CIENCIA 23(1), 30 - 38, 2015
Maracaibo, Venezuela

Kaolin as a Feedstock for a Versatile Synthesis of Composite MFI/MCM-41 with Enhanced Catalytic Properties

Freddy E. Imbert[1*], Eleida Sosa[1], Sergio L. González-Cortés[1,2], Fernando Aguirre[1], Pedro Rodríguez[1], Alvaro Uzcátegui[1], Andrés Eloy Mora[3], Gema González[4], Marlín Villarroel[1], Lynda Belandria[1], Claudio Lugo[1], and Jorge Férnandez[3]

[1]Laboratorio de Cinética y Catálisis, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101 Venezuela.
[2]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK.
[3]LAQUEM Facultad de Ciencias, Universidad de Los Andes, Mérida 5101 Venezuela
[4]Laboratorio de Materiales, Centro de Ingeniería III, Instituto Venezolano de Investigaciones Científicas, Altos de Pipe, Carretera Panamericana Km 11, Los Teques Venezuela

Recibido: 27-10-14 Aceptado: 27-02-15

Abstract

Kaolin was used as an efficient and low cost feedstock for the synthesis of MFI/MCM-41 compo-site material, zeolite type MFI and Al-MCM-41, using TPA and CTAB as structure directing agents. First, the MFI was synthesized from kaolin, the obtained MFI was treated with NaOH solutions (1-4M), subsequently the reaction mixture was treated under MCM-41 synthesis conditions and the MFI/MCM-41 composite material was obtained. The materials were characterized by XRD, nitrogen adsorption/desorption isotherms, SEMEDX, TEM and TPD-NH_3. The activity, selectivity and catalytic stability were evaluated in the m-xylene transformation reaction. In the absence of alkaline treatment two phases were observed-zeolite and mesoporous material. The alkaline treatment partially dissolved the zeolite structure, modifying the characteristic zeolite morphology, reducing its crystal domains and creating mesoporosity. The zeolitisized kaolin treated with 2 or 3M NaOH showed a significantly higher density of strong acid sites than the parent zeolites, therefore with high catalytic activity, with *p/o* and D/I selectivities similar to that of MCM-41, combining the best of both structures, the MFI high catalytic stability and activity, and the MCM-41 lack of diffusion limitation and the possibility of bulky transition state formation. The alkaline treatment eases zeolite dissolution and leads to the SBU assemble around the surfactant and into the mesoporous walls.

Keywords: composite materials; nanostructure; chemical synthesis; kaolin; MFI/MCM-41.

---

* Corresponding author: imbert@ula.ve

Caolín como materia prima para síntesis versátil de materiales compuestos tipo MFI/MCM-41 con propiedades catalíticas mejoradas

Resumen

Caolín venezolano fue empleado como materia prima eficiente y de bajo costo para la síntesis de materiales compuestos tipo MFI/MCM-41, zeolita MFI y Al-MCM-41, usando TPA y CTAB como agentes directores de estructura. Primero, se sintetizó la zeolita MFI a partir de caolín, luego la zeolita obtenida fue tratada con NaOH (1-4M), y subsecuentemente la mezcla de reacción se trató en condiciones de síntesis de MCM-41, así se obtuvieron los materiales compuestos tipo MFI/MCM-41. Los materiales fueron caracterizados mediante DRX, adsorción/desorción de nitrógeno, MEB-EDX, MET y TPD-NH_3. La actividad, selectividad y estabilidad catalítica fueron evaluadas en la reacción de transformación de *m*-xileno. En los materiales compuestos preparados sin tratamiento alcalino se observaron dos fases – la zeolita y el material mesoporoso. El tratamiento alcalino parcialmente disuelve la estructura de la zeolita, modifica la morfología característica de la zeolita, reduce el tamaño de los dominios cristalinos y crea mesoporosidad. Una vez que la zeolita es sintetizada a partir del caolín, su tratamiento con 2 ó 3M NaOH facilita la disolución y conduce al ensamblaje de las SBU de la zeolita alrededor del surfactante incorporándolas en las paredes del material mesoporoso, confiriéndoles una densidad de sitios ácidos fuertes mayor que la zeolita de partida, en consecuencia con alta actividad catalítica, similar a la de la zeolita MFI, y selectividades *p/o* y D/I similares a las del material mesoporoso MCM-41. El material compuesto obtenido combina lo mejor de ambas estructuras: la alta actividad y estabilidad catalítica de la MFI, por una parte y la ausencia de limitaciones difusionales y la posibilidad de formación de estados de transición voluminosos de la MCM-41.

