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Use of zeolites in petroleum refining and petrochemical processes: recent advances

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Abstract Zeolites and molecular sieves have revolutionized oil refining and petrochemical processes with a step change in product selectivity and operation parameters. However, stringent emission norms and depleting refinery gross margins in view of volatile crude oil price and its quality has demanded search for novel zeolytic materials. Such developments are envisaged to improve existing zeolite based processes or to develop new and energy efficient processes to enhance the product yields and quality in oil refining and petrochemical processes, respectively. As a result, focused and sustained efforts have led to discovery of novel molecular sieves such as ITQ-*n*, EMM-*n* in recent time. The present paper illustrates a brief overview of such developments and is aimed to understand the applicative potential of novel molecular sieves in terms of their novel zeolite chemistry and structural-property aspects.

Keywords Zeolites · ITQ-12, -13 · EMM-2 · UZM-8 · FCC · LOBS · MTO processes · Alkylation · C3 separation

1 Introduction

Zeolites are microporous crystalline materials that play important roles in catalysis, ion exchange, and adsorption sciences, and the molecular-sieving properties of zeolites are exploited in many industrial applications [1]. The reason for such wide range of zeolite applications is commonly ascribed to their unique shape selectivity properties. Today, this zeolite property is extensively exploited in oil refining processes such as catalytic cracking, hydrocracking, hydroisomerization of short and long paraffins, and isomerization of *n*-butenes [2, 3]. Likewise, zeolite catalyze processes namely transformation of aromatics: isomerization of C8 aromatics, disproportionation of toluene/transalkylation toluene-xylenes aromatics and alkylation of benzene by short and long olefins. Owing to their shape selectivity, zeolites are extensively practiced in the downstream petrochemical sector [2, 3].

Although, aforementioned oil refining and petrochemical processes are well established, the stringent fuel specifications and continuous increase in demand for petrochemicals has added impetus in improvements in existing processes. Such improvements are envisaged to take place through design of novel zeolitic materials rather than mere improvement in process design. This has led to focused efforts in zeolite synthesis in recent time leading to discovery of novel ITQ-*n* (Instituto de Tecnologia Quimica-*n*), EMM-*n* (Exxon Mobil Matter-*n*), UZM-*n* (UOP Zeolite Material-*n*) molecular sieve frameworks [4–11]. In the following sections, an attempt has been made to understand the applicative potential of such frameworks for product quality in oil refining and petrochemical industries especially cracking, dewaxing, alkylation and MTO processes, in terms of their structure-property relationship.

2 Oil refining catalyst

2.1 Fluid catalytic cracking (FCC) catalyst

FCC is one of the important secondary processes primarily practiced to improve yields of gasoline, LPG distillate and C3 olefin in the presence of Zeolite Y and ZSM-5 based

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catalyst and additive, respectively. General and in-depth reviews along with process advances and challenges on FCC are available in the literature [12–14].

Typically FCC catalyst comprise of the following active ingredients:

- The zeolite crystal, ion-exchanged with the desired level of rare-earth, to achieve the desired gasoline properties
- An active matrix with tailored composition and porosity to pre-crack large molecules
- A kaolin clay acting as a heat sink and filler
- A binder to maintain the integrity of the spray-dried particles

