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Synthesis of Al-MTW with low Si/Al ratios by combining organic and inorganic structure directing agents

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A rationalized combination of alkali cations and bulky dicationic organic structure directing agents (OSDAs) has allowed the synthesis of the Al-rich MTW zeolites with Si/Al ratios of ~12 and large pore accessibility. ²⁷Al MAS NMR spectroscopy indicates that most of the aluminum atoms are in tetrahedral coordination in framework positions, and *in situ* infrared pyridine adsorption/desorption spectroscopy reveals strong Brönsted acidity after cationic exchange for the Al-rich MTW. In addition, another MTW material with a Si/Al ratio of 30 has been synthesized under alkali-free conditions using a bulky dicationic molecule such as OSDA, the lowest Si/Al ratio being achieved for a MTW zeolite synthesized in the absence of alkali-cations in the synthesis media. The catalytic activity of these MTW materials has been tested for the *n*-decane cracking reaction, achieving higher catalytic activities and olefin yields than other related large pore zeolites.

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1. Introduction

MTW is a one-dimensional large pore zeolite with pore openings of 5.6 \times 6.0 Å in its structure.¹ The first synthesized MTW structure was the high-silica ZSM-12 zeolite, by researchers of Mobil Oil Co with Si/Al ratios above 40.² In addition to ZSM-12, other zeolites presenting the MTW structure have been reported in the literature, such as TPZ-12,³ Nu-13,⁴ Theta-3,⁵ CZH-5,⁶ and VS-12,⁷ where the main differences between them are the chemical composition (introduction of different heteroatoms, such as V, Fe, Ti, among others) and/or the organic structure directing agents (OSDAs) used for their synthesis. Nevertheless, the most important form of the MTW structure is aluminosilicate (Al-MTW), since the incorporation of aluminum atoms in the MTW framework creates strong Brönsted acid sites, allowing the application of Al-MTW as a catalyst for several chemical processes, such as isomerization,⁸ alkylation and disproportionation of aromatic hydrocarbons,⁹ or cracking of hydrocarbons.¹⁰

Since the discovery of the high-silica ZSM-12 zeolite, the synthesis of the Al-rich MTW material has become a clear objective to improve its acidic properties.¹¹ Okubo *et al.* have recently described the synthesis of the Al-rich MTW zeolite under OSDA-free conditions using sodium aluminosilicate gels

following a seed-assisted methodology.¹² This seeding methodology has allowed the synthesis of Al-MTW zeolite with Si/Al ratios in the final product of almost 12 when the Si/Al ratio in the synthesis gel was fixed at 30.¹² This large difference between the theoretical and the final Si/Al ratios indicates that the zeolite yields achieved in the synthesis were very low. Nevertheless, the main problem of the Al-rich MTW zeolites synthesized following the OSDA-free methodology is their very low pore accessibility, since a micropore volume of 0.006-0.035 cm3 g-1 compared to regular MTW acid materials with a micropore volume of 0.12 $\text{cm}^3 \text{g}^{-1}$ was measured.¹² The possible reason for the low micropore volume of the MTW materials presented with the OSDA-free method could be the partial blocking of the one-dimensional channels due to the presence of structural defects.¹³ Indeed, the defects would be formed by the excessive positive charges introduced by the alkali-cations when used as single structure directing agents. In that case, the alkaline content is larger than the Al framework and the excess of positive charge is compensated by Si-O- framework groups, which become internal sylanols when the alkaline content is removed.

On the other hand, during the synthesis of MTW assisted by organic structure directing agents, samples with higher framework Si/Al ratios are achieved, and the filling of the pores requires a relatively small number of organic cations within the pores of the MTW zeolite. Then, their positive charge can be compensated by the negative charge associated with the presence of the Al framework, reducing therefore the formation of structural defects (internal sylanols).