Palabras clave: materiales compuestos; MFI/MCM-41; nanostructuras; síntesis; caolín;

Introduction

There is a great deal of industrial processes that requires acid solid catalysts to replace the traditional ones, because of porous dimension constrain. The oil refining industry faces the present challenge to process heavier crudes and the demand for better quality fuels [1]. As a consequence, there is a great interest to develop molecular sieves that combine large pores and super acid sites, which may catalyze bulky bimolecular reactions, such as alkylation [2]. The zeolites are widely used as catalysts, particularly by the petroleum industry, due to their high acidity, thermal stability and high selectivity in a variety of chemical reactions. However, considering the pore dimensions, their catalytic properties are limited to molecules with kinetic diameters lower than 1 nm. This limitation can be overcame employing mesoporous materials (2-50 nm), that allow the diffusion of bulkier molecules, but they have certain limitations for their industrial use, as a consequence of their low hydrothermal stability, acidity, and ion exchange capacity. Building the mesopore wall with zeolite units represents an excellent alternative, combining the best properties of both materials. Some approaches started by synthesizing the mesopore material and then trying to zeolitisize the amorphous wall [3]; however, the low stability of MCM-41 wall, in zeolite synthesis conditions limits this method. Other methods synthesize first the zeolite and then try to assemble the zeolite to form the mesopore structure [4-12], in both cases a mixture of phases was obtained. The xylene gas phase transformation over acidic catalysts is used as a model reaction to characterize the pore structure and acidity [13,14]. Isomerization and transalkylation of alkylaromatics are used commercially to a large extent in the production of important petrochemicals [15,16].

The aim of the present work is to synthesize composite materials type MFI/MCM-41, using a low cost Venezuelan kaolin and sodium silicate as a convenient and efficient Si-Al sources, furthermore to study the effects of several parameters such as zeolitisation period, CTMAB/Si ratio, and alkaline treatment on the properties and catalytic performance of the composite MFI/MCM-41 obtained.

Materials and methods

Catalyst preparation

Whatever the synthesis venezuelan kaolin (Si/Al=1) and sodium silicate produced in Venezuela (GlassVen) were used as aluminum and silica sources, both easily accessible and economical. Tetra propylamonium Bromide (TPAB, Merck-Schuchardt, 99%) and cetyltrimetylamonium bromide (CTAB, Merck 98% TLC) were used as structure directing agents for MFI and MCM-41, respectively. The scheme followed for the zeolitisation of kaolin, the preparation of the composite material type MFI/MCM-41 (micro/mesoporous) and Al-MCM-41 is illustrated in figure 1 and

