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Additional Information

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

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1.- Introduction

MTW is a one-dimensional large pore zeolite with pore openings of 5.6 x 6.0 Å in its structure.^[1] The first synthesis description of the MTW structure was the high-silica ZSM-12 zeolite, which was synthesized 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 as 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 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 became a clear objective to improve its acid 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 was 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 compared to regular MTW acid materials with micropore volume of 0.12 cm³/g 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 by the presence of structural defects. Indeed, the defects would be formed by the excessive positive charges introduced by the alkalis when used as the single structure directing agents.^[13] In that case, the alkaline content is larger than the framework Al and the excess of positive charge is

compensate by Si-O⁻ framework groups, that become internal sylanols when the alkaline 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 to the presence of framework Al, reducing therefore the formation of structural defects (internal sylanols).

Tetraethylammonium (TEA), methyltriethylammonium (MTEA), and benzyltrimethylammonium (BTMA),^[14] have been described as the most common OSDAs for the synthesis of the 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, Zones et al. have systematically studied the synthesis of zeolites with OSDAs formed by diquatery ammonium compounds of C₄-C₆ chain lengths with different heterocyclic end-groups.^[15] They observed that when the heterocyclic end-group was N-methylpiperidine (see OSDA-C4 in [Figure 1](#)), the synthesis of aluminosilicates in alkaline media was very selective towards MTW, but the Si/Al ratios were larger than 40.^[15]

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 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 with different sizes (see [Figure 1](#)), either in combination or in absence of alkali metal cations (Na⁺ or K⁺), can direct the synthesis of Al-MTW zeolites toward materials with framework Si/Al ratios in the final solids lower than the values previously reported in the literature, 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.- OSDAs preparation

OSDA-C2. Preparation was achieved by a two-step 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°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°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 in a two-neck 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 (0.05mol) was added drop-wise and the resulting biphasic solution heated at 80°C for 12 hs. Once the reaction was finished, the organic layer was separated from the crude, and washed with water (3 x 15 ml) and Brine solution (1 x 20ml). Then, the organic layer was dried with anhydrous $MgSO_4$ 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°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 under 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 a 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 with 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 $HNO_3/HCl/HF$ aqueous solution. The organic content of as-made materials was determined by elemental analysis performed with a SCHN FISIONS elemental analyzer.

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_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. ^{27}Al MAS NMR spectra were recorded at 104.2 MHz with a spinning rate of 10 kHz and 90° pulse length of 0.5 μs with a 1 s repetition time. ^{27}Al chemical shift was referred to $Al^{3+}(H_2O)_6$.

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 673K and 10^{-2} Pa for 2 hours. After wafer activation, the base spectrum was recorded and pyridine vapour ($6.5 \cdot 10^2$ 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 623K, 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 ratio in a microactivity test unit as described previously.^[16] 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).

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

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

3.- Results

3.1.- Syntheses of Al-rich MTW zeolites

Based on the previous results,^[15] three related linear dicationic OSDAs with different sizes were synthesized and used as OSDAs for the synthesis of the Al-rich MTW zeolite (see **Figure 1**). The experimental design containing the synthesis conditions is summarized in **Table 1**. 54 synthesis experiments have been performed in where the OSDAs, Si/Al, H₂O/Si, and alkali/Si ratios where varied. The phase diagram, achieved after the crystallization process at 175°C for 14 days, show the presence of amorphous

materials and the formation of two different crystalline phases, such as NON and MTW (see Figure 2).

NON is a cage-like chlatrasil type structure with pore openings lower than 3 Å.^[17] This dense phase is preferentially obtained when using the smaller dicationic OSDAs (OSDA-C2 and OSDA-C3, see Figure 1), always in presence of alkali metal cations (both Na⁺ and K⁺) in the synthesis gels (see Figure 2). Similar structure directing effects towards chlatrasil frameworks have been described in the literature when using small OSDAs combined with alkali metal cations in zeolite synthesis under alkaline conditions.^[18]