Generally, zeolite Y based FCC catalysts are employed in two forms namely; (a) octane making and (b) gasoline making catalyst form depending upon the refiners need. The major difference in two forms of catalyst is ascribed to the rare earth (RE) content in the zeolite Y. This is due to the fact that Zeolite Y with low RE (below about 3 wt% RE_2O_3) content allows the zeolite to dealuminate strongly, thus lowering its acid site density and consequently its hydrogen transfer capability. The olefin rich gasoline has a high octane rating but is highly unstable in nature. On the other hand, Zeolite Y with high RE (up to 15 wt% RE_2O_3) content prevents the zeolite from dealuminating strongly, thus maintaining a high site density and consequently its hydrogen transfer capability. Primarily, addition of rare earth content in zeolite Y is targeted to enhance the hydrothermal stability and to retain activity of zeolite Y in the FCC regenerator wherein steam produced leads to rapid dealumination of Zeolite Y framework under hydrothermal conditions. Addition of such elements into zeolite framework is performed by means of ion exchange route which essentially bridges the three acid sites. This leads to stabilization of zeolite Y unit cell thereby its framework under hydrothermal conditions. However, improvement in hydrothermal stability demands certain minimum level of rare earth exchange as initial exchange in zeolite Y occupies highly energetic sites present in sodalite cages which are not accessible during cracking conditions to the hydrocarbon molecules. Thus, it is important to stabilize the acid sites which are responsible for hydrocarbon cracking by increasing rare earth content to minimum level (~3 wt%) depending upon the starting Si/Al ratio of Zeolite Y and intended product quality. Such exchange level allows rare earth to bridge the three acid sites, which are present in the main cage, to maintain desired acidity by controlling the ejection of framework aluminium. Thus, Lanthanum and Cerium are commonly used as rare earth elements to stabilize the zeolite activity and impart hydrothermal stability due to their natural abundant in rare earth oxide mixture. Excellent reviews on the role of rare earth in controlling the zeolite Y properties to obtain gasoline with desired properties can be found in literature [12, 13].

Table 1 Typical FCC product characteristics

LPG	Highly olefinic
Naphtha (15–220 °C)	
Olefins (wt%)	>20
Aromatics (wt%)	>20
Octane number	High
Use	Gasoline pool
Kerosene (150–250 °C)	
H (wt%)	10.4
S (ppmw)	1,000
Gas oil (250–370 °C)	
H (wt%)	9.4
S (ppmw)	5,000
Cetane number	<30

Active matrix facilitates conversion of large reactant molecules to convert into smaller molecules prior to their cracking on highly acidic zeolite porous framework during FCC operation. Such operation represents complete synergy of zeolite and matrix.

The paraffin and aromatic rich gasoline is more stable and therefore produced in higher volume. However, such gasoline needs enhancement in octane number to meet the market demand which is usually accomplished by use of ZSM-5 based octane boosting additive. Such boost up is usually accomplished by increasing the olefin content of gasoline stream. Furthermore, the aforementioned additive is often used for C3 maximization (especially propylene) by tailoring its framework Si/Al ratio [12, 13].

In view of the above, FCC product characteristics observed, based on the FCC catalyst and ZSM-5 additive employed, are given in Table 1:

Today, FCC catalyst composition is a well known art in literature and FCC process is considered to be a good route for conversion of heavy oil. However, with volatile crude oil price, stringent transportation fuel specifications and its demand, FCC catalysts and additives is facing major challenges in terms of:

- The growing diesel market, particular in European and Asian regions-Demanding diesel maximization during FCC operation
- Ever increasing demand for C3 olefin
- Stability of gasoline-Demanding substantial reduction of olefin content
- Reduction in gasoline aromatic content-Stringent fuel specifications

- Conversion of heavy crudes with high metal content-Such crudes are difficult to process due to their metals (Ni affects the coke selectivity and V, Na, Fe,… destroy or severely reduce the zeolite activity), sulfur (SO_x emissions, the S content of the FCC gasoline requiring either to process the feed upstream, the products downstream in separate units or to find effective FCC additives), nitrogen (NO_x emissions) contents and their higher coke making tendency
- Quality up-gradation of co-products (the LCO, Light Cycle Oil, a middle distillate high in aromatics and sulfur needs further upgrading to be incorporated in higher quantities in the diesel pool)
- Disposal of spent FCC catalyst containing heavy metals

Thus, it is imperative to develop a new generation of FCC catalyst and additives that provide good conversion of heavy fractions to low-aromatics transportation fuels with maximum production of light olefins (mainly propylene). Such demand in turn has led to development of novel molecular sieve frameworks namely ITQ-13/-17/-21 in recent time for maximization of propylene and minimization of olefin content, respectively, in FCC process [15–17]. Like wise, sustained efforts has led to development of ITQ-33 molecular sieve framework thus offering leverage for possible designing of diesel maximization catalyst formulation in FCC process [18, 19]. In view of this, following section deals with structural aspects of the aforementioned molecular sieves to understand their applicative potential.