Tetraethylammonium (TEA), methyltriethylammonium (MTEA), and benzyltrimethylammonium (BTMA)¹⁴ have been described as



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Fig. 1 Diquaternary ammonium compounds proposed as OSDA for the synthesis of the MTW structure.

the most common OSDAs for the synthesis of Al-MTW. Nevertheless, the lowest Si/Al ratios reported for the synthesis of pure Al-MTW phases using the above described monocationic OSDAs in combination with small inorganic cations are still limited to 25–30.¹⁴

Very recently, Li *et al.* have reported the synthesis of the Al-rich MTW structure using a bulky and complex dicationic OSDA, such as N,N,N',N'-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dypyrrolidinium, combined with the presence of potassium cations in the synthesis media.¹⁵

In addition, Zones *et al.* have systematically studied the synthesis of zeolites with OSDAs formed by diquaternary ammonium compounds of C4–C6 chain lengths with different heterocyclic end-groups.¹⁶ They observed that when the heterocyclic end-group was *N*-methylpiperidine (see OSDA-C4 in Fig. 1), the synthesis of aluminosilicates in alkaline media was very selective towards MTW, but the Si/Al ratios were larger than 40.¹⁶

The high selectivity of this linear OSDA towards MTW under alkaline synthesis conditions together with its dicationic nature, provide a unique opportunity to modulate the presence of positive charges within the MTW pores either in combination or in the absence of small inorganic cations and, therefore, to control the amount of aluminum atoms in the framework positions of MTW.

We will show here that the use of related linear dicationic OSDAs of different sizes (see Fig. 1), either in combination or in the absence of alkali metal cations (Na^+ or K^+), can direct the synthesis of Al-MTW zeolites toward materials with low Si/Al ratios in the final solids, while preserving the pore accessibility when the zeolite is activated. If this was achieved, the catalytic activity of MTW for acid catalyzed reactions should increase, opening further possibilities for its use, as will be shown here.

2. Experimental

2.1. Synthesis

2.1.1. OSDA preparation

OSDA-C2. The preparation was performed following a twostep procedure. In the first step, 1,2-bispiperidinoethane was prepared by reacting piperidine (0.1 mol) and 1,2-dichloroethane (0.025 mol) at 100 $^{\circ}$ C (80% yield). In the second step, the quaternary salt was achieved by direct alkylation of 1,1-bispiperidinoethane (0.02 mol) in acetonitrile with iodomethane (0.16 mol) at 40 $^{\circ}$ C. OSDA-C2 was obtained as a white solid.

Elemental analysis. N = 5.84; C = 35.17; H = 6.64 (found, %). N = 5.83; C = 35.02; H = 6.30 (calculated, %). Formula $(C_{14}H_{30}N_2I_2)$.

OSDA-C3. Piperidine (0.1 mol) was introduced into a twoneck round flask and, an aqueous NaOH solution (0.11 mol) was added to the flask and left to react for 15 min under vigorous stirring. Finally, 1,3-dibromopropane (0.05 mol) was added drop-wise and the resulting biphasic solution was heated at 80 °C for 12 h. Once the reaction was completed, the organic layer was separated from the crude, and washed with water (3 × 15 ml) and Brine solution (1 × 20 ml). Then, the organic layer was dried with anhydrous MgSO₄ and filtered. Finally, 1,3-bispiperidinopropane was obtained as a pale yellow oil, with 78% yield.

In a second step, 1,3-bispiperidinopropane (0.039 mol) was subjected to alkylation with iodomethane (0.195 mol) in a methanolic solution at 40 $^{\circ}$ C. The quaternary ammonium salt OSDA-C3 was obtained as white crystals after recrystallization (70% yield).

Elemental analysis. N = 5.60; C = 36.35; H = 6.64 (found, %). N = 5.67; C = 36.45; H = 6.53 (calculated, %). Formula $(C_{15}H_{32}N_2I_2)$.

OSDA-C4. 1-Methylpiperidine (0.15 mol) was dissolved in an argon atmosphere, in anhydrous *N*,*N*-dimethylformamide (50 ml). Then, under continuous stirring, 1,4-dibromobutane (0.075 mol) was slowly added and the reaction mixture was allowed to react at room temperature for 24 h. OSDA-C4 is obtained as a white solid (61% yield).

Elemental analysis. N = 6.78; C = 45.70; H = 9.21 (found, %). N = 6.76; C = 46.39; H = 8.27 (calculated, %). Formula $(C_{16}H_{34}N_2Br_2)$.

