

Review

Development of catalytic properties of mordenite zeolite via chemical modification

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ABSTRACT

Mordenite is an industrially important zeolite used as a catalyst for various reactions, viz. hydrocarbon hydrocracking, hydroisomerization, alkylation, reforming,

and dewaxing, as well as in the production of dimethyl amines. It has, recently, been used for hosting semiconductors, chemical sensors and non-linear optical materials. There have been numerous articles and patents concerning mordenite synthesis in the presence or absence of organic templates as structure directing agents that help tailoring pore openings for some selected catalytic reactions. Nano-particle (≤ 100 nm), large-crystal (7-500 micron) types of mordenite have been synthesized by conditioning the gel composition, crystallization and templating. Synthesis of such nano-particle mordenites permits applications to sorption and catalysis with developed surface properties as compared to the micro-particle ones. Mordenite's shape selectivity, acidity and thermal stability are unique features. It decomposes at 1113 K yielding amorphous *anorthite* and SiO₂ materials. In order to optimize the catalytic properties of mordenite, the zeolite has been subjected to **chemical modification** using (i) metal ion incorporation, (ii) pore size engineering, and (iii) partial dealumination. The present article reviews and assesses impacts of these various modification methods on characteristics, adsorptive and catalytic conduct of mordenite zeolite toward a number of reactions of industrial and technological importance, e.g. organic synthesis, hydrocarbon disproportionation and isomerization, NO_x selective reduction, total oxidation, and cracking reactions.

Keywords: Mordenite; Zeolite; Chemical Modification; Catalytic Properties

1 Introduction

Mordenite is a zeolite of Na₈Al₈Si₄₀O₉₆.nH₂O composition and orthorhombic crystal structure defined in the *cmcm* space group. Its framework is built on 5-

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membered rings stacked in columns parallel to the [001]-direction (Fig.1). Thus, the framework includes elliptical micropore ($6.7 \times 7.0 \text{ \AA}$) channels parallel to the c -axis and ($2.6 \times 5.7 \text{ \AA}$) channels parallel to the b -axis. Since the latter channels are too tight to sorption of most molecules, mordenite is regarded as a uni-dimensional zeolite [1]. The unit cell of sodium mordenite assumes the following dimensions: $a = 18.121 \text{ \AA}$, $b = 20.517 \text{ \AA}$ and $c = 7.544 \text{ \AA}$. The most common morphology of mordenite particles is needle-shaped with the c -axis elongated [1].

Mordenite is an industrially important zeolite used as a catalyst for various reactions, viz. hydrocarbon hydrocracking, hydroisomerization, alkylation, reforming, and dewaxing, and, also, in the production of dimethyl amines. It has, recently, been used for hosting semiconductors, chemical sensors and non-linear optical materials [2]. There have been lots of articles and patents concerning mordenite synthesis in the presence or absence of organic templates as structure directing agents that tailor pore openings for some selected catalytic reactions [3,4]. Nano-particle ($\leq 100 \text{ nm}$), large-crystal ($7\text{-}500 \text{ micron}$) types of mordenite have been synthesized by conditioning the gel composition, crystallization and templating [2,4]. Synthesis of such nano-particle mordenites permits applications to sorption and catalysis with developed surface properties as compared to the micro-particle ones [5]. Mordenite's shape selectivity, acidity and thermal stability are unique features. It decomposes at 1113 K yielding amorphous *anorthite* and SiO_2 materials. In order to optimize the catalytic properties of mordenite, the zeolite has been subjected to **chemical modification**

using various procedures, most importantly are the *metal ion incorporation*, *pore size engineering* and *partial dealumination*.

2 Metal Ion Incorporation into Mordenite

Catalysis chemists worldwide have paid much attention to mordenite loaded with transition metal ions (TMI) for use as oxidative catalysts of potential conduct. The advantage of using mordenite over organic-based ion-exchange resins and clay minerals is based on its excellent ion-exchange capacity that permits revealing the nature of both the complex interactions between the framework-metal-ions and solvent molecules, and the properties of the electrolyte solution in contact with the ion exchanger [2]. Ion exchange is well suited for zeolite modification, whereby introduction of different cations modifies the catalytic and sorption performances of the zeolite. It controls the effective pore size and modifies the electrostatic field and field gradient in the zeolite [6], thus generating active sites inside the framework capable of attracting reactant molecules and prompting their bond distortion and rupture. These are necessary molecular rearrangement events for the anticipated chemical change to occur.

Activity and shape selectivity of a zeolytic catalyst depend generally on the dispersity (particle size), structure, morphology, and composition of the incorporated TMI particles, as well as their interactions with the framework components. A fair TMI dispersion will depend on a proper selection of the precursor compound and the zeolite material (mordenite). Various TMI loading methods have been adopted (Table 1) for effecting high activity

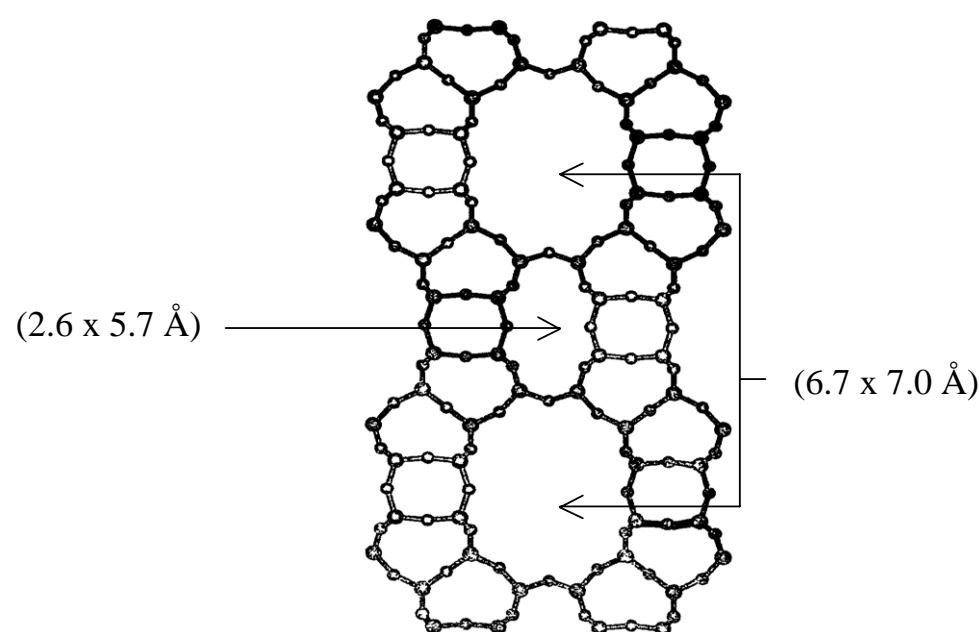


Fig. 1. The structure of mordenite as viewed down the [001] direction

and selectivity, including ion-exchange, impregnation, chemical vapor deposition (CVD) and implantation processes. Isomorphous substitution of TMI into the mordenite framework governs the zeolite selectivity, depending on synergistic effects of the TMI and the zeolite.

2.1 Transition metal ion-mordenites

Table 1 sets out typical examples of TMI-incorporated mordenites (M) and their methods of preparation and characterization, and applications to various catalytic reactions.

Modern combustion engines require a fuel with a high octane number (ON). The naphtha directly obtained by distillation of crude oil cannot meet this requirement. An ecologically sound way to increase the ON of a fuel is by increasing the concentration of branched alkanes at the expense of linear alkanes. Thus, hydroisomerization reactions find a lot of concern of many researchers, specially when performed on Pt-containing catalysts. Pt-exchanged mordenite (PtM) is very suitable for this kind of reactions, since it works as a bifunctional hydrogentaion acid-mediating catalyst for various reactions,

Table 1: Preparation features, characterization methods and catalytic applications of some selected TMI-incorporated mordenites.

TMI precursor	TMI loadings	TMI loading method	Characterization methods ^{a)}	Catalytic applications	Ref.
[Pt(NH ₃) ₄](NO ₃) ₂	0.5-5.0 Wt % -Pt/M	Ion exchange	¹²⁹ XeNMR; TEM; XRD; TPR; H ₂ adsorption	Isomerization of n-alkane; aromatization of paraffins	7,8
	5 Wt% -Pt/M	Ion exchange	¹³ C and ¹ H MAS-NMR; XPS; ¹²⁹ XeNMR	Toluene disproportionation mainly to benzene; Xylenes and cumene transformations,	9,10
Ni (NO ₃) ₂	1.4 Wt% -Ni/M	Ion exchange	¹³ C and ¹ H MAS-NMR; XPS; ¹²⁹ XeNMR	Transalkylation of C ₉ ⁺ aromatics	11
FeSO ₄ ·7H ₂ O or FeCl ₃	10-20 Wt% -Fe/M	Ion exchange, or mechanical mixing	N ₂ sorption; NH ₃ sorption; TG; XRD; FTIR; Moessbauer	Ethanol transformation; polymerization of N, N-diethanol acrylamide,	12,13
Cu(NO ₃) ₂	8.2 Wt% -Cu/M	Ion exchange	In-Situ FTIR; SEM; TPD; EXAFS; ESR	DeNOx reactions	14
AuCl ₃	5 Wt% -Au/M	Mechanical mixing and ion exchange	In-Situ FTIR	Water-gas shift reactions; CO oxidation; Formic acid decomposition	15
[Ru(NH ₃) ₆] ³⁺	3.95 Wt% -Ru/M	Ion exchange	N ₂ sorption; H ₂ chemisorption; XRD	N-alkylation of amino groups of melamine (fine chemicals)	16