MTW is the only competing crystalline phase when using small OSDAs (OSDA-C2 and OSDA-3) and aluminum in the synthesis gels (see Figure 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 Figure 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 Figure 2). Nevertheless, by properly combining potassium cations and the OSDA-C4, it was possible to synthesize highly crystalline MTW zeolite with a Si/Al ratio in the synthesis gel of 15 (see MTW-1 in Figure 2). In this case, MTW with the same Si/Al ratio than the starting gel could be obtained, as it will be shown later. Notice that the only synthesis we have found in the literature giving similar low Si/Al ratio is the OSDA-free procedure described by Okubo et al. and, as was 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 pure crystalline phase in absence of alkali-cations with OSDA-C4 and with a Si/Al ratio of 30 (see MTW-2 in Figure 2). It has to be remarked that the synthesis of Al-MTW under alkali metal cations-free 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.^[19] 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 Figure 3), and scanning electron microscopy (SEM) images show similar average crystal size ($\sim 1\text{-}2\ \mu\text{m}$) for both MTW materials (see Figure 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, 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 ^{27}Al MAS NMR spectroscopy. MTW-1 and MTW-2 show a single band at $\sim 55\ \text{ppm}$ that has been assigned to tetrahedrally coordinated Al in framework positions (see Figure 5). If this is so, then it can be said that the synthesis methodology presented here allows the efficient introduction of aluminum atoms in framework positions of the MTW materials.

N_2 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 N_2 isotherm of the MTW-1-Exc material indicates high microporosity (see Figure 6), with micropore surface area and micropore volume of $261\ \text{m}^2/\text{g}$ and $0.12\ \text{cm}^3/\text{g}$, respectively (see Table 2). 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 N_2 adsorption isotherm of the 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 [Figure 6](#) and [Table 2](#), MTW-2 also shows high microporosity, with a micropore area of 274 m²/g and a micropore volume of 0.13 cm³/g.

The acid properties of the Al-rich MTW-1 material have been characterized by IR spectroscopy of adsorbed pyridine. The results in [Figure 7](#) show that the characteristic IR band of pyridinium ion at 1545 cm⁻¹, which is associated to the presence of Brønsted 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 to 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 exchanged 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 adsorption (see MTW-1-Exc in [Figure 7](#)). The intensity of this band remains important after increasing the pyridine desorption temperature, even at 350°C (see MTW-1-Exc in [Figure 7](#) and [Table 2](#)), revealing a strong Brønsted acid behavior of the MTW-1-Exc zeolite, that should be useful for carbocation type reactions.

When the Brønsted acidity of the sample MTW-2 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 Brønsted acid sites per gram of zeolite were determined from the area of that IR band using the extinction coefficient reported by Emeis,^[20] 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 x 7.0 Å), which are slightly higher than those of the MTW zeolite (6.0 x 5.6 Å),

interconnected by 8-ring pores (3.4 x 4.8 Å). In general, the results presented in Table 4 show that MTW samples present higher catalytic activity in terms of kinetic rate constant than mordenites. This higher catalytic activity compared to 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 to C3-C4 olefins compared to MOR zeolites, with remarkable higher propylene yield (see Table 4). The reason for that 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/isobutene 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 favored 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 for the first time 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 Brønsted 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 absence of alkali-cations, 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 the n-decane cracking and show lower extension of hydrogen transfer reactions leading to higher yield of olefins compared to other large pore zeolites, as mordenites.

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Figure 1: Diquaternary ammonium compounds proposed as OSDA for the synthesis of the MTW structure

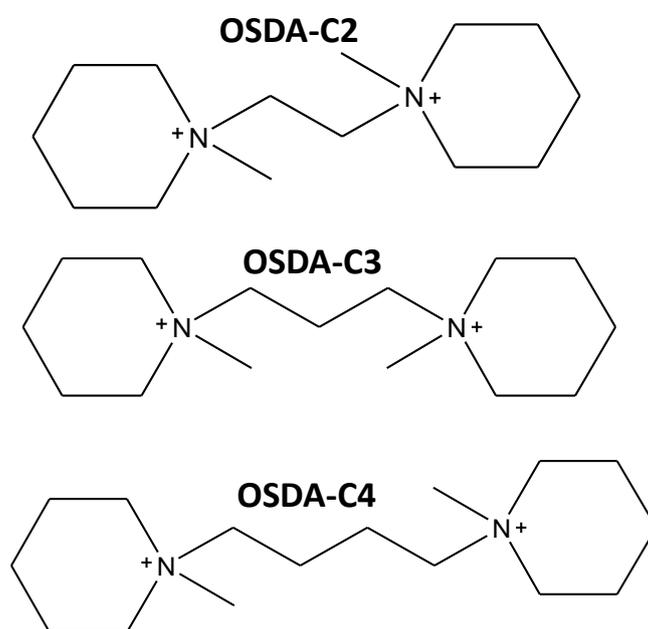


Figure 2: Phase diagram obtained for the synthesis of zeolites using different diquatery ammonium compounds