2.1.2. Zeolite synthesis. In a typical synthesis, alumina (74.6%, Condea) was dissolved in an aqueous solution formed by the hydroxide salts of the OSDA and the alkali cation (Na⁺ or K⁺). Colloidal silica (Ludox AS-40, Aldrich) was then added, and the gel was allowed to reach the desired silica to water ratio by evaporation. Finally, the gel was transferred to Teflon lined stainless autoclaves and heated at 175 °C for 14 days. The solids were recovered by filtration, extensively washed with distilled water, and dried at 90 °C overnight.

2.2. Characterization

Powder X-ray diffraction (PXRD) measurements were performed using a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 45 kV and 40 mA, and using Cu K_{α} radiation ($\lambda = 0,1542$ nm).

The chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO₃/HCl/HF aqueous solution. The organic content of as-made materials was determined by elemental analysis performed with a SCHN FISONS elemental analyser.

The morphology of the samples was studied by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope.

Textural properties were obtained from the $N_{\rm 2}$ adsorption isotherms measured at 77 K with a Micromeritics ASAP 2020 apparatus.

Solid NMR spectra were recorded at room temperature with a Bruker AV 400 MAS spectrometer. ²⁷Al MAS NMR spectra were recorded at 104.2 MHz at a spinning rate of 10 kHz and a 9° pulse length of 0.5 μ s with 1 s repetition time. ²⁷Al chemical shift was referred to as Al³⁺(H₂O)₆.

Infrared spectra were measured with a Nicolet 710 FT IR spectrometer. Pyridine adsorption–desorption experiments were made on self-supported wafers (10 mg cm⁻¹) of original samples previously activated at 673 K and 10^{-2} Pa for 2 hours. After wafer activation, the base spectrum was recorded and pyridine vapour (6.5×10^2 Pa) was admitted in the vacuum IR cell and adsorbed onto the zeolite. Desorption of pyridine was performed in vacuum over three consecutive one-hour periods of heating at 423, 523 and 623 K, each of them followed by the IR measurement at room temperature. The spectra were scaled according to the sample weight.

2.3. Catalytic test

n-Decane cracking experiments were performed at 500 °C, 60 s time on stream, and different zeolite to *n*-decane ratios in a microactivity test unit as described previously.¹⁷ Zeolites were pelletized, crushed, and sieved, and the 0.59 to 0.84 mm fraction was taken and diluted in 2.5 g of inert silica. For each catalyst, five experiments were performed, maintaining the amount of catalyst (cat) constant and equal to 0.5 g, and varying the *n*-decane amount fed (oil) between 0.77 and 1.54 g. Apparent kinetic rate constants were calculated by fitting the conversions (*X*) to a first-order kinetic equation for a plug flow reactor (1), assuming that the deactivation is enclosed in the kinetic constant and taking into account the volumetric expansion factor (2).

$$K = -(\operatorname{cat} \operatorname{oil}^{-1} \operatorname{TOS})^{-1} \left[\varepsilon X + (1 + \varepsilon) \ln(1 - X) \right]$$
(1)

$$\varepsilon = (\sum \text{molar selectivities of products}) - 1$$
 (2)

3. Results

3.1. Syntheses of Al-rich MTW zeolites

Based on the previous results,¹⁶ three related linear dicationic OSDAs with different sizes were synthesized and used as OSDAs for the synthesis of Al-rich MTW zeolites (see Fig. 1). The experimental design containing the synthesis conditions is summarized in Table 1. 54 synthesis experiments have been performed where the OSDAs, Si/Al, H₂O/Si, and alkali/Si ratios where varied. The phase diagram, achieved after the crystal-lization process at 175 °C for 14 days, shows the presence of amorphous materials and the formation of two different crystal-line phases, such as NON and MTW (see Fig. 2).

Variable	Values
OSDA type Si/Al H ₂ O/Si OSDA/Si Alkali/Si	OSDA-C2, OSDA-C3, OSDA-C4 INF, 30, 15 10, 30 0.25 (for alkali-free), 0.2 (for synthesis with alkali cations) 0, Na/Si = 0.1, K/Si = 0.1



Fig. 2 Phase diagram obtained for the synthesis of zeolites using different diquaternary ammonium compounds.