^{a)} ¹²⁹XeNMR, ¹²⁹Xe nuclear magnetic resonance spectroscopy; TEM, transmission electron microscopy; XRD, X-ray diffractometry; TPR, temperature-programmed reduction; ¹³CNMR, ¹³C nuclear magnetic resonance spectroscopy; XPS, X-ray photoelectron spectroscopy; MAS-NMR, magic angle spinning nuclear magnetic resonance spectroscopy; TG, thermogravimetry; Moessbauer, Moessbauer spectroscopy; FTIR, Fourier-transform infrared spectroscopy; TPD, temperature programmed desorption; EXAFS, extended X-ray absorption fine structure spectroscopy; ESR, electron spin resonance spectroscopy; SEM, scanning electron microscopy; ²⁷Al MAS-NMR, ²⁷Al magic angle spinning nuclear magnetic resonance spectroscopy.

e.g. normal alkane isomerization, paraffins aromatization and aromatic alkylation [7-10,17,18]. For example, benzene hydrogenation activity of PtM depends on the metal particle size, zeolite Brönsted acidity and the hydrogen molecule dissociation at the metal boundary [19]. Optimal activity is achieved upon partially replacing the content of Na cations by H ions. The activity is rendered even higher at high H_2 pressure in the presence of thiophene as a reducing agent. Catalysts modified to allow for the synthesis of fine bulky chemicals, as the alkylation of melamine on Ru-exchanged Mordenite (RuM), showed external surface activity so that considerable unwanted side reactions were found to coincidentally take place [16]. Such side reactions must be suppressed. Implantation is another method of inserting Ti in M, using $TiCl_4$ vapor deposition. TiM, thus produced, is distinguished by high activity for ammoximation of ketones into oximes [20-21]. Effects of reaction variables and the shape-selectivity for various ketones were studied to elucidate the reaction mechanism, which was, accordingly, suggested to be as schematized in Fig. 2.

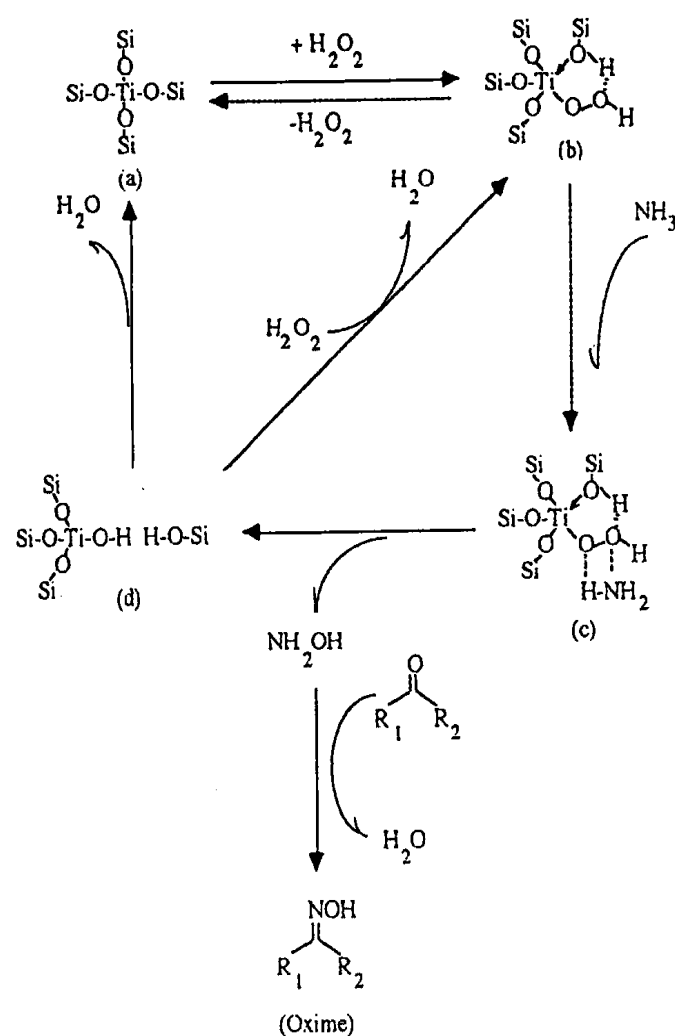


Fig. 2. Schematic representation of ammoximation reaction mechanism, as adapted from ref. [20]

Selective oxidation reactions are important to the chemical industry, particularly those used to activate alkanes, alkenes and arenes. Titanium-containing zeolites are highly selective oxidation catalysts when hydrogen peroxide is the oxidant. Catalytic hydroxylation of phenol, oxidation of styrene and epoxidation of propylene with aqueous H_2O_2 have been efficiently carried out on TiM [22]. Nano-sized particles of TiO_2 , particularly when confined inside mordenites, are expected to show different physical and chemical properties from those of bulk TiO_2 . Their photocatalytic activity is enhanced not only because of their increased surface area, but also due to changes in their surface structure (e.g. generation of lattice defects) following Ti incorporation into mordenite. Photocatalytic degradation of aromatic pollutants over TiM occurs till almost complete decomposition (mineralization) in a short period of time. This has been explained in view of the open structure and the high surface area the mordenite has. The shape selectivity-favored liquid phase hydroxylation of aromatic hydrocarbons with H_2O_2 has been studied over two kinds of titanosilicates, the large pore TiM with MOR structure and medium pore TS-1 with MFI structure. The liquid phase diffusion of the aromatics into both catalysts was compared in the presence of H_2O and H_2O_2 to find out the origin of the shape selectivity. The hydroxylation rate of TS-1 decreased monotonically with increasing the molecular size in the order: benzene > Toluene > ethylbenzene > cumene, whereas TiM showed the maximum rate for toluene hydroxylation [23]. It has been concluded that a bulky Ti-peroxo species (Ti-OOH) formed by the interaction of Ti sites with H_2O_2 molecules mainly cause a transition-state shape selectivity favouring the hydroxylation of bulky aromatics in titanosilicate/ H_2O_2 systems [24].

For some specific reactions, an in-situ incorporation of TMI during the mordenite synthesis is important, as for the latter reaction. However, such preparations are usually correlated with the stability of TMI in tetrahedral oxygen surroundings. It has been estimated that the tetrahedral surrounding could be stable for cations with $0.414 > \rho > 0.225$, where $\rho = r_m/r_O$, and r_m and r_O are the radii of the cation and the oxygen, respectively. Within this context, isomorphous substitution of Fe^{3+} in the framework of mordenite has been successfully affected under hydrothermal template-free conditions, using various gel compositions of $SiO_2/Al_2O_3+Fe_2O_3$ [25]. This type of catalysts showed high activity in liquid phase oxidation reactions, using H_2O_2 as an oxidant.

In a way of getting over problems caused by homogeneous catalysis of polymerization reactions [25],

such as color formation and the difficulty of separating the products, FeM was successfully used in catalyzing the polymerization between N,N-diethanol acrylamide (DEAA) and phthalic anhydride (PA) to polyesteramide (PEA) resin [13]. This reaction was kinetically followed to show that it is completed in only 25 min compared with 170 min when using homogeneous catalysts (e.g., *p*-toluene sulphonic acid). Moreover, FeM exhibited a strong catalytic performance in the selective catalytic reduction (SCR) of NO either by NH₃ or hydrocarbons [26-27]. It has been shown that the SCR of NO by NH₃ on FeM surpasses the activities observed for Fe/HEU, Fe/FER, Fe/BETA and Fe/CHA zeolite catalysts [26]. The activity has, moreover, been shown to increase upon decreasing the Si/Al ratio of the M zeolite with 100% NO-conversion. SO₂ and SO₂+H₂O additives to the reaction did not cause any loss on the NO reduction activity but rather improved it. TPR and FTIR studies [27] indicated the presence in the FeM catalyst of approximately 73%-Fe³⁺ and 27%-Fe²⁺. They informed, moreover, that the reaction between NO₂ and a pair of NH₄⁺ ions to generate an active intermediate, which then react with NO to produce N₂ and H₂O, is a prerequisite for a firm NO reduction. For the FeM catalyst, there existed a good correlation between the N₂ selectivity in the selective catalytic oxidation (SCO) reaction and the activity in the SCR of NO with ammonia; viz., the higher the SCR activity is, the higher the N₂ selectivity in SCO [28].

A preferential oxidation of CO remaining in reformed H₂ fuels, the future clean technology, is one of the most important reactions carried out on FeM promoted by Pt in a way of avoiding a serious poisoning of anode catalysts in the fuel cells. The crucial requirement to be fulfilled by the catalyst is high CO oxidation-rate and selectivity at < 473 K [29]. Methane partial oxidation to methanol over zeolitic α -oxygen sites has also been performed using FeM and FeZSM-5 catalysts. α -oxygen can be formed on dinuclear iron sites in zeolites by N₂O decomposition at elevated temperatures and is independent of the zeolite structure. A range of preparative and activation conditions was studied preceding methane conversion. Proper activation is essential to maximize the catalyst selectivity, e.g. activation with N₂O at 523 K and reaction with methane at 473 K. Structure-activity mutual impacts are presumed to take part in the reaction [30].