2.2 ITQ-13

Propylene maximization in FCC operation is routinely practiced by employing ZSM-5 based additive. The practice of such additive favors formation of light olefins through shape selective cracking of n-olefins. Thus, sound understanding of shape selectivity is found to be extremely essential to develop superior additive for C3 enhancement than the existing one. Accordingly, investigation on numerous cracking studies of model hydrocarbons over a large number of zeolites with different pore dimensions and topologies coupled with molecular simulations led to predictions that zeolites with a bidirectional or tri-directional pore system formed by 9 or 9 × 10 MR should be very adequate FCC additives for boosting propylene [20]. In view of this, successful synthesis of germanium silicate based ITQ-13 framework is recently accomplished which has a tri-directional set of channels in which one of them has 9 MR (4.0 × 4.9 Å) openings and the other two channels are straight (4.7 × 5.1 Å) and sinusoidal 10 MR (4.8 × 5.7 Å) [20]. In order to examine the applicative potential of such framework, post- as well as direct synthesis attempts have been made to generate framework acidity via. Al-incorporation. Interestingly, direct synthesis approach is found to favor generation of acid sites as strong or even stronger than ZSM-5. The catalytic studies over such framework have found to demonstrate higher selectivity for propylene vis-à-vis ZSM-5 during cracking of model feed as well as vacuum gas oil (Tables 2, 3).

Table 2 Catalytic cracking of 1-hexene and 4-methyl-1-pentene over ZSM-5 and ITQ-13 [15]

Catalyst	ZSM-5		ITQ-13	
Feed	1-Hexene	4-Methyl-1-pentene	4-Methyl-1-pentene	1-Hexene
Cat/oil	0.05	0.05	0.09	0.09
Conversion (wt%)	54	9	49	54
Liquids (wt%)	25.81	21.84	16.03	18.37
Gases (wt%)	27.85	26.82	32.31	34.81
Coke (wt%)	0.35	0.34	0.67	0.53
H_2 (wt%)	0.01	0.01	0.009	0.003
C_1 (wt%)	0.04	0.05	0.1	0.06
C_2 (wt%)	0.13	0.07	0.06	0.14
$C_2^=$ (wt%)	2.67	2.33	2.02	2.43
C_3 (wt%)	1.7	1.65	0.88	0.6
$C_3^=$ (wt%)	**11.91**	**11.21**	**19.17**	**20.86**
$ic_{4,}$ (wt%)	1.54	1.47	0.6	0.5
nc_4 (wt%)	0.73	0.72	0.18	0.2
$t2C_4$ (wt%)	1.81	1.84	2.03	2.14
iC_4 (wt%)	1.94	1.95	1.94	2.07
iC_4 (wt%)	3.88	3.95	3.76	3.86
$C2C_4$ (wt%)	1.48	1.55	1.66	1.74

As seen from Table 2 that ITQ-13 demonstrates higher selectivity for propylene over propane as compared to ZSM-5.

Like wise, vacuum gas oil, having following properties [16], when cracked over conventional FCC catalyst USY and catalyst system comprising of USY along with 20% olefin max ZSM-5 additive and ITQ-13, respectively, demonstrated higher propylene/propane ratio with ITQ-13 additive (Table 3).

Density 15 °C, g/cc	0.917	ASTM D-1,160 (°C)
Aniline point (°C)	79.2	5%–319
S (wt%)	1.65	10%–352
N (ppm)	1,261	30%–414
Na (ppm)	0.18	50%–436
Cu (ppm)	<0.3	70%–459
Fe (ppm)	0.3	90%–512
Ni (ppm)	0.2	
V (ppm)	0.4	

The observed increase in propylene selectivity is ascribed to strong electric field gradient in ITQ-13 due to its smaller pore dimensions coupled with the strong acidity and shape selectivity as compared to ZSM-5 framework [20]. The presence of strong acidity in ITQ-13 is expected based on its smaller 9-membered pore diameter as it is commonly believed that the acid strength of the zeolites should increase with decreasing pore diameter. This effect is explained based on the differences in the distribution and density in the electric field gradients within the zeolites with different pore diameters as well as the differences in Van der Waals adsorption effects [20].