NON is a cage-like chlatrasil type structure with pore openings lower than 3 Å.¹⁸ This dense phase is preferentially obtained when using the smaller dicationic OSDAs (OSDA-C2 and OSDA-C3, see Fig. 1), always in the presence of alkali metal cations (both Na⁺ and K⁺) in the synthesis gels (see Fig. 2). Similar structure directing effects towards chlatrasil frameworks have been described in the literature by using small OSDAs combined with alkali metal cations in zeolite synthesis under alkaline conditions.¹⁹ MTW is the only competing crystalline phase when using small OSDAs (OSDA-C2 and OSDA-3) and aluminum in the synthesis gels (see Fig. 2). These results would suggest that bulkier OSDAs could help in directing the crystallization towards more open crystalline phases than the dense NON phase.

As expected, the use of the bulkier OSDA-C4 molecule directs the crystallization of the open crystalline MTW structure, precluding the formation of the undesired dense NON phase (see Fig. 2). MTW is preferentially achieved as pure crystalline phase when alkali metal cations, either sodium or potassium, are present in the synthesis gels under high silica or even pure silica conditions (see Fig. 2). Nevertheless, by properly combining potassium cations and OSDA-C4, it was possible to synthesize a highly crystalline MTW zeolite with a Si/Al ratio in the synthesis gel of 15 (see MTW-1 in Fig. 2). In this case, MTW with the same Si/Al ratio as the starting gel could be obtained, as it will be shown later. Note that the only synthesis we have found in the literature giving a similar low Si/Al ratio is the OSDA-free procedure described by Okubo et al. and, as said above, the resultant MTW crystalline material had low pore accessibility, due to the presence of a large number of structural defects.¹² We were also able to prepare a MTW as a pure

crystalline phase in the absence of alkali-cations with OSDA-C4 and with a Si/Al ratio of 30 (see MTW-2 in Fig. 2). It has to be remarked that the synthesis of Al-MTW under alkali metal cationfree synthesis conditions is very unusual. Indeed, zeolites synthesized with alkali metal cations require post-synthetic ion-exchange treatments before their use as acid catalyst. Very recently, researchers at BASF have reported the alkali-free synthesis of the Al-MTW zeolite using 4-cyclohexyl-1,1-dimethylpiperazinium as OSDA, and a Si/Al ratio of almost 50 was required for crystallizing this material.²⁰ Thus, MTW-2 could be synthesized in our work under alkali-free conditions with lower Si/Al ratios than those reported by researchers at BASF.

3.2. Physico-chemical characterization of the Al-rich MTW zeolite samples

PXRD patterns of the as-prepared MTW-1 and MTW-2 materials reveal the presence of the pure MTW crystalline phase (see Fig. 3), and scanning electron microscopy (SEM) images show a similar average crystal size ($\sim 1-2 \mu$ m) for both MTW materials (see Fig. 4).

Chemical analyses of the crystalline MTW materials indicate that the Si/Al ratios in the final solids are similar to the Si/Al ratios introduced in the synthesis gels (see Table 2). Interestingly, the MTW-1 material presents a Si/Al ratio in the solid of 12.5, revealing that a relatively Al-rich MTW material can be obtained by properly combining potassium cations and OSDA-C4 as structure directing agents.

The coordination of aluminium atoms in the MTW materials has been studied by solid ²⁷Al MAS NMR spectroscopy. MTW-1 and

MTW-1

MTW-2





Fig. 4 SEM images of the MTW materials.

 Table 2
 Chemical analyses and acid properties of the crystalline MTW materials

				Acidity ^{<i>a</i>} (mmol Py gr ⁻¹)		
Sample	$\left(Si/Al\right)_{gel}$	$(Si/Al)_{ICP}$	K/Al	B150	B250	B350
MTW-1 MTW-1-Exc MTW-2	15 — 30	12.5 12.6 30.3	0.3 0.005 —	0.035 0.138 0.095	0.025 0.120 0.082	0.007 0.082 0.063

 a Calculated by $in\ situ$ infrared pyridine adsorption/desorption at different temperatures.