On the other hand, CuM is deactivated while passing H₂O and SO₂ gases on the stream during the NO_x reduction, due to alteration of the copper oxidation state [31]. The physicochemical properties of

SO₂-deactivated CuM catalysts have been extensively characterized by TG, TPSR, XPS, Raman, XANES and N₂ sorptiometry. Not only the catalyst surface was deactivated by sulfur, but also the existence of S-O species, as SO₄²⁻ moieties, was revealed by Raman spectroscopy. Coq et al. [32] explained that the catalyst activity towards NO reduction is also dependent on the Cu²⁺ site density; in the sense that isolated Cu²⁺ ions are much favourable to CuO clustering. Thus, knowledge of the location and coordination of the TMI in the zeolite is indeed required. Accordingly, Attfield et al. [33] studied the locations of extraframework Cu²⁺ cations in hydrated and partially dehydrated analogues of CuM by means of single crystal X-ray diffractometry. They were, thus, able to identify two sites in the hydrated sample: one in the elliptical 8-membered ring (8-ring), and the other in the center of the main 12-ring channel. Upon dehydration three copper sites were exposed; one in the elliptical 8-ring, another above the 6-ring in the main channel, and the third in the circular 8-ring that leads into the main channel. The low coordination, but high accessibility, of the latter two Cu sites in the partially dehydrated sample provides a possible explanation for the high activity of CuM in the NO reduction [33].

Although problems still exist for the practical utilization of CuM, viz. poisoning by SO₂ and steam dealumination during the early stages in the reaction, Tost et al. [34] claimed that Cu(II)-exchanged M maintained its catalytic activity after 20h of reaction in the presence of 100 ppm SO₂. It has been found that Cu(I) ions occluded within the nanopores of M or ZSM-5, with planar three- coordinate or two-coordinate geometry, are active in photocatalytic decomposition of NO_x into N₂ and O₂ at temperatures as low as 275 K. The photocatalytic reactivity of these Cu(I)/zeolite catalysts was strongly affected by the local structure of the Cu(I) ions which could easily be modified by changing the type of zeolite and the loading level of the copper ions [35]. Some Mordenite-based catalysts including Ni and Pd showed high initial activities when either hydrocarbons or ammonia were used as reducing agents [36-37]. For the former type of catalyst (NiM), a correlation between the concentration and strength of acid sites of Ni-exchanged ZSM-5, M and MCM-22 has been found. Ni/ZSM-5 was the most active catalyst for the NO reduction by propane, due to the high concentration of strong acid sites. Using propene as a reductant, Ni/ZSM-5 and Ni/MCM-22 were rapidly deactivated, owing to the acid site-catalyzed formation of carbonaceous deposits. In contrast, Ni/M was less affected by the deposits formed because of its larger pore size.

For PdM catalysts [37], it seemed that the total number of Pd^{2+} ions and the relative abundance of the mono- and dinitrosyl species, as traced by in-situ FTIR spectroscopy, determine to a great extent the activity of Pd/PdO particles. Recent studies on PdM have indicated that this catalyst is more tolerant to the presence of either water or SO_2 at > 723 K, especially when promoted with small amounts of Pt, than the corresponding monometallic Pt or Pd-HM [38]. The inhibition occurred on PdM at < 723 K, when $\text{SO}_2 + \text{H}_2\text{O}$ coexist in the feed stream, has been attributed to an enhanced water adsorption and, thus, poisoning of the active sites.

Looking for a catalyst possessing a potential activity for NO decomposition, it has been claimed [39] that CoMFI and CoM zeolites, containing Co in the framework, have considerably larger activity for NO decomposition than does CuMFI. Selective reduction of NO with hydrocarbons in an oxidizing atmosphere on CoM showed high activities comparable to those observed on Fe and CuMFI catalysts [39]. It has been shown that Brönsted acid sites of M are active for the SCR of NO by CH_4 . CoM samples were far more active than NaM and HM samples, thus indicating that protons play a negligible role when Co is present. Co^{2+} ions dwelled in the main channels of M are the active sites for the $\text{CH}_4 + \text{NO} + \text{O}_2$ reaction [40]. Shichi et al. [41] showed that the reaction rate increases with the cobalt loading level, and that the rate over large crystals of M was slightly lower than that over small crystals of M. The pathway for selective reduction of NO_x by methane over CoM catalysts has been studied [42] by comparing rates of the individual reactions (NO oxidation, CH_4 oxidation or NO_2 reduction) with that of the combined reaction ($\text{NO} + \text{O}_2 + \text{CH}_4$). The results obtained could help proposing a bi-functional pathway for the reaction, in the sense that metal sites catalyze the NO oxidation, whereas the protons catalyze the formation of the N_2 . The activity of CoM could be improved by additives of Pd. Namely, the activity at high temperature regimes was considerably increased in an oxygen-free feed ($\text{CH}_4 + \text{NO} + \text{H}_2\text{O}$) and the temperature window of CoM became wider. XPS and TPR examinations [43] revealed that cobalt is uniformly distributed as Co^{2+} in fresh Pd/CoM samples, whereas Pd exists as Pd^0 and Pd^{2+} on the surface. The presence of Pd was found to shift the reduction temperature of Co^{2+} cations at exchange positions to lower regimes [43].

Incorporation of TMI into the mordenite framework can, also, be achieved by post-synthesis methods (solid-liquid interaction and solid-gas interaction). In this regard zincosilicate analogues of mordenite was synthesized

in the presence of citric acid acting as a complexing agent. This system has been found [44] to exhibit a high catalytic activity in aromatization and dehydrogenation reactions.

2.2 Alkali ion- and rare earth ion-mordenites

Research has shown that mordenite zeolite is deactivated via carbonaceous deposits, which block the active acid sites. The selectivity to oxygenated products can be significantly enhanced using a form of mordenite in which the protons have been exchanged by alkali metal cations such as Li, K and Cs. Alkali cation exchange, such as of Na^+ ions, causes significant modifications to the acidic and catalytic properties of mordenite towards *m*-xylene transformation at 623 K. This extends to the product distribution, leading to an increase in the selectivity to isomers at the expense of disproportionation products. This effect has been attributed [45] to a decrease in the proximity of protonic acid sites, as observed by FTIR spectroscopy. Obtained FTIR spectra showed the Na-exchange to lessen the intensity of absorptions corresponding to bridging OH-groups, with those located inside pockets being more affected than those in large channels [45]. Accordingly, protonic sites inside pockets have been suggested to be the active sites, and that reactions of *m*-xylene are much affected by internal diffusion, whereas the unidimensional channel system gives products with the lowest *para/ortho* ratio. Hence, *m*-xylene has been found to enable the characterization of medium, large and extra-large pore zeolites [46], under identical experimental conditions. NaHM was also found to catalyze the pyrolysis of n-hexane to ethylene, following a carbenium ion mechanism [47].

The acidic and basic properties of M, with or without metal modification, were characterized using NH_3 -TPD and CO_2 -TPD, respectively [48]. To increase the ethylene selectivity, non-acidic NaM was the best candidate catalyst. It has been shown [48] that the location and diffusion of Na cations depend on the Si/Al ratio. Monte Carlo simulation of dielectric relaxation in NaM indicated that the Na^+ hops are responsible for the polarization change and thus the activity. Oxidative methylation of toluene was carried out over BaO-modified mordenite to produce ethylbenzene and styrene in comparison with X, Y and ZSM-5 containing BaO catalysts [49]. The Si/Al ratio, structural geometry and the accessibility of BaO have been found to control the catalyst activity. Side chain alkylation of 4-picoline by formaldehyde was investigated at 570 K over alkali and alkaline earth cations (Li, Na, K, Rb, Cs, Mg, Ca, Sr

and Ba) modified zeolites (M, ZSM-5 ion, X, Y and MCM-41) to determine their reactivities. Amongst the test catalysts, alkali (Li, Na, K, Rb, Cs) modified ZSM-5 and M showed the highest conversion of picoline and selectivity to vinylpyridine. The characterization results suggested a correlation to exist between the catalyst basicity and activity in the side chain alkylation. In addition, they attributed the decrease in activity of the alkaline earth containing catalysts to their larger ionic radii [50] as compared to the alkali metal ions.

Most researchers have used ion exchange to achieve maximal metal ion dispersion. Unfortunately, this method triggers a marked drop in the zeolite Brönsted acidity [12-13]. So, one has to make a fair compromise that maintains acidity as well as selectivity features. In this regard, one may sacrifice the external surface acidity by poisoning with ceria (CeO_2), for instance, for gaining a better shape selectivity catalysis that mainly occurs inside the zeolite structure. Ceria-modification [51] of M is an effective method for the suppression of reactions proceeding at the external surface, leaving a better chance to those occurring within the pores. On the other hand, the amount of NO_2 formed on CeM during NO reduction [52] was comparable to that formed on NaM, suggesting that Ce ions, which adsorb propene and NO_2 , are the active sites for the $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ reaction. Accordingly, it has been suggested [52] that the active sites in CeM are Ce ions exchanged at the Na sites. One expects much progress in the near future, both with respect to the development of environmentally benign technology and in the scientific understanding of the catalytic deNOx action.

3 Pore Size Engineering of Mordenite

The tailoring of porous materials, particularly zeolites, poses a broad challenge best appreciated by considering the range of applications where certain types of new porous materials are needed in devices or systems that perform specific functions. Examples include shape-selective gas or liquid separation and catalysis. Because of difficulties usually encountered while tailoring such porous materials, it has been attempted to modify zeolites, particularly mordenite (M), with some specific groups either for internal or external modification. This indeed facilitates changes in both surfaces to desired performances.