		OSDA/Si=0,25		OSDA/Si=0,20 NaOH/Si=0,10		OSDA/Si=0,20 KOH/Si=0,10	
		H ₂ O/Si		H ₂ O/Si		H ₂ O/Si	
		10	30	10	30	10	30
OSDA-C2	Si/Al=INF						
	Si/Al=30						
	Si/Al=15						
OSDA-C3	Si/Al=INF						
	Si/Al=30						
	Si/Al=15						
OSDA-C4	Si/Al=INF						
	Si/Al=30	MTW-2					
	Si/Al=15					MTW-1	

	Amorphous
	NON
	NON-MTW
	MTW-amorphous
	MTW

Figure 3: PXRD patterns of the as-prepared crystalline MTW-1 and MTW-2 materials

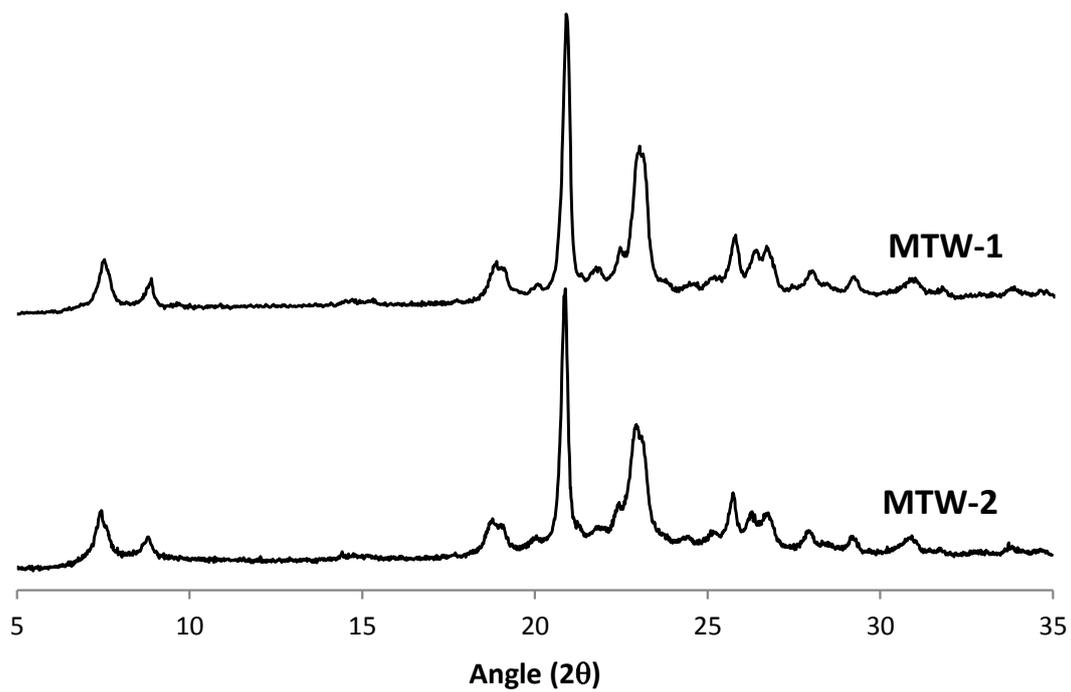


