Synthesis of Hierarchical MWW Zeolites and Their Catalytic Properties in Petrochemical Processes (Review)

A. V. Shkuropatov^a, E. E. Knyazeva^{a, b}, O. A. Ponomareva^{a, b, *}, and I. I. Ivanova^{a, b}

^aFaculty of Chemistry, Moscow, Moscow State University, Moscow, 119991 Russia ^bTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia *e-mail: oaponomareva@phys.chem.msu.ru Bacairod March 14, 2018

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Abstract—Approaches to the synthesis of hierarchical MWW zeolites by the pillaring, delaminating, and recrystallization methods are surveyed and systematized. The influence of the characteristic features of the micro—mesoporous structure of MWW on their physicochemical and catalytic properties has been assessed. The results of investigation of the catalytic activity and selectivity of hierarchical MWW zeolites in petro-chemical processes are discussed.

Keywords: MWW zeolite, hierarchical zeolite, pillaring, delamination, recrystallization, petrochemical processes

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Hierarchical zeolites are a new class of molecular sieve materials characterized by the presence of pores of various diameters in their structure. The creation of a mesopore system in microporous zeolites leads to an increase in the accessibility of active sites within the channels and to elimination of diffusional limitations, thereby increasing their activity and on-stream stability. Thus, there are good prospects for the use of microporous zeolites in deep oil refining, as well as in the creation of new petrochemical and organic synthesis processes. Zeolite MCM-22 (Mobil Composition Materials) developed in 1990 by Mobil (structural type MWW) has a unique porous structure that differs from the structure of other zeolites by three-dimensional organization by stacking of microporous layers of a 2.5 nm thickness.

Currently, MWW zeolites are almost the only available layered structures characterized by high aluminum content, which is crucial for their high activity in catalytic processes. This zeolite has found widespread application as an acid component of catalysts for benzene alkylation with lower olefins [1-3]. Today, the MWW zeolite family continues to be under the close attention of researchers from various scientific groups and schools as the most interesting object from the scientific and practical point of view for obtaining hierarchical zeolite materials.

Various methods and approaches to the fabrication of micro-mesoporous (hierarchical) materials based on MWW zeolite have been the subject matter of many studies in recent decades; their results have been surveyed in reviews [4–7].

There have been also studies on the use of these materials in various catalytic processes. The catalytic properties of hierarchical MWW zeolites were tested in

alkylation [8–13], acylation [14, 15], isomerization and hydroisomerization [16, 17], cracking [18–21], hydrogenation [20], dehydrogenation [22, 23], oligomerization [24, 25], and alkene oxidation [26–28] reactions. In 2012, Diaz [5] published a review on the catalytic application of pillared and delaminated materials based on MWW. However, that review has little coverage of petrochemical processes; in addition, many new publications on the use of hierarchical MWW zeolites (HZ-MWW) in various catalytic processes have appeared over the past five years.

The aim of this paper is to systematize and analyze approaches to and methods for the synthesis of hierarchical MWW zeolites, as well as to survey their application in petrochemical processes.

SYNTHESIS OF MICRO–MESOPOROUS ZEOLITES BASED ON MWW

Traditionally, MWW zeolite is produced by hydrothermal synthesis at a temperature of 150° C using reaction mixtures with SiO₂ source (silica sol, silica gel, aerosil), sodium aluminate, sodium hydroxide, and the hexamethyleneimine (HMI) directing agent [29]. Immediately after hydrothermal synthesis, flat oval crystals of zeolite MWW with a size of 2 × 5 µm and a thickness of 150–300 nm appear as plate aggregates of nanoscale layers of 2.5 nm in thickness separated by HMI molecules and linked with one another by hydrogen bonds between the silanol groups of adjacent layers (scheme). Such a material is commonly called precursor for obtaining MWW with an hierarchical structure; hereinafter, it will be referred to as LP-MWW (layered MWW precursor).

In the course of calcination to remove the directing agent, hydrogen bonds are destroyed; as a result, due to