3.1 Internal surface modification

The channel-like structure of zeolites of precise geometry with pores of uniform shape, throughout the entire crystal, is an essential requirement for molecular

sieves that can be used for separating gas mixtures by selective adsorption. Practically, the separation capability of zeolites can be achieved or altered by chemical modification, using modifiers containing silicon or boron hydride functional groups. Silylation of large port (LP) HM, carrying varying amounts of OH groups, results in the chemisorption of SiH_4 . Amounts of physisorbed SiH_4 and liberated H_2 revealed a global estimation of the extent of the occurring reactions [53]. After silylation, the unstable Si-H groups were oxidized to Si-OH groups by successive water vapor treatments at room temperature and dehydration at 633 K in vacuo. Adsorption of inert gases of different size on pure and silylated HM revealed a relationship to exist between the modification parameters and the obtained structure of the zeolite [53]. Room temperature modification with increasing amounts of SiH_4 showed that a gradual decrease of the pore size was obtained [53]. In Fig. 3, the adsorption kinetics at 273 K of Kr and Xe on HM, before and after silylation, are illustrated.

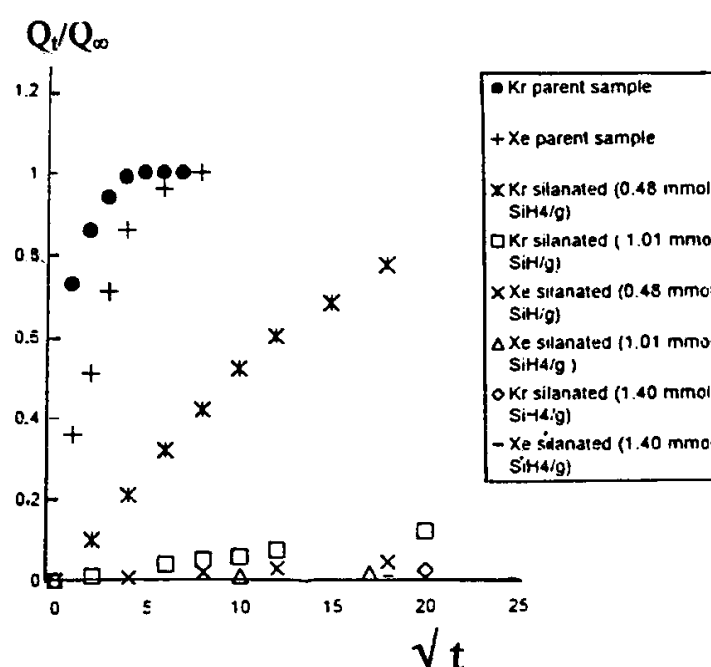


Fig. 3. Xe and Kr sorption at 273 K on LP mordenite at different degrees of silylation and oxidation. Q_t/Q_∞ : sorption amount at time t relative to the maximal sorption on pure zeolite after equilibrium, as adapted from ref. [53]

The results presented in Fig. 3 indicate that the effective pore size of the original mordenite (0.62 nm) was reduced to 0.35-0.4 nm, which was responsible for enhancing C_2 and C_3 products during C_7 and C_8 cracking.

Silylation at high temperatures affected the rate of adsorption of molecules like CO , O_2 and N_2 at 77 K [54]. Interestingly, reaction equilibrium for such small

gas molecules could not be reached for any used time scale. A fast desorption of the gases at 273 K is attained while an increase of the adsorption at 77 K was observed. This behaviour was typical for narrow sieves, like CaM, and was found to be due to an activated diffusion [54]. Several applications of silylated zeolites were attempted. A very important application is the encapsulation of gases, e.g. long term storage of radioactive ^{85}Kr . It has been reported [55,56] that new immobilization techniques for gases having much smaller, similar or greater dimensions than the zeolite pores were adopted, including: chemisorption-adsorption-oxidation (CAO), adsorption-chemisorption-oxidation (ACO), and hydration polymerization.

3.2 External surface modification

Disilane is another modifying agent for H-mordenite that can be used for either modifying the external or internal surface separately [57]. The influence of the reaction temperature on the porosity was studied by synthesizing two samples at 273 and 373 K, with equal disilane loadings [54]. A marked decrease in the total pore volume was observed for the sample modified at 273 K on using O_2 , Ar and Kr as adsorbates. Whereas the sample modified at the higher temperature (373 K) led to no change in the pore volume, implying the susceptibility of only the external zeolite surface to the chemical modification, i.e. pore blocking without significant change in the adsorption capacity and surface acidity. It has been proven [58] that the disilylated M could be used for cracking reactions with high reactant and product shape selectivity. Upon increasing the extent of disilylation of the zeolite, the percentage of cracked hexane and 2,2 dimethylbutane

are presented in Fig. 4a. The product shape selectivity during hexane cracking is shown in Fig. 4b. It is shown that the amount of isobutane decreases in favor of the formation of propane with increased disilylated. It may be anticipated that the sterically hindered molecules formed during cracking are further decomposed prior to desorption.

The former modifying agents are used for modification of either external or internal surfaces depending on temperature, whereas some other reagents are only restricted to external surface modification such as tetramethoxy silane (TMOS) and tetraethoxy silane (TEOS). Thus, they are excellent modifiers to estimate shape selectivity of catalysts without adversely affecting the inherent activity of the zeolite [59]. In addition, polymerization reactions on the M surface could still take place [54]. Impacts of varying the silylation procedure of TEOS (chemical vapor and liquid deposition) as well as the contact time and deposition cycles on the silylation of M, ZSM-5 and β -zeolites have been studied [60]. Experiments were carried out with the view of characterizing the extent to which the external sites were inertised and the pore openings narrowed. Unidimensional channel structures (mordenite) were found to be more affected with respect to pore mouth narrowing than the siliceous three-dimensional zeolite ZSM-5. The adsorption properties of modified M allowed the separation of mono- and dibranched hydrocarbons (n-hexane and 2-methylpentane, respectively) based on restrictions of the size of the pore entrances [61]. At high temperatures, the presence of H_2O has been found [61] to increase the rate of TEOS deposition, reducing the extent to which pore mouth blocking occurs.

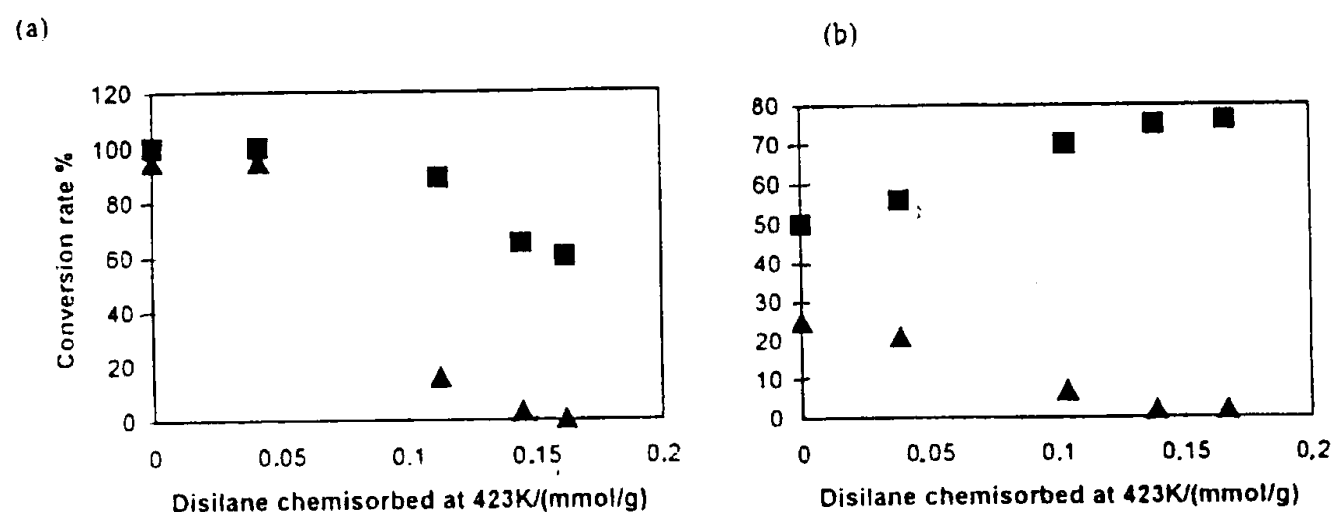


Fig. 4. (a) Reactant shape selectivity of disilylated H-Mordenite: ■ n-hexane cracking and ▲ 2,2- dimethylbutane cracking; (b) product shape selectivity of n-hexane cracking on disilylated H-Mordenite: ■ propane and ▲ isobutane, as adapted from ref. [53].

Chemical vapor deposition (CVD) of the silicon alkoxides $\text{Si}(\text{OCH}_3)_4$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ has been proposed by Niwa et al. [62] as a useful method for enhancing the shape-selectivity of zeolites. The alkoxides react with terminal silanol groups, leading, upon decomposition, to the coverage of zeolite crystal surfaces. The deposition process involved results in the formation of a thin layer of silica on external surfaces, which, thus, deactivates acid sites thereon exposed, without changing the internal surface properties [63]. This method has been applied to HM and its shape selectivities have been found to improve in hydrocracking of paraffins, cracking of octane isomers, methanol conversion, and alkylation of toluene [64]. It has, also, been found that the silicon concentration required for the deactivation of external surfaces of M, does not depend on the Si/Al ratio.