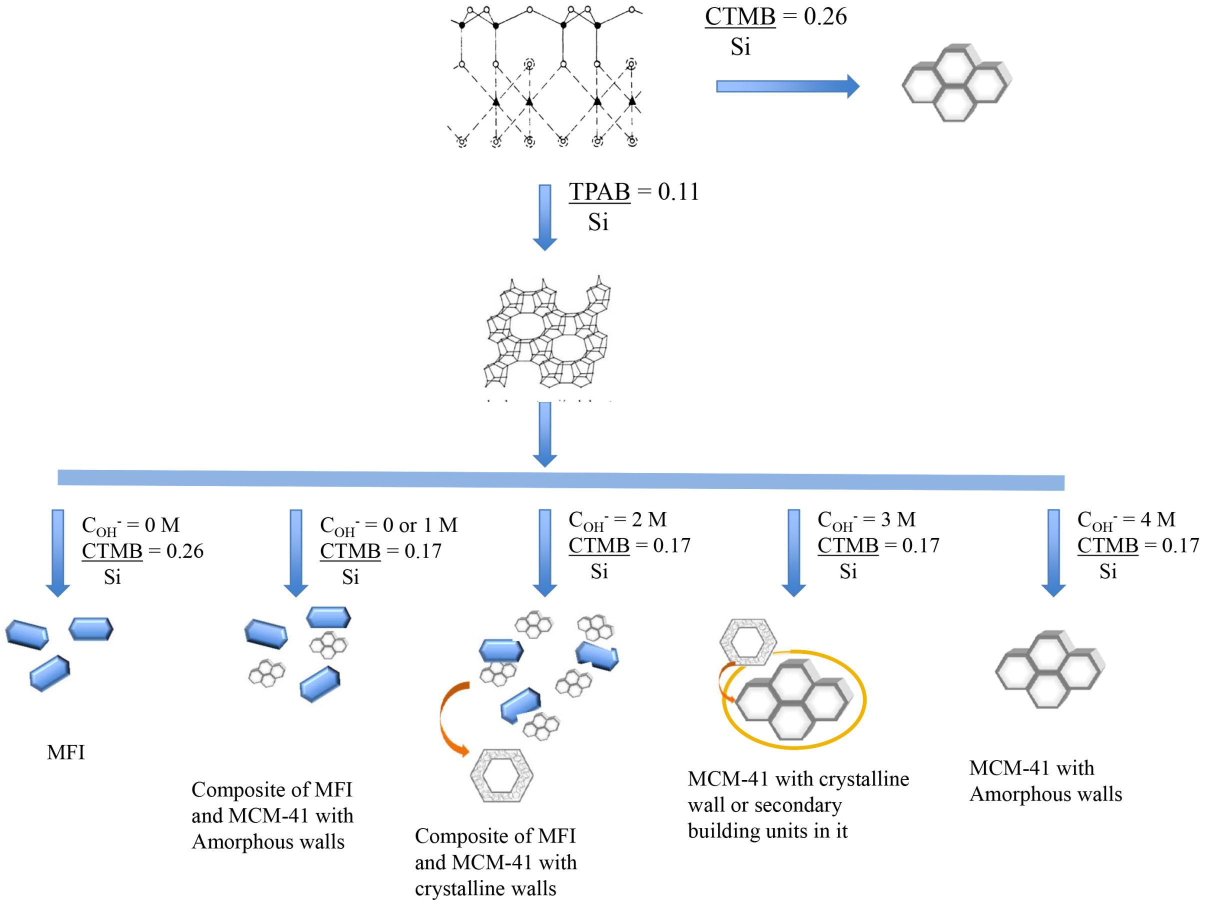

Figure 1. Scheme of kaolin transformation to MFI, Al-MCM-41 and composite materials type MFI/MCM-41. Effect of CTAB/Si ratio and of alkaline concentration.

was already reported elsewhere [17- 21]. The samples of MFI were coded MFI(t_{ZC}), in brackets the crystallization period, the composite MFI/MCM-41 samples were coded: ZM17***x*-*t*$_{zc}$**, when prepared directly from the previously synthesized zeolite: ZM17-18, ZM17-24, ZM26-18 and ZM26-24, where CTAB/Si was 0.17 for the first two, and 0.26 for the last two; the numbers -18 or -24 correspond to the kaolin zeolitization period (i.e., 18 or 24 h); when an alkaline treatment was applied the ***x*** represents the molarity of the NaOH (1, 2, 3 or 4 M) solution; thus, for example, the code: ZM172-18 indicates that the sample was obtained from a zeolite treated with NaOH 2M and CTMAB/Si = 0.17. To obtain the acid form, the samples were ion exchanged with NH_4NO_3, then filtered, washed, dried and calcined at 520°C for 6 h.

Characterization

The X-ray diffractograms were recorded with a diffractometer PHILLIPS PW 1050/25. Low angle X-ray diffractograms were recorded on a Siemens model D5005 diffractometer, using a Cu Kα (λ=1.5406Å) radiation, in the 2θ interval from 1 to 7° and a path of 0.02° a time step of 0.8s. The unit cell parameter (a_0) for MCM-41 was calculated taken into account, that it has a hexagonal symmetry ($a_0 = 2d_{100}/\sqrt{3}$). The surface areas and pore volume were measured in a Micromeritics analyzer, model ASAP 2010 at 77K. The scanning electron microscopy was done on a Hitachi model S-2500 with a THERMO NORAN SYSTEM SIX for imagine capture and EDX chemical semi-quantitative analysis. The transmission electron microscopy analysis was made on a Philips model CM10. The acidity was evaluated by NH_3 programmed thermodesorption measurements, carried out on a Micromeritics TPD/TPR 2900.