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Modification	Modification conditions								
method	number of steps	modifying agent and technological operations	starting material	<i>T</i> ,°C	τ, h	medium	Ref.		
Silanization	1	Vapor deposition Diethoxydimethylsilane $(CH_3)_2Si(OC_2H_5)_2$ or dichlorodi- methylsilane $Cl_2Si(CH_3)_2$	LP-MWW	100	20	Acidic	[9, 33]		
Delamina- tion	2 1	Drying Swelling Aqueous solution of $(C_{16}H_{33})(CH_3)_3NBr$ mixture with $(C_3H_7)_4NOH$	LP-MWW	Unspecified 80	Unspecified	Alkaline	[34]		
Pillaring	2 3 4 1	Sonication—50 W, 40 kHz, 1 h Centrifugation, 10000 rpm Drying Swelling		Room 60	12	Acidic			
C		Aqueous solution of $(C_{16}H_{33})(CH_3)_3NBr$ mixture with $(C_3H_7)_4NOH$	LP- MWW	Room	16	Alkaline	[35]		
		Aqueous solution of $(C_{16}H_{33})(CH_3)_3NCl$ mixture with $(CH_3)_4NOH$	LP- MWW	Room	12	Alkaline	[36]		
		Aqueous solution of (C ₁₆ H ₃₃)(CH ₃) ₃ NOH	Wet precipitate after LP- MWW washing	100	96	Alkaline	[37]		
	2	Ultrasonic treatment, 2 h				[35, 37]			
	3	Centrifugation at 10000 rpm and 10 cycles				[35]			
	4	Pillaring $Si(OC_2H_5)_4$	Washed delam- inated MWW	80	25	Argon			
	5 6	Drying Calcining	Pillared MWW Dry pillared MWW	40 450	6 6	Nitrogen Nitrogen			
Recrystalli- zation	1	Hydrothermal treatment Aqueous solution of $(C_{16}H_{33})(CH_3)_3NBr$ mixture with NaOH	MWW zeolite free of directing agent	100	24	Alkaline followed by adjusting to pH 8 5	[13, 16]		
	2	Aqueous solution of $(C_{16}H_{33})(CH_3)_3NBr$ mixture with silica sol Filtering, washing	LP-MWW	100	72	Neutral			
	3	3 Drying, calcining							

Table 1. Methods and conditions for preparing hierarchical MWW zeolites

the formation of siloxane bonds and the "crosslinking" of the nanolayers, a "hard crystal" is formed (designated MCM-22 in the scheme). The microporous MWW structure of MCM-22 is comprised of two types of pores:

the first type is formed by a system of zigzag channels, the size of which is limited by ten-membered silicon—oxygen rings to be about 0.55 nm, and the second type is associated with 0.7×1.8 nm cavities (supercages).

In 1993–1994, Mobil Oil designed and patented a method for increasing the interlayer spacing in MWW zeolite by swelling with the use of surfactants followed by intercalation of an inorganic pillaring agent [30, 31]. The method was called pillaring. A few years later, a team of Spanish scientists led by Prof. A. Corma extended the possibilities of the method, supplementing it with the stage of ultrasonic treatment [32]. Under ultrasonic wave irradiation, the MWW layers were disordered to form the micro–mesoporous "card house" structure.

Mesopores located between MWW layers provided maximal accessibility to hemicages on the surface of zeolite layers. The works performed have given a strong impetus to research in the synthesis of hierarchical MWW zeolites and investigation of their properties.

To date, several routes for preparing HZ-MWW have been formed as presented in the scheme. All of them involve the use of LP-MWW as a starting material. Postsynthetic treatments of LP-MWW suggest physical or chemical procedures detailed below.

The physical procedures include calcinlation to make the MWW layers crosslinked as a result of dehydration. The resulting MWW zeolite (MCM-22) is a semifinished product for preparing recrystallized micro-mesoporous zeolite materials.

The chemical modification of LP-MWW can include direct silanization of MWW zeolite with organosilicon compounds to form bridges that expand the space between MWW layers and prop the layers apart. The second method of chemical modification involves the replacement of HMI molecules by cationic surfactant (for example, cetyltrimethylammonium bromide CTMAB) molecules and the formation of oriented surfactant layers in the zeolite interlayer space (scheme). The resulting MWW–CTMAB material is a precursor for subsequent delaminating procedures (to obtain ITQ-2 material) or for pillaring (to obtain MCM-36 zeolite).

Scheme of postsynthetic treatments for preparation of hierarchical MWW zeolites.



Modification	SiO ₂ /Al ₂ O	3, mol/mol	Surface a		
method	before modification	after modification	before modification	after modification	Ref.
Silanization	66	79	622	674	[38]
Delamination	26	20	_	>700	[32, 16]
Pillaring	62	44	400-500	800-950	[37]
Recrystallization	26	29	520	855	[13]

Table 2. Properties of hierarchical MWW zeolites obtained by different methods, before and after modification

Table 1 specifies the conditions of procedures for preparing HZ-MWW by various methods, and Table 2 shows the chemical composition and characteristics of the porous structure of HZ-MWW.

Silanization of the LP-MWW is carried out in a vapor-phase treatment mode. The high volatility of alkylated and chlorinated silane derivatives renders them able to react with the zeolite at a sufficiently low temperature of 100°C. In the interlayer space, the silane derivatives are oxidized via the reaction: $Cl_2Si(CH_3)_2 + 3O_2 \rightarrow SiO_2 + 2HCl + 2CO_2 + 2H_2O.$ The hydrochloric acid formed partially dealuminates LP-MWW; as a result, the SiO_2/Al_2O_3 ratio increases from 66 to 79 (Table 2). The resulting highly dispersed silica is located in the interlayer space, preventing the collapse of the layers and facilitating the preparation of a material with a more developed surface; by this modification, the surface area will increase from 622 to $674 \text{ m}^2/\text{g}$. The increase in the surface area is due to a change in the diameter of micropores as a result of the modification. As shown by the micropore size distribution curves calculated from argon adsorption isotherms, along with pores of a 5.5 Å size, the silanized MWW zeolite have pores with a size of 7 Å, which can be due only to the intercalation of silica particles in the interlayer space [39].