Other compounds have, also, been reported to passivate external surfaces of M by deposition of bulky organometallic complexes, such as Abu_4 , APh_4 (where A= Sn or Ge), ZrNP_4 and MgNP_2 , followed by calcination. Consequently, an improvement of the catalytic conduct of M in the isomerization of C_8 aromatics has been accomplished [65]. The exchange of Al atoms with Ge led to M with a non-conventional Si/metal lattice. This GeM has been synthesized by grafting an organometallic complex of Ge at the pore entrances of M, and found to demonstrate high activity towards the Diels-Alder reaction of 2,3-dimethylbutadiene with p-benzoquinone. Indeed, GeBu_4 has led to thermally resistant surface organometallic fragments, $\text{Si}\dots\text{O}\dots\text{GeBu}_3$, to heating up to 673 K under vacuum [66]. Modification of external surfaces of zeolite by metal surfactants, such as carboxylic soaps, can deposit the corresponding metal oxides following decomposition of the soap. Consequently, catalytic properties, particularly of the external surfaces, were influenced by the modifying metal oxide [67].

Also amination of ethanol over M catalysts has been shown to improve a great deal following silylation of the outer surface of the zeolite, thus forming a thin silica layer blanketing the acid sites of the outer surface together with decreasing the diameter of the pore mouth opening [68,69]. Silylation of the outer surface, however, enhances the rate of formation of monoethylamine (MEA) as well [69]. The decrease in pore mouth diameter hinders the higher substituted amines to leave the pores generating a higher degree of alkylation of the alkylammonium ion [70]. The smaller pore mouth could also enhance the concentration of reactants in the zeolite, thereby enhancing the reaction rate. Modified M, on the other hand, resists the deactivation that could be posed during the reaction due to the strength of the

acid sites and the pore structure. The important role to be played by the zeolite side pockets in ethanol amination has, also, been evident in the variation of the rate of amination upon varying the exchange degrees. The turn over frequency (TOF) over the acid sites in the side pockets has been found to be 1.5 times that determined over the acid sites in the main channel [71]. The selectivity enhancement to lower substituted amines, the desired products, has been attributed to the inability of the trimethylamine (TMA) to leave the pores of the modified (silylated) M, thus enhancing the disproportionation of TMA to the desired products [72]. A surprising side effect has been shown to be the significant decrease in formation of dimethylether (DME), the main side product, after Silylation [70, 71].

Generally, one may conclude that in microporous materials, not only the reaction parameters, but also the porosity, play a decisive role in the reaction course. Depending on the type of the reaction end products, either pore narrowing or pore blockage may be chosen. In the former case, microporous materials may be used to capture hazardous gases, whereas in the latter case the modified zeolite has practically the same catalytic activity of the original zeolite but with improved product selectivity.

4 Dealumination of Mordenite

4.1 Dealumination processes

Three basic procedures have been developed for dealuminating the mordenite framework [73-76]: (i) hydrothermal (steaming), (ii) chemical (by acids, salts, chelating agents, SiCl_4 or other halides), and (iii) a combination of thermal and chemical methods. It has been found that most of the literature dealing with M dealumination is principally directed to acid-treatments, since they exclusively create a secondary pore structure, thus increasing the accessibility of M channels to either large molecules or to appreciable amounts of modifying cations [77-79], by leaching the extra-framework Al deposited inside the channels.

4.2 Acidity of dealuminated mordenite

Acidity in zeolites can be introduced by a number of different ways, and can be achieved due to the particular charge balance of zeolitic frameworks. The existence of Al(III) in tetrahedral framework with Si(IV) in zeolite structure requires the existence of compensating cations that are, in turn, accessible to ion exchange, and, thus, acidity can be achieved by: ion exchange with NH_4^+ , hydrolysis of ion exchanged polyvalent

cations, as well as reduction of exchanged metal ions to lower valency states. Knowledge of the number and strength of acidic sites, and the type of acidity (Brönsted, protonic; and Lewis, aprotic) involved is extremely important as it helps to explain the mechanism of reactions occurring at the surface of these catalysts, and to select the best catalyst for a given reaction [80-84]. The large body of data available on reactions revealed a similar trend with the aluminium framework content [81], for limited Si/Al ranges. The presence of Lewis acid sites also has some influence on the Brönsted acidity strength. Inductive effects exercised by Lewis sites on neighboring protonic sites increase the latter's acid strength, resulting in an enhancement of some reactions thereon catalyzed [85-86].

4.3 Characterization of dealuminated mordenites

Characterization of dealuminated mordenites is often conducted by means of a range of techniques, including XRD or IR of lattice vibrations [87]. To probe the integrity of the pore voids of zeolites following dealumination, techniques such as ^{27}Al and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) and temperature dependent ^{129}Xe NMR spectroscopy [80] are successfully used. Dealumination affects the pore structure, depending on the dealumination process applied. Either extra-lattice aluminum species may be

deposited inside zeolite channels, such as when using steaming and SiCl_4 treatments, or help generating a secondary pore structure, such as when using acid dealumination. Xenon and N_2 adsorption isotherms could communicate useful information concerning the pore structural consequences of these treatments. The adsorption of some molecules, including t-butylamine (as Hammett indicator) and methane, was measured before and after dealumination to assess acidity and check on the restrictions posed by ions such as Na^+ and H^+ [88]. Knowledge of the acidic properties following M dealumination, has, usually, been depicted during a stepwise temperature programmed desorption (STPD) or FTIR spectroscopy [89] of adsorbed base molecules (e.g. NH_3 or pyridine). On the other hand, X-ray photoelectron spectroscopy (XPS) has been used, in combination with other techniques, to trace the possibility of finding non-framework Al at the surface as a result of its migration out of the pore entities [74].

5 Catalysis on Dealuminated Mordenites

According to the previously mentioned advantages of dealuminated M, researchers have been focusing on the catalytic utilization of these materials. Table 2 summarizes some of the most prominent catalytic reactions carried out on dealuminated M together with their preparation and characterization methods.

Table 2: Preparation and characterization methods of dealuminated mordenites, as well as reactions thereon catalyzed.

Metal ion (If any)	Dealumination method ^a	Characterization method ^b	Reaction performed	Key factors of activity enhancement	Ref.
	AL(HCl)	FTIR	Synthesis of ethylenediamine from ethanolamine	Brönsted acid sites	90
	HT/AL(HCl)	Sorptiometry of benzene, water, ammonia	Disproportionation of ethylbenzene	Changes in microporosity; Evolution of large pores	91
	Mild Steaming (673 K)	Sorptiometry; Microcalorimetry; XRD; FTIR (Pyridine)	Isopropylation of naphthalenes; Acylation of naphthalenes	Acid site density & strength	92,93
	AL(HCl)	Spectroscopy; Calorimetry	Hydroisomerization of n-hexane	Lewis acid sites (Al_{EF})	94

Pt	AL(HCl)/ Steaming	²⁷ Al MAS-NMR; FTIR	n-hexane cracking	Dual Lewis- Brönsted site	95
Pt	AL Acid leaching	N ₂ sorptiometry; TPD; TGA; HRTEM	Hydroisomerization of n-hexane	Mesopore& 3-D micropore	96
	Acid leaching	N ₂ sorptiometry; TPD; TGA; HRTEM	Adsorption & diffusion reaction of n-hexane	Brönsted sites, Mesopores; Interacrystalline diffusion	97
	Steaming	¹³ C & ¹ H MAS-NMR	Xylene disproportionation	Strong acid sites	98
Ce	AL(HNO ₃)	Density function calculations; N ₂ sorptiometry; Acidimetry	Isopropylation of biphenyl	Microporosity, mesoporsity & acidity	99
	HT/ AL(HNO ₃)	SEM; Sorptiometry of furfuryl alcohol	Hydroxymethylation of furfuryl alcohol with formaldehyde	Hydrophobic character	100
	HT/AL	FTIR; ICP; XRD; XPS; TPR	CO-based reactions	Lewis acid sites	74
Au	HT/AL	²⁷ Al MAS-NMR; ¹²⁹ Xe NMR; FTI; XRD	NO reduction by methane	Lattice Al species	101
	HT/AL	²⁹ Si MAS-NMR; FTIR; UV-VIS DRS	Hydroxylation of aromatics	Large pores	102
Ti					

^a AL = acid leaching; HT = heat treatment

^b ICP, Inductively coupled plasma; UV-VIS DRS, Diffuse reflectance UV-visible spectroscopy; HRTEM, High resolution transmission electron microscopy; SEM, scanning electron microscopy.

5.1 Organic synthesis

As it can be seen in Table 2, acid-dealumination of M successfully enhances the formation of ethylenediamine (EDA) from ethanolamine and ammonia, due to a consequent increase in the amount of Brönsted acid sites [90]. The breadth of utilities of EDA has ignited as active research on its preparation [103]. Results obtained have consolidated the believe that the increase of the amount of the acid sites, necessary for the EDA formation, is due to the localization of electrons between acid sites and SiOH groups. They also helped concluding that over certain Si/Al ratios, the catalytic activity and selectivity for EDA formation decreased

owing to collapse of the framework structure and, thus, loss of acid sites [103]. Hydrophobicity effects following M dealumination (Si/Al ratios varying from 7 to 100) was also examined on two reactions carried out in aqueous/alcohol media: (i) hydroxymethylation of furfuryl alcohol via aqueous formaldehyde, and (ii) hydration of phenylacetylene. For both reactions, initial rates and TOF values increased significantly with the Si/Al ratio. Differences observed for the TOF values were found characteristic of variations in the hydrophobicity of the dealuminated M, as traced by TG analysis [103]. Hydrophobic character of the zeolite has been discussed in terms of the softness and acidity of Brönsted acid sites [104].