Table 3 Catalytic cracking of vacuum gas oil over USY in the presence of ZSM-5, ITQ-13, respectively [15]

Catalyst	USY (2.432 nm)	ZSM-5 (20%)	ITQ-13 (20%)
Cat/Oil	0.69	0.48	0.50
Gasoline (wt%)	41.95	34.57	36.82
Diesel (wt%)	14.56	11.77	12.83
Gases (wt%)	12.53	21.83	18.69
Coke (wt%)	1.46	1.82	1.38
Gas yields (wt%)			
H_2	0.07	0.03	0.00
C_1	0.41	0.19	0.53
$C_2^=$	0.8	1.59	1.18
C_3	1.19	3.19	2.14
$C_3^=$	2.32	5.17	4.45
iC_4	3.88	4.82	4.46
nC_4	0.89	1.81	1.41
$t2C_4$	0.67	1.00	0.8
IC_4	0.85	0.82	1.03
iC_4	0.82	2.02	1.93
$c2C_4$	0.63	0.97	0.63
Butene/butane ratio	0.62	0.72	0.75
Propylene/propane ratio	1.95	1.62	2.08

2.3 ITQ-33

The continuous increase in diesel demand in Europe and Asian market has led to designing of high through put synthesis methodology to explore possibility for synthesis of extra large pore molecular sieve with increased micropore volume. This has led to successful crystallization of germanium silicate based molecular sieve framework. Structural elucidation of such framework has revealed the presence of 18- and 10- membered ring structure with pore dimension of 1.2 nm as compared to 12-membered ring structure with 0.8 nm pore diameter [18, 19]. Such open framework upon aluminium incorporation has been investigated for its cracking potential. Accordingly, it is reported to favor diesel maximization as seen in the Table 4.

Furthermore, special microporous structure of ITQ-33 is reported to favor the formation and diffusion of the alkylation products while reducing the undesired propylene oligomerization during benzene alkylation process. Typically, the large 18-MR pores allow the formation of multialkylated products, such as di-isopropyl- and tri-isopropylbenzene, in larger proportions [19]. Interestingly, selectivity of ITQ-33 framework for n-propylbenzene is reported to be <100 ppm which is an advancement over the specifications for commercial cumene processes, such as UOP Q-Max (250–300 ppm) or ENI SpA (<500 ppm) [19].

2.4 ITQ-21

It is well known in FCC art that conventional faujasite based FCC catalyst demands extensive post-synthesis treatment to produce an ultrastable form, and has a large cavity accessible through four 0.74 nm-wide windows and thus limits the access of oil molecules to the catalytically active sites [12–14]. Therefore, it is envisaged that the use of zeolites with better accessibility to their active sites should result in improved catalyst efficiency. Accordingly, novel germanium silicate based zeolytic 12-membered ring ITQ-21 framework with a 3-D pore network containing 1.18 nm-wide cavities, each of which is accessible through six circular and 0.74 nm-wide windows, is introduced recently [21] which has been reported to favor better

Table 4 Catalytic cracking of Arabian light vacuum gas oil at 500 °C and 60s time on-stream [18]

Catalyst	Conversion (%)	Yields (%)			Molar ratio	
		Diesel	Gasoline	Propylene	C3 = /C3	Isobutene/isobutane
USY						
Catalyst/oil = 0.62	92.5	15.7	40.4	4.7	1.0	0.1
Catalyst/oil = 0.47	88.3	19.5	39.5	4.4	1.3	0.1
ITQ-33						
Catalyst/oil = 0.70	89.2	22.6	34.5	4.2	1.9	0.4
Beta						
Catalyst/oil = 0.70	84.0	14.1	32.3	7.5	1.9	0.5
USY + 20% ZSM-5	87.0	17.0	33.2	7.2	1.5	0.3
ITQ-33 + 20% ZSM-5	86.1	23.3	25.1	9.0	3.7	1.1

USY Unit cell size-2.432 nm

conversion and less olefin content in FCC gasoline but high aromatic content *vis-à-vis* USY based FCC catalyst [17].