According to the data reported in [39], the presence of highly dispersed SiO₂ fragments stabilized the MWW structure, as followed from the results of X-ray diffraction analysis, which revealed a shift of the diffraction maxima to larger 2 θ angles in the calcined LP-MWW compared to the initial one. The shift of the diffraction maxima confirmed the fact that calcination of LP-MWW leads to changes in the crystal structure of the starting material. Silanization of LP-MWW using diethoxydimethylsilane followed by calcination did not alter the positions of the diffraction maxima of LP-MWW, thereby giving indirect evidence for the stabilization of the crystal structure [39].

Delamination of MWW zeolite is carried out with the aim of disordering the MWW layers and obtaining an openwork structure in which the MWW layers are randomly oriented with respect to each other and form a porous card-house type system. To carry out delamination, the following steps are successively undertaken: <u>LP-MWW swelling</u> by introducing a surfactant into the interlayer space (the procedure is carried out in an alkaline medium created by adding tetraalkylammonium hydroxides into the system (Table 1)); <u>ultra-</u> <u>sonication</u> of an LP-MWW suspension in an alkaline surfactant solution to obtain HZ-MWW; <u>isolation</u> of HZ-MWW (ITQ-2) from the suspension by the reduction of pH value of alkaline suspension to 2 with concentrated hydrochloric acid followed by centrifugation; and <u>drying</u> HZ-MWW under mild conditions.

A comparison of high-resolution TEM images of the precursor material LP-MWW and the solid phase isolated after the swelling process confirm the increase in the interlayer spacing. The HZ-MWW isolated after the sonication step is randomly oriented MWW monolayers with a thickness of 1.3 nm [32]. This material has an exceptionally developed outer surface of 550 [18] to 700 [32] m²/g according to data of different authors.

The characteristics of the porous structure of the MWW zeolite and the delaminated HZ-MWW obtained from the same precursor LP-MWW (Table 3) show that the delamination process is accompanied by degradation of the microporous structure [18]. This is indicated by a significant decrease in the micropore surface and micropore volume (Table 3). The deterioration of crystallinity in delaminated materials is confirmed by a decrease in the intensity of reflections on the diffraction patterns of MWW materials isolated after individual steps of the delamination process (Fig. 1).

Differences in the chemical composition between the initial and delaminated materials (Table 2), namely, a decrease in the SiO_2/Al_2O_3 molar ratio from 26 to 20, can be associated with silicon leaching during the initial steps of the process.

Pillaring of LP-MWW includes the steps required for the delamination process, followed by treatment of the material with a silicon-containing compound, for example, tetraethoxysilane Si(OC_2H_5)₄, and calcination. It has been shown [33–35] that the list of compounds necessary for carrying out the swelling step can be extended by varying combinations of surfactants and quaternary alkylammonium hydroxides (Table 1). The alkaline medium and the elevated temperature (80°C) of the reaction mixture exert a

$(S_1O_2/Al_2O_3 = 19)$ [18]									
Sample	$S_{ m micro},$ m ² /g	S_{outer} , m^2/g	$V_{\rm micro},$ cm ³ /g	V, cm ³ /g					
MWW	352	117	0.16	0.28					
HZ-MWW	153	551	0.07	0.63					

Table 3. Porous structure characteristics of zeolite MWW and HZ-MWW obtained using the delamination method $(SiO_2/Al_2O_3 = 19)$ [18]

destructive effect on the zeolite structure during swelling, which leads to a decrease in the Si/Al ratio, so it was suggested in [40] to swell samples at room temperature. As a result of that study, it was found that dissolving the silica contained in the zeolite structure leads to the formation of mesopores during swelling, in addition to those created by pillaring. The average pore diameter decreases from 2.7 nm to 1.8 nm as the swelling temperature decreases from 80 to 25°C. The sample treated at 80°C has a random structure, whereas the sample treated at 25°C demonstrates a more ordered structure. Thus, lowering the swelling temperature leads to retaining the microporous structure of the layers in pillared zeolites and a slight increase in temperature will make it possible to control the degree of degradation of the zeolite structure.

A crucial parameter for conducting the pillaring process is the degree of washing to remove excess surfactant solution. It was shown that the number of washing cycles should be at least 10, but the best results were achieved with 40 cycles. In addition, an inert medium is necessary for effective modification, which is achieved by creating an argon atmosphere above the liquid layer during the course of pillaring (see Table 1). Such energy- and resource-intensive modifying conditions make the pillaring process unpromising for application at an industrial scale.