5.2 Hydrocarbon disproportionation and isomerization

The disproportionation of ethylbenzene [91] is a probe reaction for void enlargement following dealumination of M. Dealumination has been found to enhance the reaction as a result of consequent pore enlargement [105]. Also, alkylation of naphthalenes with isopropyl and acetic anhydride [92-93] is now carried out using dealuminated M (dM) instead of the conventional Friedel-Crafts catalysts, relying on the advantages of the shape selectivity M has. Complications may arise from differences in the diffusion rate of various products within the zeolite pores, which are caused by several factors [106]: size of the product molecules, existence of mesopores, acid site density and strength, and the location and consistence of coke deposits.

Isomerization/cracking of medium sized paraffins such as normal hexane [94,95] depends on the method employed for M dealumination. For example, hydroisomerization proceeds on steam-dealuminated samples [107], due to exposure of Lewis acid sites at the expense of extra-framework Al embedded inside the channels. In contrast, cracking usually necessitates appreciable presence of Brönsted acidity, irrespective of the presence of Lewis acidity. This is confirmed in ref. [95], which shows a marked enhancement in hydroisomerization of n-hexane, along with appreciable cracking activity, following steam dealumination of mordenites. This was explained [95] on the basis of increasing the heat of adsorption as a result of the presence of extra-framework Al, and, thus, increasing the surface concentration of reactant molecules. Also, the activity and selectivity of hydroisomerization of n-hexane were markedly enhanced over Pt-incorporated acid-leached M [96,97]. This was ascribed to the fact that the reaction requires a bifunctional catalyst consisting of a (de)hydrogenating metal function and a protonating acid function [108]. Thus, the first step requires a noble metal, such as Pt. Following migration of alkenes to the acid site, protonation takes place leading to a branched carbo-cation [109] via a cyclopropyl intermediate. This is usually the rate-determining step of the reaction. The formed carbo-cation is deprotonated and, after migration to a metal site, hydrogenated yielding a branched alkane. Acid-leaching renders the catalyst more active by generating new external surfaces. Due to lesser diffusion limitations and easier desorption from the surface after leaching, the residence time of products on the surface decreases so that fewer secondary reaction products are formed.

In order to realize impacts of the acid-leaching on the n-hexane adsorption/desorption cycle, results obtained on HM parent (H-MOR-P), Pt/H-MOR-P, H-MOR-L and Pt/HMOR-L; where L means leached, are graphically represented in Fig. 5. It can be clearly seen that desorption of hexane is the best on Pt/H-MOR-P, a behaviour that has been attributed to the formation of branched products which remained entrapped as immobile species inside the parent M channels thus hindering desorption of the products.

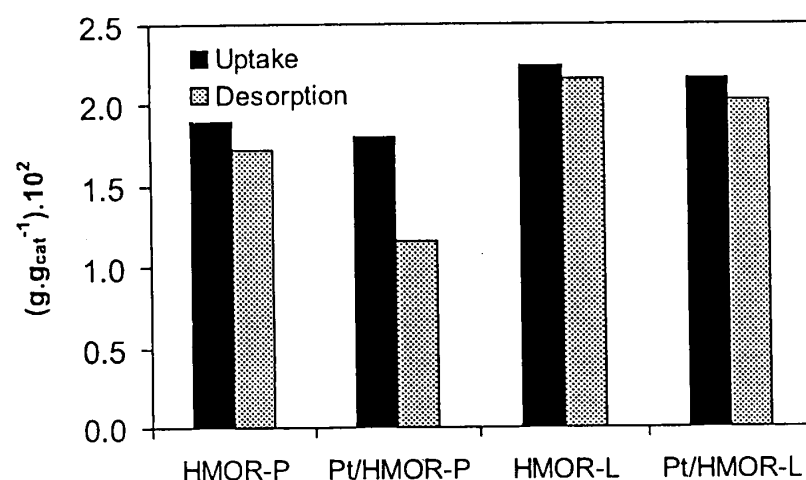


Fig. 5. Amounts of adsorption and desorption of n-hexane as determined on the samples indicated, at 523 K and a H₂/nC₆ molar ratio of 1:1, as adopted from ref. [110].

No noticeable change in steady state diffusivities has been observed [110] after the acid leaching, which has been considered indicative of an intact one-dimensional M structure. During hydroisomerization, methylpentane is formed as a primary product. On Pt/HM-P, the transport of branched products across the crystal is more difficult as the diffusion pathlength is longer, which results in the formation of secondary products [110]. However, opening up the structure, as done by acid leaching, results in a faster exchange of reaction products and, thus, nullifying the selectivity towards other unwanted products, such as methylpentane and dimethylbutane. On the other hand, it has been shown [95] that cracking of C₆ compounds either to C₄/C₃ or C₄/C₂ compounds is dependent on the pore accessibility, on the first place, and the availability on the surface of dual Lewis-Brönsted pair sites [95]. It has been shown [95] that hexane is transformed to the more active hexene, which reacts rapidly with the remaining structural hydroxyl groups present in the 12-ring channels.

Xylene disproportionation/transformation is another

very interesting type of acid-catalyzed reactions, which depends on the accessible void volumes, particularly those facilitated in 10- and 12-ring structures [98]. The disproportionation reaction of xylenes has been investigated by means of *ab initio* calculations inside the 12-ring M framework, and found possibly to follow either of two bimolecular mechanisms [98]. In the first mechanism, the reaction is assumed to proceed via unstable methyl cation as a transition state. The second, and more energetically favourable mechanism, implies the formation of benzylic-like carbo-cation that subsequently converts into a trimethyldiphenylmethane, known as DPM intermediate. The stability of this intermediate governs largely the disproportionation reaction and, thus, the steric constraints that might be induced in 12-rings. Indeed, dealumination is the key parameter behind improving this type of reactions. One of the most important such reactions carried out on dM is the *m*-xylene transformation that is critically dependent on the pore structure [111]. In fact, one may generalize that the smaller the pore size, the more favorable should be the formation of the smaller isomer *p*-xylene. Thus, it has been found that the ratio of bimolecular reaction rates (of disproportionation or coke formation) to the monomolecular reaction of isomerization is directly related to the maximal space available to formation of intermediates or transition states, emphasizing the importance of exactly knowing the channel size following any dealuminating treatment.

Alkylation of polynuclear aromatics, such as the isopropylation of biphenyls (BP), has drawn the attention to the area of shape-selective catalysis. It has been shown [112] that a high selectivity of this reaction is achieved over dM. This is because the dealumination not only reduces the number of acid sites, but also modifies the pore size distribution, resulting in a considerable increase in the mesopore proportion. Some authors used ceria to eliminate the external acid sites responsible for producing non-regioselective mixtures of isomers, thus directing the reaction to proceed mainly inside pores [113]. Horniakova et al. [99] attempted to corroborate achievements of other researchers by deactivating the external acid sites using ceria, as well as enlarging the pore volume via acid dealumination, and managed, thereby, to enhance the selectivity towards formation of isopropylbiphenyl.

5.3 NO_x selective reduction

Nitrogen oxides (NO_x), mainly produced in fuel combustion processes, are harmful pollutant gases to the environment. One of the most attractive ways to reduce

amounts of NO_x in the atmosphere is their catalytic decomposition to molecular nitrogen and oxygen or their selective catalytic reduction with various hydrocarbons [114]. M has been found [114] to be deactivated by water, SO₂, or acidic gases such as HCl, which are commonly contained in the flue gas from industrial waste incinerators [114]. Modification of M by dealumination has been found [101] to help improving its structural tolerance to the existence of such compounds. However, further research studies are still required to eliminate other reasons responsible for its early deactivation [115]. Fig. 6 shows, for instance, the effect of the Si/Al ratio (5.9-16.9; following acid-dealumination) on the conversion of NO to N₂.

Fig. 6 shows, moreover, the importance of framework Al to enhancing the reaction reactivity that, indeed, suffers from dealumination. Although dealumination might be a reason for the hydrothermal stability of M zeolite, presence of appreciable amounts of framework Al is required as active sites for the reaction. Hence a fair compromise is demanded. Compatibly, Descorme et al. [116] have found that a strong catalytic reduction of NO by methane over Pd-exchanged non-dealuminated or dealuminated M necessitates the presence of oxygen. These authors revealed that, for accessibility reasons, Pd ions in the main channels are more reactive than those in small cavities. The activity has been shown to increase by the addition of 10 vol %-water, which is in contrast to the behaviour of metal-loaded zeolites. This phenomenon has been attributed to migration of Pd ions from hidden to accessible sites in the non-dealuminated M. However, the observed deactivation of dM has been ascribed to conversion of isolated Pd into PdO particles located outside the zeolite matrix [116].