Catalytic test

The catalytic behavior was evaluated in the *m*-xylene isomarization at 350°C, the reactant was fed to the reactor at 2 cm^3h^{-1} using a perfusion pump (Harward Apparatus), as a carrier gas was employed N_2 with a flow of 30 cm^3min^{-1}. The effect of time-on-stream (*tos*, s) was measured between 60 and 180 s. The *m*-xylene/N_2 mixture was fed to a pyrex down flow continuous fixed bed reactor, in line with a gas chromatograph (Hewlett Packard 5890), equipped with an Chrompack Cp-Cresol capillary column (100 m x 0.2 mm x 0.5 μm film), a FID, and an Hewlett Packard integrator model 3392A. The catalyst mass (0.1 g) was pre-treated in situ at 450 ºC in 30 cm^3min^{-1} of N_2.

Results and discussion

The calcined kaolin an economical source of Si and Al was employed successfully for the synthesis of pure phases of microporous type MFI, mesoporous type MCM-41 and micro/mesoporous composite materials type MFI/MCM-41 as evidenced by SEM, TEM, XRD and N_2 adsorption at 77 K and reported previously [18,19,21]. The acidity was evaluated by TPD-NH_3 where the peak position in the thermogram is related to the acid site strength; those peaks at T < 300ºC (**A1**) are due to weak acid sites and to physisorbed ammonium and the peaks at T > 300°C correspond to chemisorbed ammonium associated to strong acid sites (**A2**) catalytically active [22-25]. The deconvolution results of TPD-NH_3 profiles (A1 and A2) are given in table 1. The composite material synthesized from kaolin without alkaline treatment or with low NaOH concentration (1 M) have strong acid density similar to the starting zeolite materials (see fig 2). However, when the treatment is carried out with 2 or 3 M, the strong acid site density is significantly higher than that of the parent zeolite. This effect of the alkaline treatment on the acidity is shown in figure 2. Thus, the incorporation of zeolite secondary building units (SBU) into mesoporous walls, in these conditions, creates greater amount of acid sites and as strong as those of the parent zeolite. In these conditions the silicon and aluminum species coming from both the media and the zeolite are arranged into the mesoporous walls in such way that contributes to the increasing

Table 1.
Acidity (TPD-NH3) of MFI, mesoporous and composites MFI/MCM-41 synthesized from kaolin with CTAB/Si = 0.26.

Solids	Total Acidity (mmol/g)	A1 (mmol/g)	A2 (mmol/g)
Al-MCM-41	1.39	1.05	0.34
MFI (3h)	1.43	1.32	0.11
MFI (6h)	1.30	1.07	0.23
MFI (12h)	1.40	1.03	0.37
MFI (18h)	1.81	1.37	0.44
MFI (24h)	1.99	1.45	0.54
ZM260-18	2.34	1.79	0.55
ZM260-24	2.72	2.15	0.57

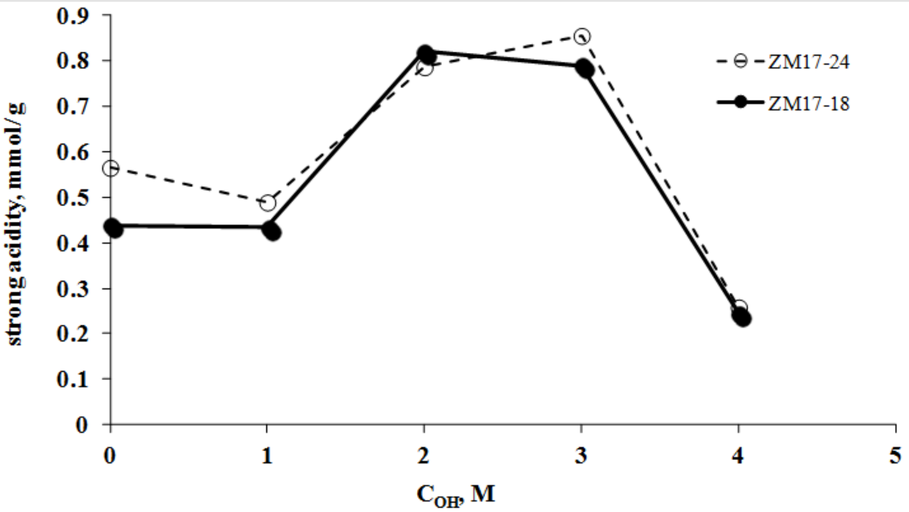

Figure 2. Effect of alkaline concentration treatment on strong acidity of composite MFI/MCM-41.

