 3.27-3.44 (m, CH_2, 4*H*).

^{13}C-NMR (75 MHz, D_2O), δ (ppm): 12.90 (CH_3); 19.28 (CH_2); 21.40 (CH_2, 2); 23.94 (CH_2); 27.24 (CH_2, 2); 50.17 (CH_3); 64.38 (CH_2, 2); 65.01 (CH_2).

1.1.2.- Synthesis of the conventional MCM-22

Standard MCM-22 was synthesized following the procedure describe in the literature (A. Corma, C. Corell and J. Pérez-Pariente, *Zeolites*, 1995, **15**, 2-8). The synthesis was carried out dissolving sodium aluminate ($NaAlO_2$; 58,9% Al_2O_3, 38,7% Na_2O, 2,4% H_2O, Carlo Erba) and sodium hydroxide (NaOH, 20% in water) in double-distilled water. After that, hexamethyleneimine (HMI 99%, Sigma Aldrich) was added to the solution while stirring. Finally, fumed silica (particle size = 0.007 µm, Sigma Aldrich) was also added. The mixture was maintained under stirring for 1 hour to obtain a homogeneous gel. The final gel composition was SiO_2 : 0.042 Al_2O_3 : 0.3 NaOH : 0.5 HMI : 40 H_2O. Sequentially, this gel was hydrothermally treated in Teflon-lined stainless steel autoclave with 60 rpm rotation at 423 K for 7 days. Finally, the quenched sample was filtered, washed with distilled water until pH<9, and dried at 363 K overnight. The organic material was removed by calcination in air at 823 K for 8 h.

To obtain the acidic material, the calcined MCM-22 was ion exchanged with a 1.0 M ammonium chloride solution (1.0 g zeolite in 10 ml solution) at 353 K for 3 h. The sample was filtered and washed with deionized water. Finally, the calcination was carried out in air at 623 K for 4 h, resulting in the acid form of the zeolite.

1.2.3.- Synthesis of the nanosized MCM-22 [MCM-22(n)]

The synthesis of the nanosized MCM-22(n) was carried out dissolving sodium aluminate ($NaAlO_2$; 58,9% Al_2O_3, 38,7% Na_2O, 2,4% H_2O, Carlo Erba) and sodium hydroxide (NaOH, 20% in water) in double-distilled water. After that, the required amount of BMH was added to the solution while stirring. Then, when all solids were completely dissolved, hexamethyleneimine (HMI 99%, Sigma Aldrich) and fumed silica (particle size = 0.007 µm, Sigma Aldrich) were added, and the mixture was maintained under stirring for 1 hour to obtain a homogeneous gel. The final gel composition was SiO_2 : 0.042 Al_2O_3 : 0.3 NaOH : 0.1 BMH : 0.4 HMI : 40 H_2O. The resultant gel was hydrothermally treated in Teflon-lined stainless steel autoclave with 60 rpm rotation at 423 K for 10 days. Finally, the quenched sample was filtered, washed with distilled water until pH<9, and dried at 363 K overnight. The organic material was removed by calcination in air at 823 K for 8 h.

To obtain the acidic material, the calcined MCM-22(n) was ion exchanged with a 1.0 M ammonium chloride solution (1.0 g zeolite in 10 ml solution) at 353 K for 3 h. The sample was filtered and washed with deionized water. Finally, the calcination was carried out in air at 623 K for 4 h, resulting in the acid form of the zeolite.

1.2.- Characterization

Synthesized samples were characterized by powder X-ray diffraction (PXRD) measurements collected on a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 35 mA, and using Cu Kα radiation (λ = 0.1542 nm).

The chemical analysis was determined by a Varian 715-ES ICP-Optical Emission spectrometer, after dissolution of the solids in HNO_3/HCl/HF aqueous solution.

The morphology of the samples was studied with a Field-Emission Scanning Electron Microscopy (FESEM) using a ZEISS Ultra-55 microscope and with Field-Emission Transmission Electron Microscopy (TEM) using a JEM 2100F microscope.

Nitrogen adsorption isotherms at -196°C were measured on a Micromeritics ASAP 2020 with a manometric adsorption analyzer to determinate the textural properties of the samples.

The solid-state NMR spectra were recorded at room temperature with a Bruker AV 400 MAS spectrometer. ^{27}Al MAS NMR spectra were recorded at 104.2 MHz with a spinning rate of 10 kHz and 9^{o} pulse length of 0.5 µs with a 1 s repetition time. ^{27}Al chemical shift was referenced to $Al^{3+}(H_2O)_6$.