The essence of the *recrystallization* method consists in the degradation of zeolite, followed by the assembly of the resulting fragments in the presence of a surfactant [41]. Typically, the destruction of the zeolite is carried out in an alkaline medium, the use of which results in partial or complete degradation of the zeolite structure as a result of desilication. The next step involves assembling the zeolite fragments, formed as a result of degradation, into a mesoporous phase which, depending on the degree of zeolite degradation, can cover the surface of zeolite crystals, enter the zeolite– mesoporous phase composite, or completely replace the zeolite.

It should be outlined that despite the simplicity and effectiveness of the recrystallization method, the number of publications devoted to the synthesis and study of the properties of recrystallized MWW zeolites has been extremely limited to date. Meanwhile, the simplicity and mild conditions of the technological operations used in [13, 16], namely, the hydrothermal treatment at 100°C, separation of the solid phase by filtration followed by drying and calcining demonstrate the promise of this method for the production of HZ-MWW. Note that the recrystallization process leads to the smallest changes in the chemical composition of the initial precursor (see Table 2).

Figure 2 presents low-temperature nitrogen adsorption isotherms for HZ-MWW samples obtained using delaminating (Fig. 2a), pillaring (Fig. 2b), and recrystallizing (Fig. 2c) methods. The isotherm for the initial MWW zeolite is of the Langmuir type, it consists of a segment up to $p/p_0 = 0.01$ corresponding to micropore filling and a horizontal portion. For the hierarchical samples, the isotherms have a slope, with the sorbed volume of the HZ-MWW obtained by delaminating (Fig. 2a) and pillaring (Fig. 2b) monotonically increasing with increasing p/p_0 , thereby indicating that these samples contain mesopores with a broad size distribution. The recrystallized samples are characterized by a rise in the curve at $p/p_0 = 0.3-0.4$ (Fig. 2c), which indicates the formation of mesopores



Fig. 1. Change in the crystal structure of a layered precursor during the course of delamination and calcination procedures: LP-MWW is the layer precursor, SP-MWW is the layered precursor after swelling, HZ-MWW is the hierarchical zeolite material, MWW is the microporous material after calcination of LP-MWW [18].

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		SiO ₂ /Al ₂ O ₃ , mol/mol		Characteristics of porous structure				Po
No.	Second directing agent	In reaction mixture	In zeolite	$S_{ m micro},$ m ² /g	S_{outer} , m ² /g	$V_{\rm micro},$ cm ³ /g	V, cm ³ /g	ference
1	Dimethyloctadecyl(3-trimethoxysilylpro- pyl) ammonium chloride (60% solution in methanol)	32	38	184	122	0.13	0.44	[9]
1a*	_	32	38	332	54	0.15	0.23	
2	<i>N</i> -Hexadecyl- <i>N</i> '-methyl-1,4-diazabicy- clo[2.2.2]octane**	Unspecified	Unspecified	240	301	0.12	2.06	[43]
2a*	_	Unspecified	Unspecified	350	145	0.15	0.99	
3	Adamantane derivative*** Ada- i -16, where $i = 4, 5$, or 6 is the number of linker methyl groups	38	32	_	513	0.13	1.01	[42]
3a	-	Unspecified	Unspecified	—	121	0.14	0.29	

Table 4. Properties of nanoscale MWW zeolites synthesized by the dual-template method

* Characteristics of the MWW zeolite synthesized as a reference sample in the work.



of a certain size (about 30 Å). A comparison of the isotherms in Fig. 2 and the surface area values presented for these materials in Table 2 shows that materials with similar porous-structure characteristics can be obtained using different methods.

A special group of studies on the synthesis of HZ-MWW is made by those published in 2015–2016 and devoted to dual-template synthesis [9, 42, 43]. The main approach in dual-template synthesis is associated with the introduction of a second structuredirecting agent, usually a high-molecular-weight organic compound, into the reaction mixture crystallizing into zeolite MWW (Table 4). The presence of one or more functional amino groups in the "head" of the directing agent impart to these compounds the capability of chemical interaction with MWW layers, and the presence of an inert hydrocarbon "tail" in the form of long alkyl radicals interferes with the interaction of the layers: as a result, the hierarchical structure is formed already at the stage of hydrothermal crystallization without using energy- and material-intensive procedures of postsynthetic modification (Table 1).

* * *

According to the results of investigation of the porous structure of HZ-MWW (obtained by dual templating) and HZ-MWW (synthesized as reference samples), as given in Table 4, the dual-template method makes it possible to increase the external surface of the zeolite material by a factor of 2.5–4. When *N*-hexadecyl-*N*-methyl-1,4-diazabicyclo[2.2.2]octane was used as the second structure-directing agent, the amount of mono- and bilamellar particles made 70% of the total mass of the HZ-MWW solid phase [43].