number of strong acid sites. Given the facts that, the morphology observed by SEM for ZM173-18 or ZM173-24 was homogeneous [18, 21], i.e. MFI morphology was not observed, the MFI XRD peak showed broadening and lower intensity, and the acidity grew (table 1), the incorporation SBU of the MFI into the mesoporous structure could be a possibility. Just the incorporation of aluminum atoms in the mesoporous framework would not explain the composite acidity. It is necessary the SBU of MFI in the mesoporous wall to achieve the acid strength observed.

The *m*-xylene conversion on Al-MCM-41 decreased with *tos* [18], while on zeolites type MFI synthesized from kaolin showed catalytic stability [18], and the conversion increased with zeolite crystallization time, since the amount of structural aluminum increased and therefore the number of acid sites, as shown in fig. 3. The activity per acid site increased up to t_{zc} = 18 h. Thus, the catalyst synthesized for t_{zc} = 18 and 24 h showed the highest activity per acid site (turn over frequency, TOF). The zeolite MFI (24h, Si/Al = 27) showed 59 % higher acidity and a catalytic activity above 3 fold higher than that of Al-MCM-41 (Si/Al = 32). However, the initial (*tos* = 60 s) conversion on Al-MCM-41 appeared similar to that of a MFI synthesized between 6 and 12 h (figure 3).

The *m*-xylene conversion, for the composite MFI/MCM-41 materials synthesized from kaolin, showed that the catalytic activity as function of *tos* is stable and that the initial conversions depend lineally on the strong acidity amount (A2), see figure 3, resembling the MFI behavior and in contrast to MCM-41 behavior [18]. Furthermore, the samples treated with 2 or 3 M alkaline solution showed higher acidity and higher catalytic activity (i.e., ca. 35 %) than that for MFI (24) (i.e., ca. 28 %) (fig. 3). This can be possibly due to the higher acidity and accessibility to the acid sites caused by the removal of Si debris by the alkaline treatment. The possible effect of a particular arrangement of the SBU within the composite material walls that forms acid sites more active than those of parent zeolite are not rule out. Furthermore, Huang *et al* [4] reported for a MCM-41/ZSM-5 composite an improved catalytic activity compared to MCM-41 and to a mechanical mixture of MCM-41+ZSM-5, they explained this by an improved acidity and the presence of interconnected meso and micropore channel system. For solid treated with 4M NaOH the conversion drops drastically, even though its Si/Al ratio is still 30, perhaps as a result of an increase in Al_{octa}, according to the literature [13], and the zeolite SBU are completely destroyed.

The *p/o* selectivities are compared for typical MFI (18), Al-MCM-41 and a representative sample of the MFI/MCM-41 composite series (i.e., ZM173-24) in the figure 4. The *p/o* ratio for the series ZM17*x*-18 and ZM17*x*-24 are independent of *tos*, and are lower than that for MFI, as is clearly illustrated figure 4, Thus the composite retain the high activity of MFI eliminating diffusion limitation. Plotting *p/o* ratio as function of alkaline concentration (fig. 5), one can see that for the range of 0 to 1M, the ratio is constant and closed to the typical value of MFI, while decreasing at concentrations higher than 1M and below 3M. Then it stabilizes at 1.43-1.48 for 3-4 M (fig. 5), where as a consequence of alkaline treatment the zeolitisized kaolin is completely transformed to the mesopore structure. Thus, the samples treated with 2 or 3M reached higher acidity than that of MFI, while at the same time show a *p/o* selectivity of mesoporous solid.