5.4 CO-based reactions

The interest in CO-based reactions (to obtain hydrocarbons, oxygenated compounds and CO₂) has been revived by environmental necessities of decreasing CO levels in the atmosphere. Within this context, the application of bifunctional metal-zeolite catalysts has been lately investigated in hopes of combining the catalytic potential of some precious metals (Pt or Au) with the shape selectivity of zeolites [117]. One of the obstacles encountered using this catalyst system is the facile sintering of metal particles at relatively high temperatures and, thus, catalyst deactivation. It has also been shown [118,119] that Au⁺ ions act as active sites for many reactions including NO+CO and NO decomposition. Mohamed et al. [74] have managed to stabilize Au⁺-CO species on dM, provoking the formation of extraframework

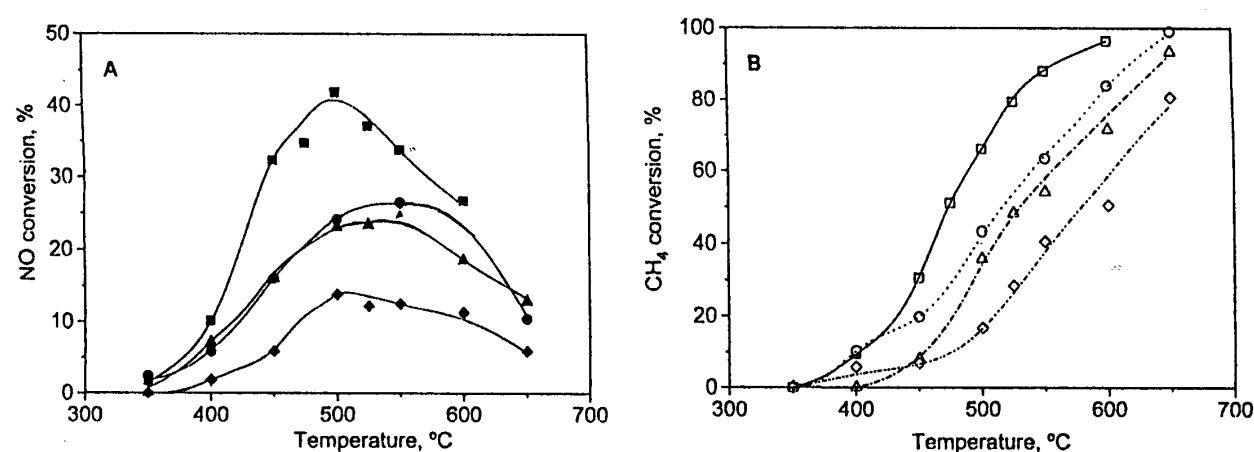


Fig. 6. Effect of the Si/Al ratio on the conversion of (A) NO to N₂: ■, 5.9; ●, 7.3; ▲, 11.0; ♦, 16.9, and (B) CH₄ to CO₂: □, 5.9; ○, 7.3; △, 11; ◇, 16.9, as adopted from ref. [115].

Al species following dealumination via steaming. Fig. 7 compares in situ FTIR spectra taken of CO adsorbed (at room temperature) on dealuminated AuM sample, as well as TPR profiles of the same sample in comparison with those of non-dealuminated M and NaY zeolite samples.

The IR spectra (Fig. 7a) evidence the stability of the $\nu\text{Au}^+\text{C-O}$ band (2192 cm^{-1}) to thermal evacuation up to 473 K. Moreover, a higher H₂ consumption as compared to the other test samples is TPR-determined for the Auⁿ⁺/dM sample.

5.5 Hydroxylation and total oxidation of organic compounds

Liquid phase hydroxylation of aromatics, using H₂O₂ as an oxidant and titanium-containing (TS-1) or iron-containing (Fe-FSM-16) zeolites as catalysts [120,121], has, recently, received a great deal of interest due to favorably high activity. It has been concluded that the catalytic activity usually relies on isolated, tetrahedrally coordinated Ti sites in the framework. However, they are restricted to oxidation of relatively small molecules because of their medium-pore structures (TS-1, ZSM-5) [122]. Thus, implanting Ti in dM has been carried out to compare its catalytic activity towards hydroxylation of various aromatics with that of TS-1 [102]. It has been revealed that TiM with a low Al content (dealuminated) assumes superior activity to TS-1 especially when bulkier aromatics are used. Fig. 8A compares turn-over-numbers (TON) of TS-1(a) and Ti dealuminated TidM (b) for the hydroxylation of benzene aromatics with a single alkyl group: toluene, ethylbenzene, cumene and t-butylbenzene. Fig. 8B shows the same for the hydroxylation of xylene isomers over TS-1 and TidM. It can be seen that electron-donating alkyl groups

attaching to the benzene ring would increase the electrophilicity of the substrate and, consequently, promote the ring hydroxylation in the following order: $-\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{CH}_2\text{CH}_3 > -\text{CH}_3$. TidM shows surprisingly the highest activity towards yielding phenol from cumene, thus indicating that TidM has a potential for bulky molecules that is usually governed by diffusion limitation.

Another very important reaction that measures the potentiality of titanium-containing dM is D-glucose oxidation by H₂O₂ as an oxidant [123]. This reaction is very important from microbial, enzymatic and pharmaceutical point of views, which mainly produce gluconic, glucuronic, tartaric, glycolic and glyceric acids. It was shown that TidM gives tremendous activity comparable to that of Ti MCM-41, with a preferential selectivity to gluconic and glycolic acids [124]. This indicates that approximately the same titanium species existed in the above-mentioned zeolites.

5.6 Cracking reactions

Motivated by recent tendencies towards recycling polymeric plastics to diminish their negative impacts on the environment, an active research has been directed nowadays to help overcoming this problem. Waste plastics, namely of polyethylene, polypropylene and polybutadiene-polystyrene, have been successfully converted into useful fuels (gasoline and high olefinic compounds) by means of fluid catalytic cracking (FCC) catalysts consisting of rare earth oxides incorporated into dealuminated mordenites [125, 126]. Shape selective effects of the catalysts influence significantly the prevalence of the various reactions, because they could retard those undergoing bulky transition states, like styrene oligomerization or hydrogen transfer, while recycling polystyrene into fuels on M, ZSM-5 and Y zeolites [127].

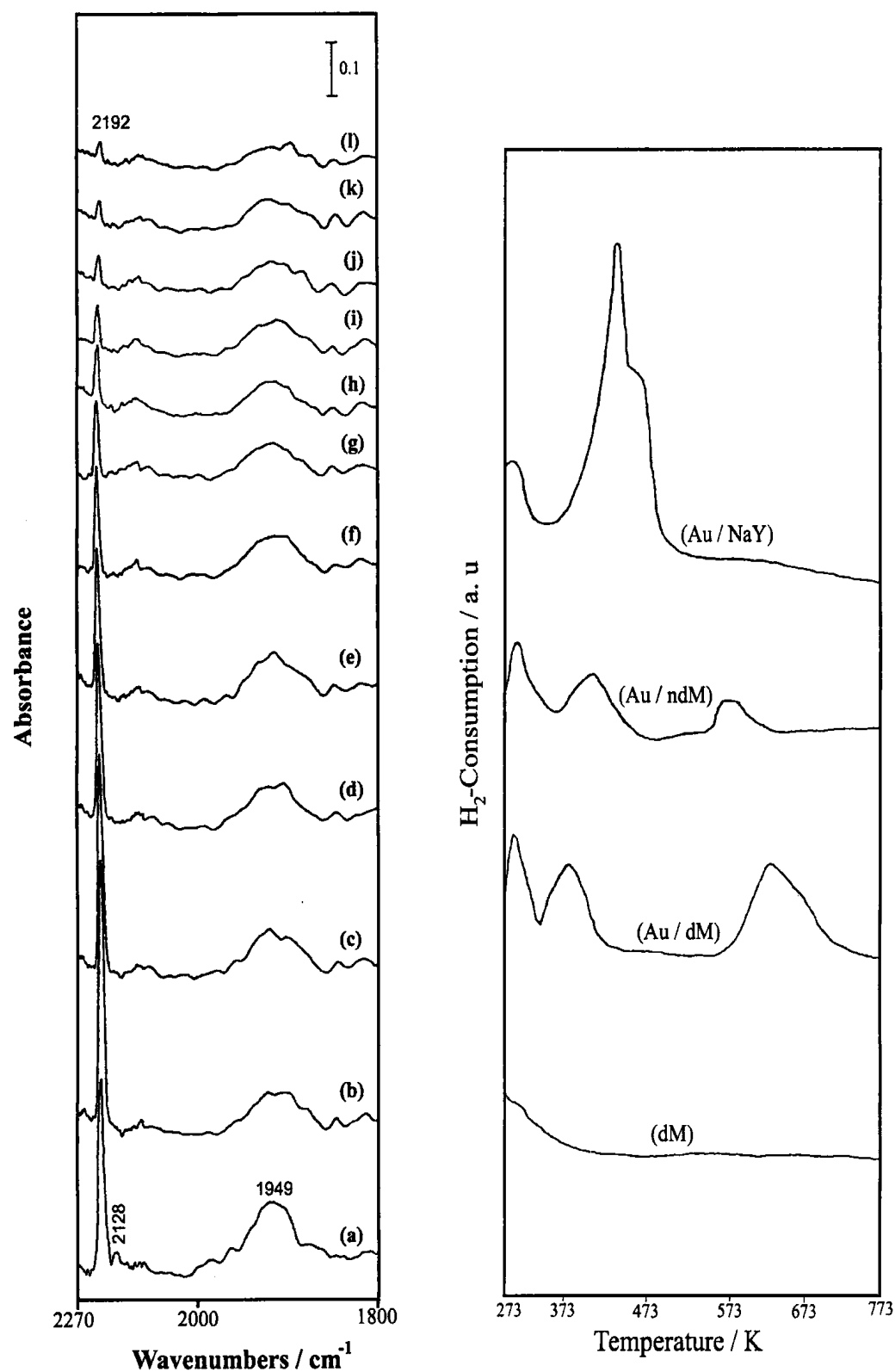


Fig. 7. (a) FTIR spectra of CO adsorbed at room temperature on Au^{n+}/dM sample followed by thermo-evacuation till 473 K, and (b) TPR profiles of dealuminated H-Mordenite (dM), Au^{n+} encapsulated dM, (ndM) and NaY zeolite catalysts, as adopted from ref. [74], where a=343, b=363, c=373, d=383, e=393, f=g=403, h=413, i=423, j=433, k=443, and l=473 K.