According to Margarit et al. [42], the use of the adamantane derivative made it possible to obtain exclusively monolamellar zeolite particles, since the experimentally obtained value of the external surface area of 513 m²/g (Table 4) corresponds to the maximum possible value of the external surface area of 517 m²/g found as a result of calculations. It should be noted that in the HZ-MWW obtained by dual templating, the micropore volume is 0.13-0.14 cm³/g, which is twice the volume of micropores in the HZ-MWW prepared by delamination (Table 3). Thus, the dual-template method ensures the preparation of high-quality HZ-MWW.

Reaction	Zeolite	Si/Al	Conditions	Process characteristics	Reference
Alkylation of ben- zene with propyl-	MWW	19–25	Benzene/propyl- ene ratio 3.5–6,	Propylene conversion 35–99.7%, selec- tivity for isopropylbenzene 60–84.8%	[8, 9]
ene	HZ-MWW/D	23.7-25	3.0–3.5 MPa, 90– 140°C	Propylene conversion 95–99.6%, selec- tivity for isopropylbenzene 80–86.9%	
	HZ-MWW/P	21.5		Propylene conversion 90%, selectivity for isopropylbenzene 90%	
Alkylation of ben- zene with pro- pene–butene	MWW	13.9	Benzene/olefins ratio 2/1, 3.5 MPa, 200°C	Conversion 99.01–98.03%, selectivity for isopropylbenzene 35.59%, selectivity for isobutylbenzene 36.61%	[10]
mixture	HZ-MWW/Des	8.6		Conversion 97.99–97.20%, selectivity for isopropylbenzene 45.67%, selectivity for isobutylbenzene 42.76%	
Alkylation of tolu- ene with methanol	MWW	50	Microreactor, 225–400°C	Toluene conversion 13.7–30.2%, selectiv- ity for xylenes 67.4– 81.1%, selectivity for trimethylbenzenes 18.9– 32.6%	[11]
	HZ-MWW/P	50		Toluene conversion 7.3–12.1%, selectivity for xylenes 86.7–90.3%, selectivity for trimethylbenzenes 9.7– 13.3%	
Alkylation of biphenyl with pro-	MWW	50	Biphenyl/propyl- ene ratio 4, biphe-	Biphenyl conversion ~4%, selectivity for isopropylbiphenyl 82.0%,	[12]
pylene	HZ-MWW/D	50	nyl feed rate 1.96 mol/h, 250°C	Biphenyl conversion ~4%, selectivity for isopropylbiphenyl 89.8%	
Alkylation of phe- nol with <i>tert</i> -buta-	MWW	50	145°C, <i>tert</i> -buta- nol/phenol 2.5,	Conversion 94.0%, selectivity for 2,4-di- <i>tert</i> -butylphenol 30.6%	[13]
nol	HZ-MWW/R	50	feed space velocity 2.2 h^{-1}	Conversion 93.3%, selectivity for 2,4-di- <i>tert</i> -butylphenol 53.9%	
Acylation of anisole	MWW	11.0	110°C, 1.0 MPa, feed space velocity	Conversion 51.4%, selectivity for methoxyacetophenone 47.3%	[14]
	HZ-MWW/R	10.6	$10.2 \ h^{-1}$	Conversion 88.5%	
Acylation of furan	MWW	13.8	60°C, stirring	<i>k</i> (mmol/(min g)) 14.3	[15]
	HZ-MWW/Des	14.9		<i>k</i> (mmol/(min g)) 178.8	
Cracking of triiso- propylbenzene	MWW	15	Microreactor, 350°C	Conversion 51%; selectivity for benzene 8%, for isopropylbenzene 27%, for diisopropylbenzene 65%	[18]
	HZ-MWW/D	15		Conversion 66%; selectivity for benzene 10%, for isopropylbenzene 38%, for diisopropylbenzene 52%	
Cracking of	MWW	15	Microreactor,	Conversion 70%	[18]
cumene	HZ-MWW/D	15	350°C	Conversion 46%	
Cracking of <i>n</i> -dec-	MWW	12	500°C, cata-	$k 2.8 \text{ s}^{-1}$	[19]
ane	HZ-MWW/D	12	lyst/feedstock 0.3– 0.8 (w/w)	$k \ 1.9 \ \mathrm{s}^{-1}$	
Mild hydrocrack- ing of light frac- tions	Ni–Mo–HZ- MWW/D	50	3.0 MPa, 350– 450°C, feed space velocity 2 h^{-1}	Conversion ~55%; selectivity for C_1-C_4 14.1%, for naphtha 34.3%, for middle distillates 51.6%	[20]

 Table 5. Catalytic properties of HZ-MWW

Table 5. (Contd.)