Figure 4: SEM images of the MTW materials

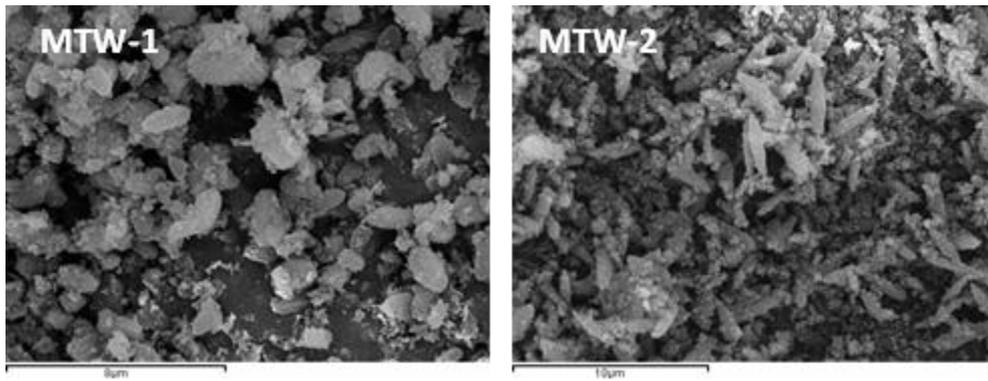


Figure 5: Solid ^{27}Al MAS NMR spectra of the MTW materials

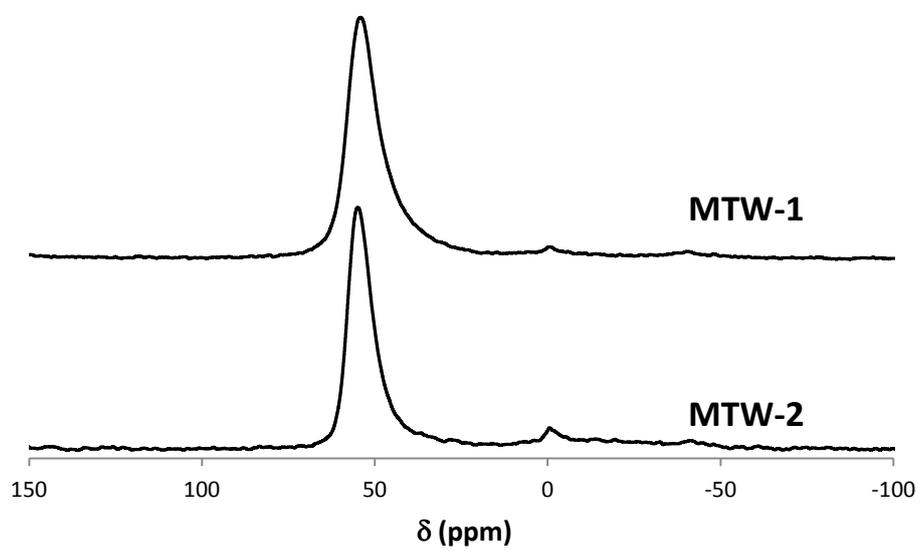


Figure 6: N₂ adsorption isotherms of the MTW materials

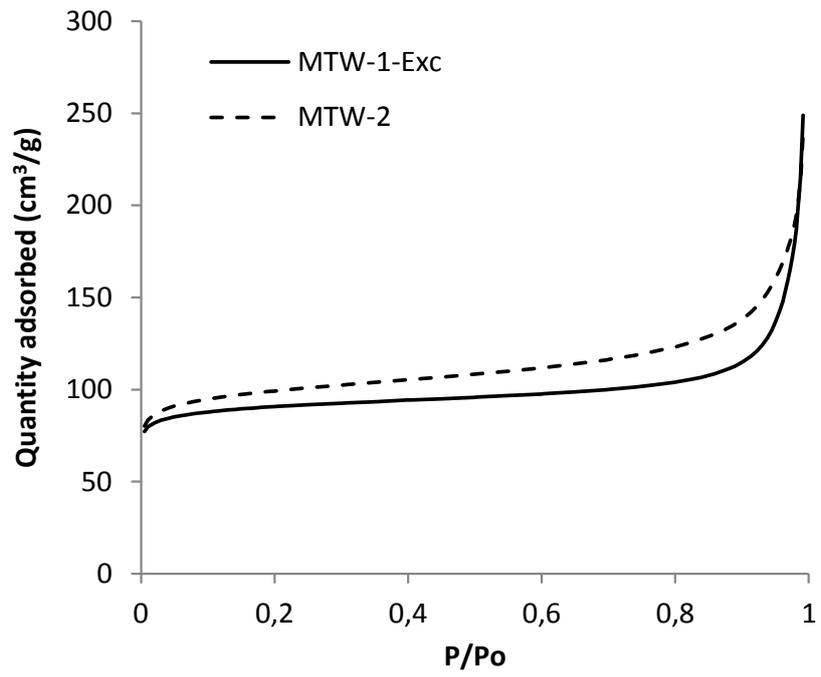


Figure 7: Transmission FTIR spectra in the stretching C–C region after adsorbing pyridine followed by desorption at 150, 250, and 350°C: (a) calcined MTW-1, (b) MTW-1-Exc, and (c) calcined MTW-2.