The disproportionation reactions involve bulky bimolecular intermediates, re-

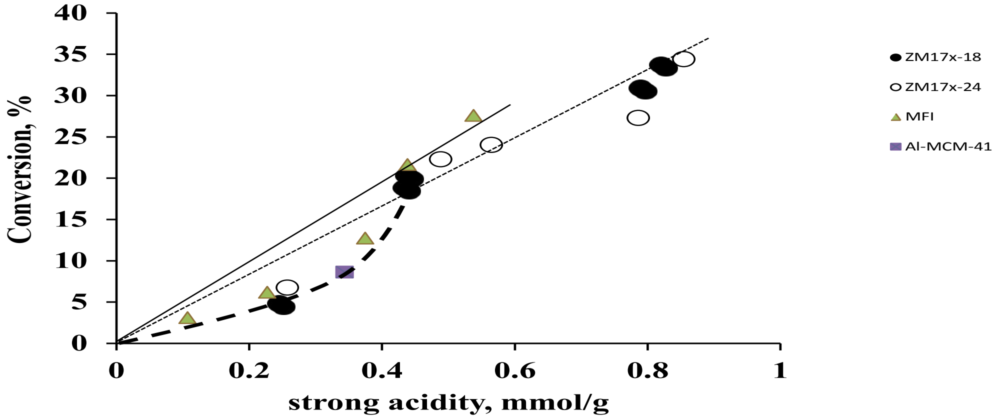

Figure 3. m-xylene conversion as a function of strong acid sites on zeolites MFI crystallized at different times, Al-MCM-41, ZM17x-18 and ZM17x-24

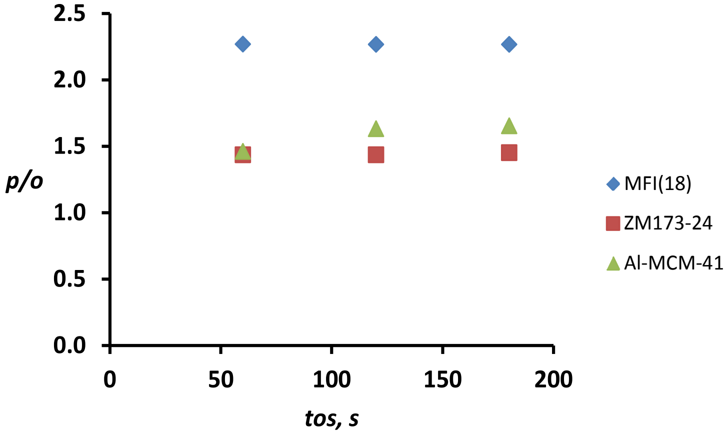

Figure 4. p/o-xylene on zeolite MFI, Al-MCM-41 and MFI/MCM-41 as function of tos.

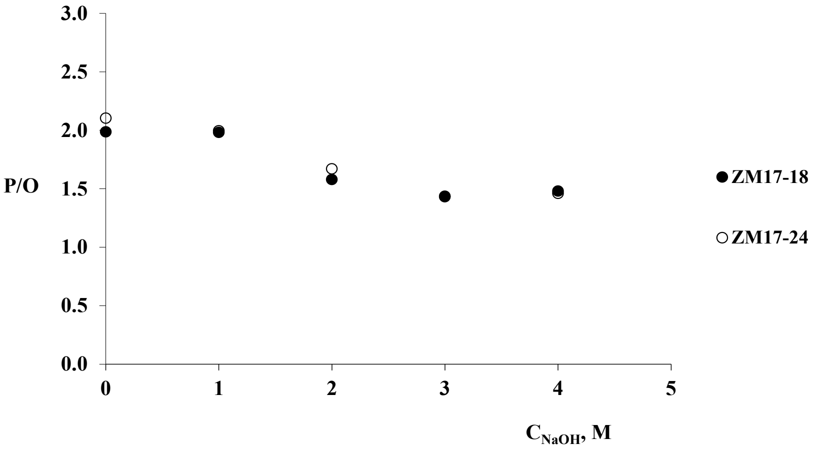

Figure 5. p/o-xylene on ZM17x-18 and ZM17x-24 as a function of alkaline concentration

quiring sufficient space at acid site for its formation, thus the Al-MCM-41 is ten times more selective to disproportionation than MFI, which are selective to monomolecular isomerization reactions. The disproportionation/isomerization (D/I) selectivity as function of *tos* for Al-MCM-41 and MFI is shown in figure 6.