MTW-2 show a single band at ~55 ppm that has been assigned to tetrahedrally coordinated Al at framework positions (see Fig. 5). If this is so, then it can be said that the synthesis methodology presented here allows the efficient introduction of aluminum atoms at framework positions of the MTW materials.

N2 adsorption measurements have been performed to evaluate the pore accessibility of the two MTW samples after calcination in air at 550 °C. As described above, pore blocking could be a critical issue for one-dimensional zeolites.¹² In the case of the calcined MTW-1 zeolite, since this material has been synthesized using potassium cations (see potassium content of MTW-1 in Table 2), a previous cationic exchange with ammonia followed by calcination at 500 °C is required to remove the extra-framework inorganic cations and properly evaluate the pore accessibility. Practically all potassium cations were removed by NH_4^+ exchange (see potassium content in MTW-1-Exc sample in Table 2), and the N₂ isotherm of the MTW-1-Exc material indicates high microporosity (see Fig. 6), with a micropore surface area and micropore volume of 261 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively (see Table 3). It is important to note that this micropore volume is similar to the values reported for highly crystalline high Si/Al MTW materials in the literature.¹¹ The N₂ adsorption isotherm of MTW-2 can be directly obtained after calcination of the synthesized sample since this sample was obtained in the absence of alkali ions and a post-synthesis cation exchange is not required to produce the acid sample. As seen in Fig. 6 and Table 3, MTW-2 also shows high microporosity, with a micropore area of 274 m² g⁻¹ and a micropore volume of 0.13 cm³ g⁻¹.

The acid properties of the Al-rich MTW-1 material have been characterized by IR spectroscopy of adsorbed pyridine.



Fig. 6 N₂ adsorption isotherms of the MTW materials.

Table 3 Textural properties calculated from N2 adsorption isotherms

Sample	BET surface area $(m^2 g^{-1})$	Micropore area $(m^2 g^{-1})$	Micropore volume $(cm^3 g^{-1})$
MTW-1-Exc	295	261	0.12
MTW-2	325	274	0.13

The results in Fig. 7 show that the characteristic IR band of the pyridinium ion at 1545 cm⁻¹, which is associated with the presence of Brönsted acid sites, is very small for the K⁺ containing MTW-1 material. This is due to the fact that K⁺ is compensating the negative charges associated with tetrahedrally coordinated aluminum atoms, and also because the relatively large size of these extra-framework potassium cations hinder the diffusion of pyridine molecules through the one-dimensional pores of MTW. After cationic exchange of MTW-1 with ammonia followed by calcination at 500 °C, the 1545 cm⁻¹ IR band of pyridinium ions is clearly observed after pyridine



Fig. 7 Transmission FTIR spectra in the stretching C–C region after adsorbing pyridine followed by desorption at 150, 250, and 350 $^{\circ}$ C: (a) calcined MTW-1, (b) MTW-1-Exc, and (c) calcined MTW-2.

adsorption (see MTW-1-Exc in Fig. 7). The intensity of this band remains important after increasing the pyridine desorption temperature, even at 350 $^{\circ}$ C (see MTW-1-Exc in Fig. 7 and Table 2), revealing a strong Brönsted acid behavior of the MTW-1-Exc zeolite, which is useful for carbocation type reactions.

When the Brönsted acidity of the MTW-2 sample was measured, pyridine adsorption results show a lower intensity of the 1545 cm⁻¹ band for MTW-2 than for MTW-1-Exc. The amount of Brönsted acid sites per gram of zeolite was determined from the area of that IR band using the extinction coefficient reported by Emeis,²¹ and the values are given in Table 2.