Reaction	Zeolite	Si/Al	Conditions	Process characteristics	Reference
Cracking of tetralin	MWW	15	0.1 MPa, 450°C	Selectivity for benzene 13.4%, ole- fin/naphthenes—aromatics 28.9%, selec- tivity for naphthalene 17.1%	[21]
	HZ-MWW/D	15		Selectivity for benzene 15.2%, ole- fin/naphthenes—aromatics 25.%, selec- tivity for naphthalene 18.8%	
Cracking of decalin	MWW	15	0.1 MPa, 450°C	Selectivity for propylene 16.3%, for C_4 fraction 30.3%	[21]
	HZ-MWW/D	15		Selectivity for propylene 17.1%, for C_4 fraction 30.6%	
Hydroisomeriza- tion of heptane	Ni–MWW	13.1	0.5 MPa, H ₂ /C ₇ 19.6, 240°C	Conversion 20.1%, selectivity for <i>iso</i> -C ₇ 78.35%	[16]
	Ni–HZ- MWW/R	13.1		Conversion 15.6%, selectivity for <i>iso</i> -C ₇ 82.20%	
Hydrogenation of naphthalene	Pt-HZ- MWW/D	50	10% naphthalene in <i>n</i> -decane, 5.0 MPa, 275°C, stirring 1000 rpm	$k 1.82 \times 10^{-4} (\mathrm{s}^{-1} \mathrm{g_{cat}}^{-1})$	[20]
Dehydrogenation of propane	Ga–MWW	20	600°C, C ₃ H ₈ /CO ₂ 2.5/5.0, 0.1 MPa	Conversion 20.6%, selectivity for C_3H_6 64.1%	[22]
	Ga–HZ- MWW/D	20		Conversion 14.5–19.7%, selectivity for $C_{3}H_{6}$ 73.7–84.5%	
Dehydrogenation of isobutane	MWW	15	70°C, feed rate $10^{-6} - 10^{-4}$ (mol of	k_{cracking} 3.3 (mol (mol H ⁺) ⁻¹ s ⁻¹ bar ⁻¹),	[23]
	HZ-MWW/P	20	alkane g ⁻¹ s ⁻¹)	k_{cracking} 4.2 (mol (mol H ⁺) ⁻¹ s ⁻¹ bar ⁻¹), $k_{\text{dehydrogenation}}$ 4.2 (mol (mol H ⁺) ⁻¹ s ⁻¹ bar ⁻¹)	
Oligomerization of ethylene	Ni–MWW	14	4.0 MPa, 70–150°C, stirring	Output 1.1–2.5 ($g_{prod}/g_{cat}h$), selectivity for C ₆ –C ₈ 17–18%	[24, 25]
	Ni–HZ- MWW/P	26	1000 rpm	Output 10–46 ($g_{prod}/g_{cat}h$), selectivity for C_6-C_8 14–40%	
Oxidation of hex- ene-1	Ti-MWW	44*	60°С, 0.1 МРа, Н ₂ О ₂	Conversion 26.2–58.7%, selectivity for hexene oxide 96–99.5%	[26, 27]
	Ti–HZ-MWW/S	49*		Conversion 29.5%, selectivity for hexene oxide 99%	[26]
Oxidation of cyclo- hexene	Ti–MWW	44*	60°C, 0.1 MPa, H ₂ O ₂	Conversion 12.7%, selectivity for cyclo- hexene oxide 62%	[26]
	Ti–HZ-MWW/S	49*		Conversion 20.3%, selectivity for cyclo- hexene oxide 71%	
Epoxidation of propylene	Au–Ti–MWW	45-160*	200°C, 0.1 MPa, feed rate	Conversion 0.6–2.1%, selectivity 33.3–63.1%	[28]
	Au–Ti–HZ- MWW/P	30-94*	$7000 \text{ cm}^3/(\text{hg}_{\text{cat}})$	Conversion 0.6–1.6%, selectivity 41.4– 94.5%	

* Si/Ti.



Fig. 2. Low-temperature nitrogen adsorption-desorption isotherms on (1) MZ-MWW and (2) HZ-MWW prepared using (a) delaminating [44], (b) pillaring [16], and (c) recrystallization [13] methods.

CATALYTIC PROPERTIES OF HIERARCHICAL MWW

Hierarchical zeolites have a more open structure compared to the MWW zeolite, which facilitates the elimination of diffusional limitations for reactant and product molecules within the zeolite crystal and increases the accessibility of acid sites, leading to an enhancement of the activity and selectivity of such catalysts in reactions involving large molecules. On the other hand, the choice of the HZ-MWW synthesis procedure leads to a change in the strength and number of acid sites. Therefore, hierarchical zeolites appear to be more active catalysts than their microporous precursors in reactions involving weak acid sites and bulky reactant molecules, whereas the activity of HZ-MWW having less strong centers is lower than that of strongly acidic zeolites in processes where strong acid sites are needed. The catalytic properties of HZ-MWW in the petrochemical processes are systematized in Table 5. Hierarchical MWW zeolites prepared by pillaring, delamination, silanization, desilication and recrystallization are designated HZ-MWW/P, HZ-MWW/D. HZ-MWW/S. HZ-MWW/Des, and HZ-MWW/R, respectively in the table.