The series of composite material prepared from kaolin shows, on one hand, that the D/I ratio is low and constant for 0 to 1 M of alkaline concentration. At low concentration essentially the pore structure corresponds to MFI, and as the concentration of the alkaline treatment grows, the D/I ratio increased up to 3 M (fig. 7), due to the rise of both the mesopore volume and the acid density, which allows the formation of bulky biphenyl methane intermediates and the desorption of trimethylbencenes. Though, for the highest concentration tested (4M), D/I selectivity drops as a consequence of diminished density (fig. 2 and 3) and strength of acid sites. For the composite materials ZM173-18 or -24, the D/I ratio is even higher than that for MCM-41 (fig 6), due to higher density and strength of the acid sites of the composite materials respect to Al-MCM-41. In turn this might suggest that some MFI SBU´s are incorporated in the mesopore wall.

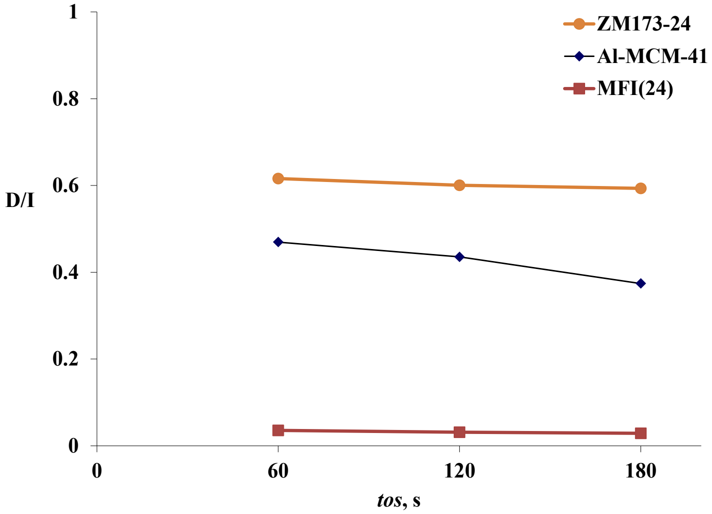

Figure 6. D/I selectivity as function of tos for: zeolites type MFI(24), Al-MCM-41 and ZM173 -24.

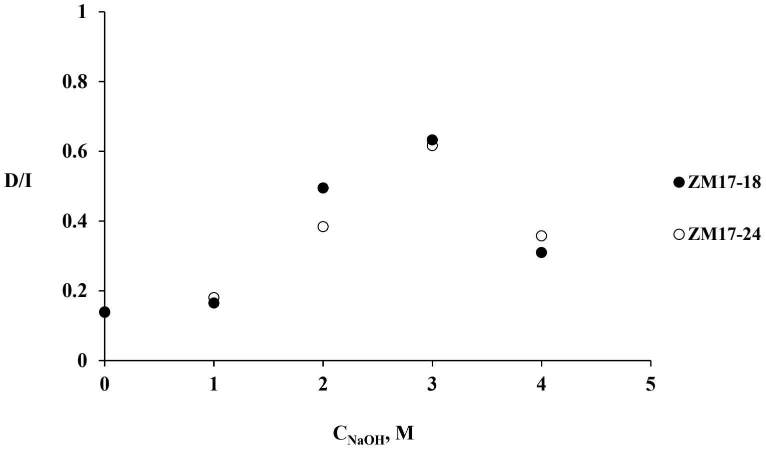

Figure 7. D/I selectivity on ZM17x-18 and ZM17x-24 as function of alkaline concentration.

Conclusions

Calcined kaolin is a good easily accessible and economical raw material for synthesizing MFI/MCM-41 composites materials using TPA and CTAB as structure directing agents. Also the calcined kaolin can be used to obtain both zeolite type MFI at relatively short crystallization time and Al-MCM-41. The CTMA/Si ratio affects the structural composition of the composite material, at higher ratio only MFI is obtained and as the ratio decreases a second phase - Al-MCM-41- appears. The MFI/MCM-41 composite materials obtained from zeolitisized kaolin synthesized with 2 or 3 M alkaline solution (ZM172-18 or ZM173-24) showed stable catalytic activity and higher activity than that of highly crystalline parent MFI (18) or MFI (24), due to a combination of a higher accessibility to the acid sites, and the particular arrangement of the MFI SBU within the composite material. Furthermore, these materials showed *p/o* and *D/I* selectivities characteristic of mesoporous solids.