Infrared spectra with adsorption-desorption of pyridine were carried out on self-supported wafers (10 mg·cm^{-1}) activated at 673 K and 10^{-2} Pa for 2 h. After sample activation, pyridine vapor (6.5x10^{2} Pa) was admitted into the vacuum IR cell and adsorbed onto the zeolite at room temperature. Desorption was performed under vacuum over three consecutive 1 h periods of heating at 423, 523, and 623 K, each followed by a Nicolet 710 FT-IR spectrometer measurement at room temperature. All spectra were scaled according to the sample weight. Adsorption of ditertbutyl pyridine (DTBP) was performed similarly, but with desorption done only at 423 K.

1.3.- Catalytic test

The acidic materials were used to catalyze the liquid-phase alkylation of benzene with propene at 398 K, 3.5 MPa, and a space velocity of 100 h^{-1}. The reaction was performed in a stainless-steel fixed-bed reactor, and the composition of the outlet stream was analyzed on-line on a Varian-450 gas chromatograph equipped with a 30 m 5% phenyl / 95% dimethyl polysiloxane capillary column connected to a flame ionization detector.

2.- Tables

Table S1: Acidity of the calcined materials as determined by FT-IR combined with absorption of basic probe molecules followed by desorption at different temperatures

Sample	Acidity – Pyridine (μmol·g^{-1})						Acidity – DTBP (μmol·g^{-1})	Accessibility factor (AF)
	B150	B250	B350	L150	L250	L350	B150´	B150'/ B150
MCM-22	364	342	259	77	61	-	101	0.28
MCM-22(n)	308	296	234	105	83	-	126	0.41