Alkylation processes. The activity of HZ-MWW was studied in the alkylation of benzene with alkenes [8–10], biphenyl with propylene [12], toluene with methanol [11], and phenol with *t*-butanol [13]. Corma et al. [46] suggested that the reaction of benzene alkylation with olefins is catalyzed by Brønsted acid sites located on the external surface of the zeolite [46]. Comparison of the activity of zeolites MWW and HZ-MWW/D in the reaction of liquid-phase alkylation of benzene with propylene showed that the activity of the hierarchical zeolite at 90°C and a pressure of 3.0 MPa

is higher than that of MWW (99.0 and 95.6%, respectively). This difference was explained by the fact that HZ-MWW/D has a significantly higher surface area than MCM-22 and, accordingly, more acid sites located on the external surface [8]. By means of the TPD-NH₃ [8] and IR-Py [12] techniques, it was found that the concentration of strong acid sites in HZ-MWW/D is lower than in MCM-22, which results in a higher selectivity of the micro-mesoporous catalyst for monoalkylated products and a lower selectivity of the formation of products of deeper alkylation [8, 12]. Similar results were obtained by Liu et al. [10], who studied the process of benzene alkylation with a mixture of C₃ and C₄ alkenes. Thus, due to the optimal acidity and hierarchical structure, hierarchical MWW zeolites are more active and selective catalysts for cumene synthesis compared to MWW [45].

The creation of mesopores in MWW in the case of toluene alkylation with methanol leads to an increase in the selectivity for xylenes and a decrease in the selectivity for trimethylbenzenes, with the proportion of the ortho-isomer in xylenes substantially increasing. In contrast to HZ-MWW/P, about 70% p-xylene of the total xylenes is formed by alkylation over MCM-22, which is explained by the fact that the formation of the *p*-isomer mainly occurs in 10-membered ring channels and 12-membered ring cavities located inside the MCM-22 crystal, in which the formation of the o- and m-isomers and polyalkylated compounds is limited [11]. At the same time, the comparison of the catalytic characteristics of MCM-22 and HZ-MWW/P zeolites showed that the toluene conversion on HZ-MWW/P is lower, a difference that is associated by the authors with a smaller amount of

acid sites in the latter because of the blocking of acid sites on the surface by silica bridges.

Song et al. [13] showed that a material with an hierarchical structure prepared using the recrystallization method exhibits high activity in the phenol alkylation reaction with tert-butanol. With close phenol conversion values of 94.0 and 93.3% for MWW and HZ-MWW/R, respectively, the selectivity for disubstituted 2,4-di-tert-butylphenol was 30.6 and 53.9 mol %, respectively, which is due to the removal of diffusional constraints for large organic molecules in the porous HZ-MWW structure. In contrast to Song et al. [13], Meloni and co-workers [32] found that the presence of mesopores in HZ-MWW obtained by pillaring and delamination did not significantly influence the catalytic activity in the alkylation reaction of phenol with tert-butanol. It is believed that this can be due to a change in the acid properties of the samples during the preparation of hierarchical zeolites [33].

The creation of a hierarchical structure in MWW has an effect on the on-stream stability of the catalysts. Tempelman et al. [9] explained an increase in the onstream stability of delaminated MWW in the liquidphase alkylation of benzene with propylene by greater accessibility of Brønsted acid sites. Corma et al. [47] revealed that MWW with a hierarchical structure obtained by pillaring is less resistant to deactivation in benzene alkylation with propylene, a fact that correlates with the low content of Brønsted acid sites in the sample. In contrast to Corma et al [47], Dumitriu et al. [11] found that HZ-MWW/P operated stably over the time on stream. Diaz et al. [33] noted that HZ-MWW prepared by pillaring or delamination are resistant to deactivation, unlike MCM-22, which activity is markedly reduced in alkylation of phenol with tert-butanol over time.

Acylation processes. The catalytic properties of HZ-MWW prepared by desilication using the treatment of MWW zeolite in an alkali solution were studied in the acylation of anisole [14] and furan [15] with acetic anhydride. The creation of mesopores, elimination of diffusional limitations, enhancement of the access to active sites, and an increase in the density of acid sites led to an increase in the conversion of anisole by more than a factor of 1.7 and in the furan acylation rate by a factor of 12.5 over HZ-MWW compared to MWW.