Acknowledgements

The authors wish to acknowledge the financial support from CDCHT-ULA through the projects C-1603-08-08-EM, C-1460-07-08-A and C-1601-08-08-AA.

References

1. CORMA A., MARTÍNEZ A. ***The Chemistry of Catalytic Processes*** in: GUISNET M, GILSON JP (eds) ***Zeolites for Cleaner Technologies***. Imperial College Press. London. 29-56. 2002.
2. TAO Y., KANOH H., ABRAMS LL, KANEKO K. ***Chem Rev*** 106: 896-910. 2006.
3. HUANG L., GUO W., DENG P., XUE Z., LI Q. ***J Phys Chem*** B 104: 2817-2823. 2000.
4. LEE D, LIU T. ***React Kinet Catal Lett*** 72(2): 209-218. 2001.
5. MASIKA E., MOKAYA R. ***Chem Mater*** 23(9): 2491-2498. 2011.
6. WANG S., DOU T., LI Y., ZHANG Y., LI X., YAN Z. ***J Solid State Chem*** 177: 4800-4805. 2004.
7. HABIB S., LAUNAY F., LAFORGE S., COMPAROT J., FAUST A., MILLOT Y., ONFROY T., Montouillout V., Magnoux P., Paillaud J., Gédéon A. ***Appl Catal A: Gen*** 344: 61-69. 2008.
8. PÉREZ P., LÓPEZ C., SAZO V., URBINA C. ***Avanc Quím***, 5(2): 107-116. 2010.
9. LÓPEZ C., SAZO V., PÉREZ P., BUHMAN S., URBINA C., GARCIA A. ***Avanc Quím***, 6(2): 29-37. 2011.
10. NA K., CHOI M., RYOO R. ***Micro and Meso Mater*** 166: 3-19. 2013.
11. IVANOVA I.I. and KNYAZEVA E.E. ***Chem Soc Rev*** 42: 3671-3688. 2013.
12. Li X., Li B., Xu J., Wang Q., Pang X., Gao X., Zhou Zh., Piao J. ***Appl Clay Sci***, 50(1): 81-86. 2010.
13. GUISNET M., GNEP S.N., MORIN S. ***Micro Meso Mater*** 35-36: 47-59. 2000.
14. GIANNETTO G., MONTES A., RODRÍGUEZ G. ***Zeolitas***. Editorial Innovación Tecnológica, Caracas. 2000
15. HAIZMANN R. and SECHRIST P. A., US Patent US20120271071 A1
16. MARCILLY C. ***J. Catal***. 216: 47-62. 2003.
17. CONTRERAS Y. (2002) Síntesis de zeolitas tipo MFI y Mordenita a partir de alumino silicatos naturales. Trabajo Especial de Grado, Universidad de Los Andes
18. SOSA E. (2011) Síntesis y Caracterización de Aluminosilicatos Micro y Mesoporosos a Partir de Caolin Venezolano. Trabajo Especial de Grado MSc, Universidad de Los Andes
19. SOSA E., AGUIRRE F., RODRÍGUEZ P., UZCÁTEGUI A., MORA A. E., FÉRNANDEZ J., GONZÁLEZ G. AND IMBERT F. E., ***Acta Microscop***, 20(2): 157-164. 2011.
20. KANG F., WANG Q., XIANG Sh. ***Mater Lett*** 59: 1426-1429. 2005.
21. SOSA E., AGUIRRE F., RODRÍGUEZ P., UZCÁTEGUI A., MORA A. E., FÉRNANDEZ J., GONZÁLEZ G. AND IMBERT F. E., ***Avanc Quím*** 7(1): 65-75. 2012.
22. KATADA N., IGI H., KIM J-H., AND NIWA M. ***J Phys Chem B***, 101: 5969-5977. 1997.
23. NIWA M. AND KATADA N. ***Catal Surv Jpn*** 1: 215-226. 1997.
24. GONZÁLEZ-CORTES S.L., HERNÁNDEZ J.C., UZCÁTEGUI A., IMBERT F.E. ***Rev Soc Venez de Quím*** 21 (3): 11-21. 1998.
25. KATADA N. AND NIWA M. ***Catal Surv from Asia*** 8 (3): 161-170. 2004.