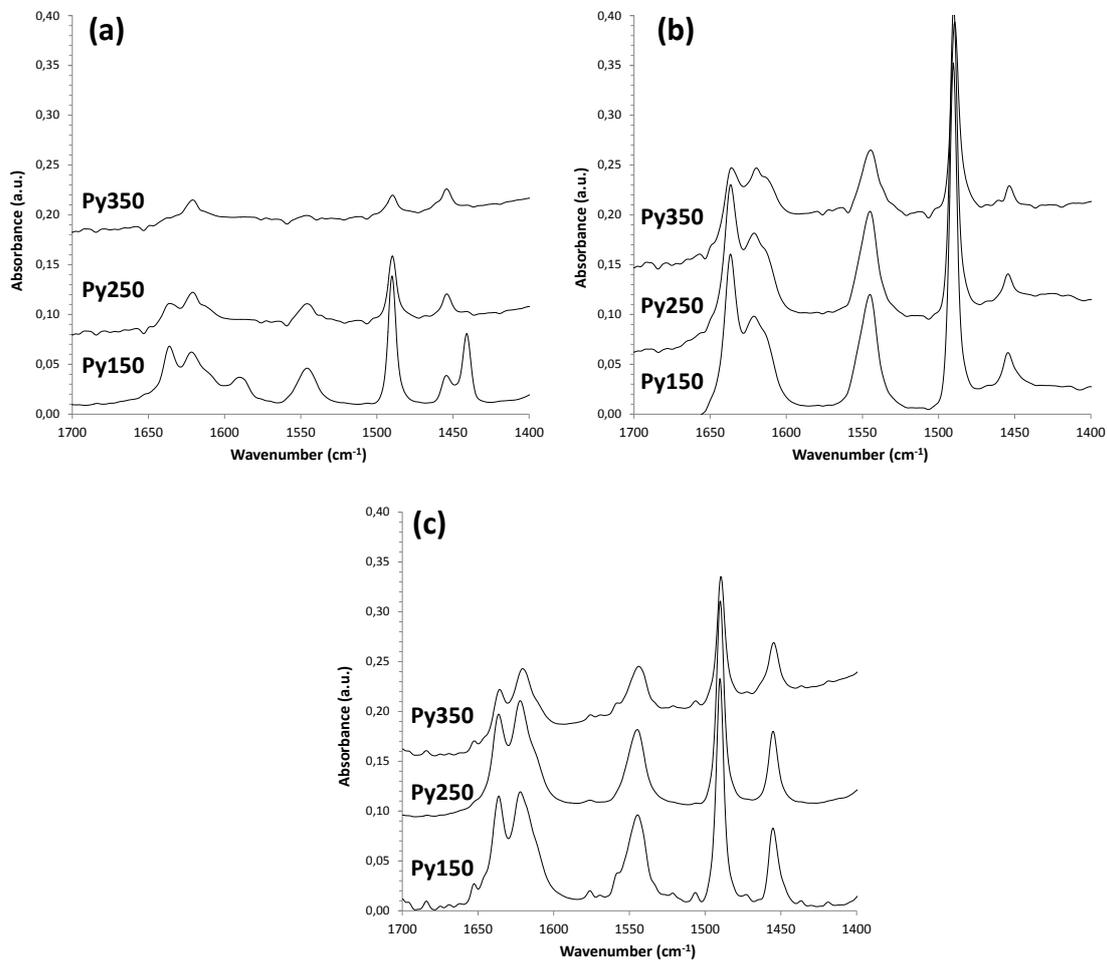


Table 1: Experimental design for the synthesis of zeolites using different diquatery ammonium compounds

Variable	Values
<i>OSDA type</i>	OSDA-C2, OSDA-C3, OSDA-C4
<i>Si/Al</i>	INF, 30, 15
<i>H₂O/Si</i>	0.8, 0.9
<i>OSDA/Si</i>	0.25 (for alkali-free), 0.2 (for synthesis with alkali cations)
<i>alkali/Si</i>	0, Na/Si = 0.1, K/Si = 0.1

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

Sample	Si/Al) _{gel}	Si/Al) _{ICP}	K/Al	Acidity (mmolPy/gr) ^a		
				B150	B250	B350
MTW-1	15	12.5	0.3	0.035	0.025	0.007
MTW-1_Exc	---	12.6	0.005	0.138	0.120	0.082
MTW-2	30	30.3	---	0.095	0.082	0.063

^a Calculated by in-situ infrared pyridine adsorption/desorption at different temperatures

Table 3: Textural properties calculated from N₂ adsorption isotherms

Sample	BET surface area (m²/g)	Micropore area (m²/g)	Micropore volume (cm³/g)
MTW-1-Exc	295	261	0.12
MTW-2	325	274	0.13

Table 4: Catalytic activity of MTW samples in the cracking of n-decane at 500°C and 60s Time On Stream compared with Mordenite samples.

Catalyst	MOR-1	MOR-2	MTW-1-Exc	MTW-2
Si/Al	10	20	15	30
Kinetic constant ($g_{\text{decane}} g_{\text{cat}}^{-1} s^{-1}$) *100	4.09	3.26	7.04	4.30
Yields (wt%) at 50% conversion of decane				
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
N-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/normalc4	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
ethylene/propylene	0.29	0.30	0.31	0.19

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