Cracking of hydrocarbons. Hierarchical zeolites MWW are effective catalysts for the cracking of large molecules. Studies of HZ-MWW in the cracking of triisopropylbenzene [18, 19], *n*-decane [19], cumene [18], tetralin, and decalin [21] and hydrocracking of light gas oil fractions [20] made it possible to determine the effect of the porous structure on the catalyst activity. The delamination procedure increases the accessibility of acid sites for large molecules, but it simultaneously decreases the strength of acid sites [47], the detriment caused by the harsh conditions

necessary for preparing HZ-MWW/D [41]. Therefore, HZ-MWW/D activity in the cracking of small molecules, such as *n*-decane [19] and cumene [18], which can freely pass through ten-membered channels but require strong acid sites for their conversion, is lower than for MWW. Comparison of the activity of the microporous and the hierarchical zeolite in the cracking reaction of larger molecules, such as triisopropylbenzene [18, 19], tetralin, and decalin [21], has shown that the presence of mesopores significantly increases the activity of the catalyst, since the creation of the hierarchical structure increases the accessibility of active sites and eliminates diffusional limitations.

Isomerization of n-alkanes. Kollar et al. [16] studied the effect of the hierarchical structure of bifunctional Ni-loaded zeolite on the catalytic characteristics in the hydroisomerization of *n*-heptane. Comparthe ison of catalytic and physicochemical characteristics showed that the desired isomerization reactions occur in 10-membered ring channels. It was found that isomers with higher branching are produced on hierarchical zeolites than on the microporous ones due to the presence of larger pores. The passage through the internal 10-membered channels in the zeolite takes a longer time than the residence time at the external acid sites, which could lead to a greater contribution of cracking to side processes. However, the amount of cracking products is almost the same in the cases of microporous and hierarchical zeolites, thereby indicating that the heptane cracking reaction occurs on identical acid sites located on the external surface of the materials.

Hydrogenation and dehydrogenation processes. Hierarchical zeolites are active in the dehydrogenation of light alkanes [22, 23] and in the hydrogenation of naphthalene [20]. The effect of the acidity and porosity of the MWW structure on propane dehydrogenation was studied in [22]. The catalysts were prepared by depositing Ga_2O_3 onto MCM-22 and HZ-MWW/D. The acid and porosity characteristics of HZ-MWW/D were tuned by varying the sonication time from 1 to 4 h. A more open structure, a larger specific surface area, and a lower concentration of strong acid sites made Ga/HZ-MWW/D more stable and more selective for propylene relative to the Ga/MWWcatalyst.

Oligomerization of ethylene. Nickel-loaded MCM-22 and HZ-MWW/P were prepared by ion exchange and studied in the ethylene oligomerization reaction. The Ni–HZ-MWW/P catalyst exhibited higher catalytic activity and selectivity for C_6-C_8 olefins than Ni-MCM-22, a difference that is explained by greater accessibility of active sites and a lower amount of acid sites in the catalyst with the hierarchical structure. An increase in the nickel loading and elevation of the reaction temperature enhance the activity of the catalyst and promote an increase in the proportion of C_6 – C_8 oligomers in the products [24, 25].

Oxidation of alkenes. Hierarchical titanosilicates with the MWW structure are active in the oxidation of hexene-1 and cyclohexene in the presence of H_2O_2 [26, 27], and Au-modified Ti-HZ-MWW mediate the epoxidation of propylene [28]. The introduction of a silanol dimer into the titanosilicate structure resulted in a more selective (99 versus 96%) catalyst with a hierarchical structure for the hexene-1 oxidation reaction, although it was less active (conversion of 29.5 versus 54.2%). The use of a catalyst with a hierarchical structure in the cyclohexene oxidation reaction leads to an increase in conversion from 12.7 to 20.3% and the selectivity for cyclohexene oxide from 62 to 71%. Xu et al. [26] believe that the cyclohexene oxidation reaction proceeds predominantly on the external surface at acid sites located in large hemicages. This feature is due to the fact that cyclohexene experiences difficulties in diffusion in narrow sinusoidal MWW channels, since its molecular size is 5.0 Å, which is comparable to the size of the 10-memberred MWW channels. The creation of mesopores in MWW facilitates the access of substrate molecules to the active sites, thereby leading to an enhancement of the activity of HZ-MWW.

CONCLUSIONS

The analysis of the literature on the synthesis of hierarchical zeolites of the MWW structure has shown that pillaring, delamination, and recrystallization are effective techniques of creating a mesopore system in MWW crystals, with recrystallization being the only method that makes it possible to obtain samples with a unimodal size distribution of mesopores. Recrystallization is also the simplest and most effective way of synthesizing micro-mesoporous materials. The analvsis of published data on the catalytic properties of hierarchical MWW zeolites structure has shown that they are promising catalysts for various petrochemical processes. These prospects concern to a greater extent the processes of alkylation of benzene with olefins and phenol with tert-butanol, as well as cracking of triisopropylbenzene.

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