3.- Figures

Figure S1: TEM images of the conventional MCM-22 zeolite

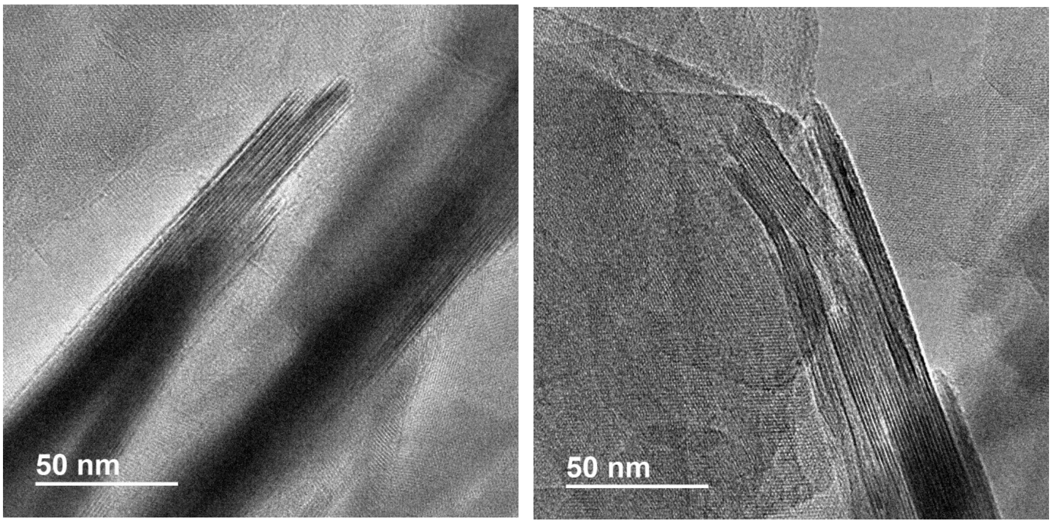

Figure S2: TEM images of the nanosized MCM-22(n) zeolite

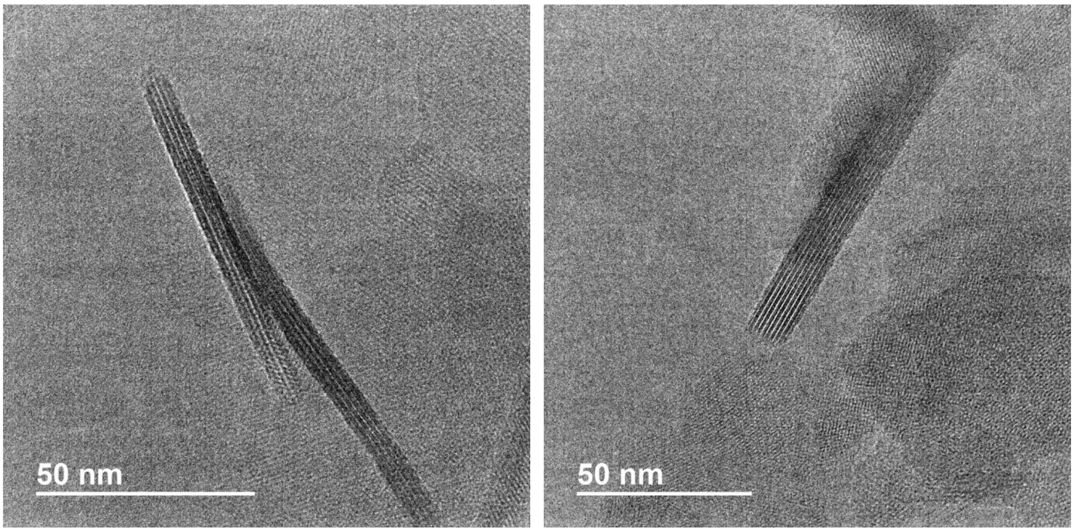

Figure S3: ^{27}Al MAS NMR spectra of the calcined MCM-22 samples

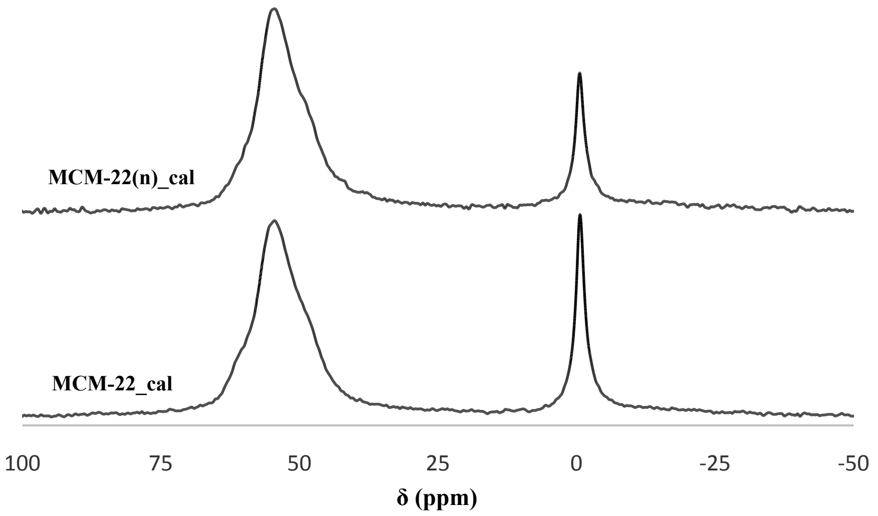

Figure S4: Transmission FT-IR spectra in the stretching C-C region of the different MCM-22 samples after adsorbing pyridine (a) and DTBP (b) followed by desorption at 150°C

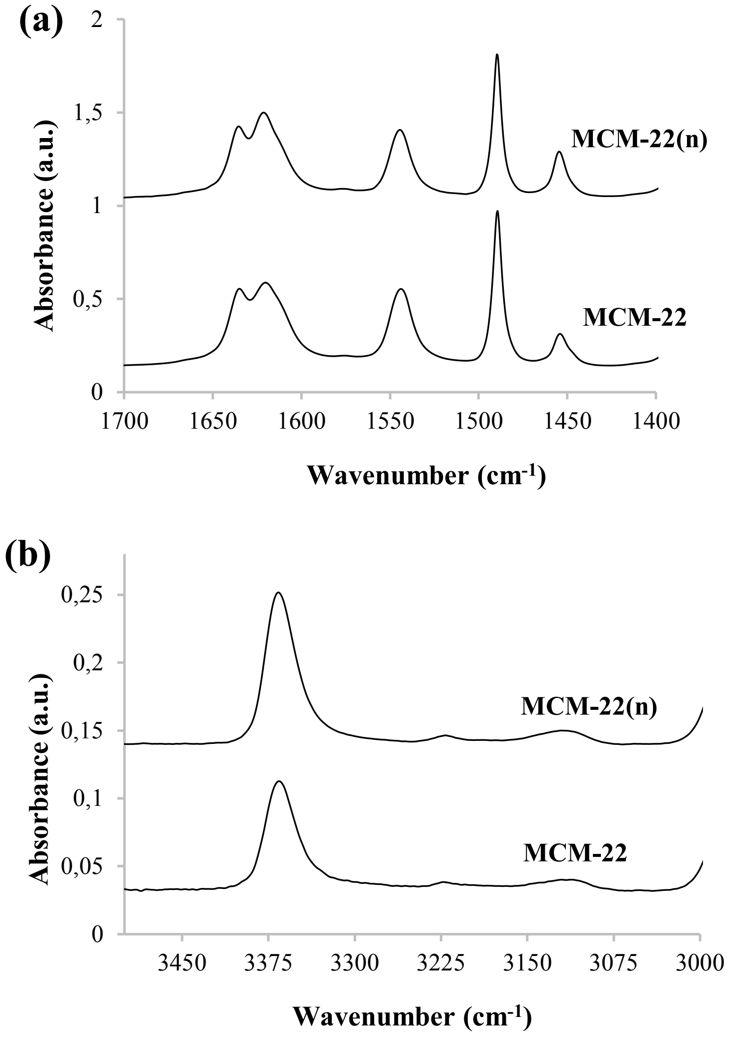

Figure S5: Selectivity to cumene (a) and di-isopropylbenzene (b) with TOS for the liquid phase alkylation of benzene with propylene using the synthesized MWW catalysts