3.3. Catalytic results

The catalytic activity of the Al-rich MTW samples has been studied here for the cracking of *n*-decane at 500 °C and 60 s of time on stream. *n*-Decane is a linear alkane able to diffuse through the one-dimensional 12-ring channels of MTW. The catalytic activity of these MTW samples has been compared with two mordenite (MOR) samples of similar Si/Al ratios. The framework of MOR contains large pores (6.5×7.0 Å), which are slightly higher than those of the MTW zeolite (6.0×5.6 Å), interconnected by 8-ring pores (3.4×4.8 Å). In general, the results presented in Table 4 show that MTW samples present higher catalytic activity in terms of the kinetic rate constant than mordenites. This higher catalytic activity compared to

Table 4Catalytic activity of MTW samples in the cracking of *n*-decane at500 °C and 60 s time on stream compared with Mordenite samples

Catalyst	MOR-1	MOR-2	MTW-1-Exc	MTW-2
Si/Al	10	20	12.5	30.3
Kinetic constant	4.09	3.26	7.04	4.30
$(g_{decane} g_{cat}^{-1} s^{-1}) \times 100$)			
Yields (wt%) at 50% con	version of d	ecane		
C5-C9	16.05	13.31	15.03	17.48
Gases H2 + C1-C4	38.39	42.34	42.14	39.85
Coke	5.55	4.34	2.83	2.67
Hydrogen	0.13	0.13	0.13	0.06
Methane	0.36	0.39	0.33	0.19
Ethane	0.45	0.59	0.73	0.46
Ethylene	1.87	2.25	2.75	1.69
Propane	11.25	12.36	10.46	7.48
Propylene	6.37	7.51	8.96	9.08
Isobutane	9.55	7.36	5.08	6.02
<i>n</i> -Butane	5.04	5.50	5.61	5.12
trans-2-Butene	1.30	1.48	1.86	2.26
1-Butene	0.98	1.10	1.43	1.66
Isobutene	2.35	2.58	3.44	4.15
cis-2-Butene	0.96	1.08	1.36	1.65
Ratios of interest				
Butene/butane	0.38	0.49	0.76	0.87
Propylene/propane	0.57	0.61	0.86	1.21
Isobutane/n-butane	1.89	1.34	0.91	1.18
C1 + C2	2.68	3.23	3.81	2.34
Isobutene/n-butenes	0.72	0.70	0.74	0.75
Isobutene/isobutane	0.25	0.35	0.68	0.69
C1 + C2/isobutane	0.28	0.44	0.75	0.39
C3/C4	0.87	1.04	1.03	0.79
IB = +IB/TOTC4	0.59	0.52	0.45	0.49
Iso/normal-C4	0.38	0.53	0.82	0.63
C1 + C2/IB = +IB	0.23	0.33	0.45	0.23
Ethylene/ethane	4.13	3.83	3.74	3.65

MOR zeolites could be attributed to the lower dimensions of the channels of MTW that are close to those of medium pore structures. In this sense, the lower dimensions of the channel of the MTW should add a stronger confinement effect boosting the activity for the activation of linear alkanes.

In terms of selectivity, MTW materials show a higher yield of C3–C4 olefins compared to MOR zeolites, with a remarkable higher propylene yield (see Table 4). The reason for this could be explained by the presence of less hydrogen transfer reactions towards saturated paraffins, such as propane or butanes. This lower extension of hydrogen transfer reactions results in higher olefinicity ratios for MTW compared to MOR zeolites (see propylene/propane, butenes/ butanes and isobutene/isobutane in Table 4). The lower contribution of hydrogen transfer reactions for MTW materials should also be attributed to the lower dimensions of the large pore channels that preclude bimolecular reactions, which are more favoured in the larger pores of MOR.

4. Conclusions

The synthesis of the Al-rich MTW zeolite with low Si/Al ratios (~ 12) and large pore accessibility has been described by using the proper combination of alkali metal cations, such as potassium, and bulky dicationic OSDAs, such as OSDA-C4. This zeolite presents all the aluminum atoms in framework positions, resulting in a material with strong Brönsted acidity after cationic exchange, as revealed by in situ infrared pyridine adsorption/ desorption at different temperatures. In addition, another MTW material with a Si/Al ratio of 30 has been synthesized under alkali-free conditions using OSDA-C4 as the only structure directing agent. This Si/Al ratio is the lowest described in the literature for the synthesis of MTW in the absence of alkalications, which is an important issue since post-synthetic cationic exchange procedures are not required to create its acid-form. These MTW samples are very active for n-decane cracking and show lower extension of hydrogen transfer reactions leading to a higher yield of olefins compared to other large pore zeolites, as mordenites.

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