Catalytic cracking of vacuum gas-oil is another very important, though challenging, reaction carried out on acid-dealuminated M catalysts. The conversion of gas-oil into gasoline and kerosene+diesel has been

correlated with the acid-amount/mesopore-volume ratio. A maximal conversion and yield is observed at an optimal acid-amount/mesopore-volume ratio, at which a good activity between two inverse tendencies is achieved. On

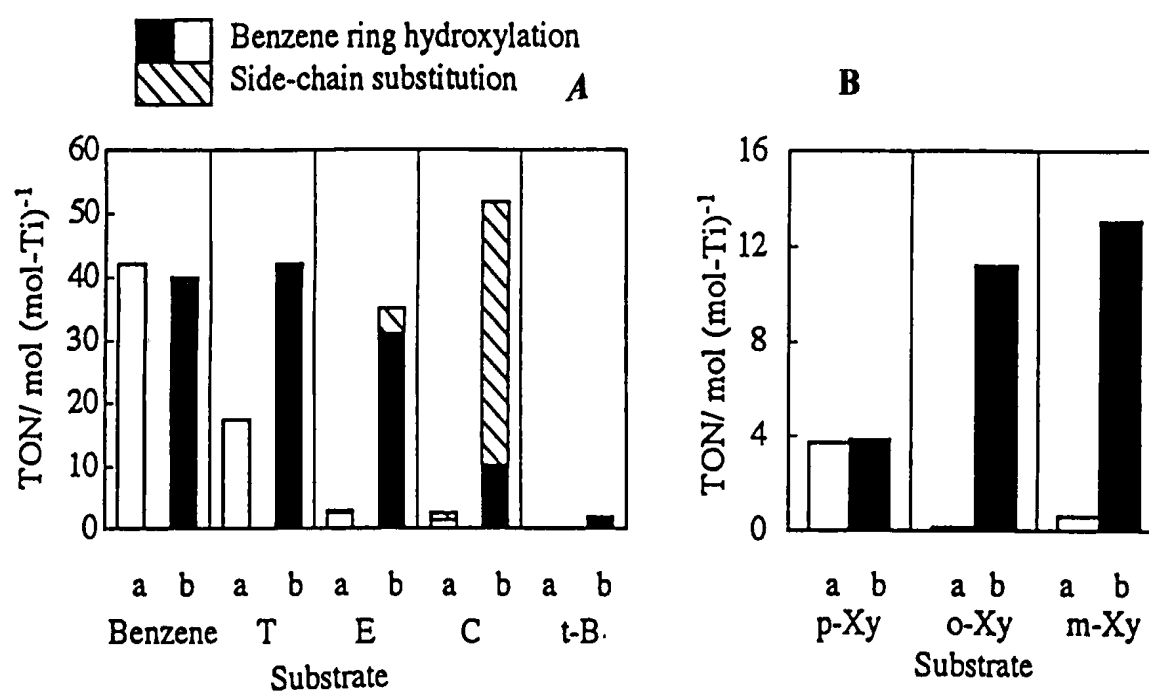


Fig. 8. (A) hydroxylation of various aromatics over TS-1 (a) and TidM (b), and (B) hydroxylation of xylene; where T= toluene, E= ethylbenzene, C=cumene, t-B= t-butylbenzene, as adopted from ref. [102]

one hand is the tendency of acid site density. On the other hand, is the tendencies of increasing the activity with the mesoporous volume. The largest content of alkyl aromatic compounds in the produced gasoline was that of toluene, a fact that was ascribed to diffusion limitation of formation of higher alkyl-branched aromatics [128].

6 Conclusive Remarks

A variety of metal ions can be chemically incorporated into mordenite framework adopting various methods, which differ in their accomplishments as regards the metal ion dispersity. Metal ion-incorporated mordenites are, often, characterized by means of powerful spectroscopic techniques, viz. the rapidly developing EXAFS, in-situ FTIR, NMR, and HRTEM for the morphology, local structure and metal ion-framework interactions of the catalysts. There are still problems facing the metal ion incorporation into mordenite, particularly when they do not fulfill for the ratio criterion of the radii of the cation to that of oxygen to be in the 0.225-0.414 range (e.g. case of Ce). However, synthesis methods of CeM zeolite have, recently, been developed [129]. Particularly that these CeM systems have been found effective in catalyzing hydrocarbon alkylation, isomerization and cracking reactions. It is believed that attempts to modify the catalytic properties of mordenite zeolite will continue to increase, either by synthetic or post-synthetic procedures. It has been shown that shape selective catalysis over mordenite occurs mainly inside the material

pores. However, regioselective reactions occurring on external surfaces are one of the factors lowering the shape selectivity for reactions occurring inside the zeolite pores. Similarly, improvement of para selectivity is commonly achieved in industrial processes by pre-coking and modification of external surfaces, thus reducing diffusivity. This will affect the activity in favor of the selectivity. Comparison of the reactivity of various mordenite catalysts suggests that transalkylation/disproportionation reactions require mild acidity, whereas isomerization reactions need strong acidity.

Silica deposition that is used in tailoring the pore size, can also be used to passivate the external surface depending on the size of the deposited alkoxy silane and deposition temperature and cycles. Future research in this area should be directed to compromise the total activity for the selectivity towards a target product. This is in the sense that for improving the latter, the former should be maintained at acceptable level. Homogeneous coating of micropore entrances in mordenite may help capturing hazardous gases. More attention should be paid to the respective roles of external and internal modifications of mordenites by silane groups (or any other groups), and to their influences on the porosity, adsorption characteristics, acidity and activity.

Dealumination that attracted a great deal of attention of many researchers working on mordenites, increases the Si/Al ratio, and, thus, the surface acidity and pore accessibility. These properties are, indeed,

sensitive to the chosen course of dealumination. Extremely high activity of dealuminated mordenites is correlated to either hyperactive sites of enhanced acidity, or favourable accessibility at a specific site. It is admitted that mesopores are responsible for the high activity towards a specific reaction, through molecule confinement (reactants, intermediates or products) that is improved as a result of pore widening. Generation of defect sites, following dealumination, renders the zeolite lattice more tolerant, thereby enabling an interaction with Brönsted protons and, hence, enhancing specific reactions.

7 Future Perspectives

Today's research for the production of environmentally benign compounds, fuels and petrochemicals demands improvements of catalysts, catalytic processes and technologies. Thus, the strong need for developing the catalytic properties of mordenite is expected to extend to the near future. It can be anticipated from what is going on nowadays concerning mordenite zeolite, that in the coming few years work will be aimed at encountering various challenges, most importantly are those given below.

1- Synthesis and application of new mordenite materials: Mordenite zeolite of Si/Al ratios as high as 60 or 100 (or even more) should be synthesized to have higher hydrothermal stability and intrinsic Brönsted acidity than mordenite zeolite of low Si/Al ratios. Improving the properties of mordenite zeolite through proposing new preparation strategies could, also, lead to maintaining large-pore structures and well-defined 3-D micropores. This would enlarge the usage of mordenite zeolite in catalysis and adsorption processes. A step forward towards accomplishing this goal could be by adopting types of templates other than the conventionally used Nitrogen-containing compounds.

2- Novel catalytic processes to remove nitrogen oxides: The growing concern on understanding and solving the problem of the removal of NO_x compounds is equally felt when catalysts are considered. Cu or Fe-incorporated mordenites are amongst the most active catalysts used. However, their stability under the extreme reaction conditions is questionable. Therefore, research endeavors are invited to synthesis versions of these, or similar mordenite based catalysts of higher stabilities to the severe conditions imposed by the deNO_x process: high temperature regimes, high space velocities, and co-existence of catalyst poisons.

3- Design and development of ultra-active photocatalyst: The generation of titanium (semi-conductor) containing mordenites as photocatalysts, operable under visible rather than UV-light, for the elimination of environmental pollutants is a current demand. This type of catalyst could also be important to biological degradation of wastewaters. Incorporating TiO₂ into mordenite is supposed to increase the surface area of the active sites, together with the benefits of the strong crystallinity of the zeolite are expected to enhance its photocatalytic activity. A large surface area would accelerate surface reactions, and a strong crystallinity would reduce crystal defects and, thus, inhibit the retrogressive recombination of electrons and holes.

4- Zeolite catalysts instead of organometallic ones: A lot of new polymeric catalysts are solids, and their preparation involves several organometallic chemical steps, which are too expensive. A more focus is being placed at mordenite zeolites as a substitute catalyst, because it combines the high activity with the selectivity. It also contributes to the quality and performance of the ultimate products because of the greater purity and uniformity of intermediates made within zeolite. Replacement of environmentally hazardous catalysts, such as AlCl₃ and BF₃, by mordenite zeolite is expected to take place on industrial scale so as to reduce waste formation.

5- Bifunctional catalysts for methane conversion into higher hydrocarbons: Effective utilization of methane in natural gas is a challenging problem for heterogeneous catalysis and will generate more concern in the coming years due to the revealed shortage in the reserved amounts of petrol all over the world. Methane activation and conversion into higher hydrocarbons is a big challenge to catalysis chemists. Studies of aromatization reactions of methane under non-oxidative conditions demand more appropriate catalysts than Mo/HZM-5. Thus, a compromise between the acidity and pore structure of the zeolite, as well as the loading level of the oxidative metal ion, is a pre-requisite for accomplishing this goal.

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