2.5 Lube oil base stock (LOBS) production

The lubricant base oil which is a refined petroleum product forms the foundation of most of the world's finished lubricants. The base oil is a complex mixture of paraffin, aromatics and naphthenic hydrocarbon type molecules, ranging in carbon number from 20 to 40+. They constitute a very important segment of the hydrocarbon industry. Normally, lube and middle distillate cuts have large amounts of wax which increases the freezing and the pour points of these cuts, because of its solid form at ambient temperature. Thus, base oil needs modification prior to its use as automotive, industrial lubricants. Manufacture of these base stocks in the past two decades or so underwent evolutionary changes due to a number of reasons. The variety of crude oils that need to be processed considerably increased with the introduction of new and improved refining processes [22]. Hydroprocessing has emerged as the most important routes for this purpose. Different processing configurations involving replacement of solvent dewaxing, and catalytic dewaxing steps have been developed. Today, base oils produced by hydroisomerization de-waxing in conjunction with severe hydrocracking process offer the following attractive features [22]:

- Very High Viscosity Index (100–130)
- Low Volatility
- Superior Oxidation Resistance
- High Thermal Stability
- Excellent Low Temperature Fluidity
- Low Toxicity

These features give performance characteristics in finished lubricants very similar to synthetics, such as poly-alpha-olefins (PAO) and are classified in various groups (Table 5) as per recommendations of the American Petroleum Institute (API) based on physical and chemical properties. Most of the above developments were possible due to continuous catalyst improvements.

Typically, medium pore zeolites and zeolite like molecular sieves are reported to be ideal candidates for wax hydroisomerization. Excellent reviews and monographs have been published in this regard. Thus, medium pore zeolites such as SAPO-11, ZSM-22/-23 have been extensively investigated both in open and patent literature [23]. Like wise, use of SSZ-32 is covered under patent literature [24]. Among SAPO family, apart from SAPO-11, SAPO-31 with puckered 12-membered ring is also found to be a good candidate; however, owing to the problems associated in crystallization of its pure form, its applicative potential is yet to be fully proven. The pore openings for these conventional zeolites are listed in Table 6.

Table 5 API—classification of base oils [22]

Group	Saturate (wt%)	Sulphur (wt%)	Viscosity index
I	<90 and/or	>0.03	>80–<120
II	≥90 and	≤0.03	≥80–≤120
III	≥90	≤0.03	≥120
IV	All poly alpha olefins (PAOs)		
V	All base stocks not included in Groups I-IV		

Table 6 Zeolite pore dimension data [25]

Zeolite	Zeolite type index	Pore opening (Å)
ZSM-22	TON	4.6 × 5.7
ZSM-23	MTT	4.5 × 5.2
SAPO-11	AEL	4.0 × 6.5
SAPO-31	ATO	5.4 × 5.4

Such zeolites with optimum acidity coupled with correct noble metal function favors wax hydroisomerization via. pore mouth/lock-key catalysis mechanism [26].

In view of the above, significant improvements have taken place in last decade to design wax hydroisomerization processes. However, it is important to note the major concerns and future challenges of hydroprocessing based LOBS production in terms of future product demand. It is noteworthy that the hydroisomerization catalyst is 5–7 times more expensive than other hydroprocessing catalyst. Furthermore, it is non-regenerable in nature and has catalyst cycle life of about 2–3 years with maximum severity of operation. Therefore, it is utmost important to improve:

- Catalyst life
- Tolerance to feed impurity namely sulfur and nitrogen
- Yields
- Product quality by increasing VI and lowering pour point without loss of yield
- Feed processing rate

Thus, sustained efforts are being made (a) to improve catalyst design and (b) to explore new zeolitic frameworks with improved conversions. In this context, synthesis of nanosized MTT has demonstrated the potential to improve the product yields [27]. Likewise, recently zeolites ZSM-12, and GUS-1 have also been identified to hold potential for hydroisomerization [28, 29]. Furthermore, intergrowth of MTT/TON is also reported to hold promise for yield improvements [30]. Recent report on synthesis of pure SAPO-31 framework could also offer an opportunity for new catalyst design [31].

3 Light olefin separation

Quest for alternate energy efficient separation process for light olefin separation especially, propane-propylene mixture has gained momentum in recent time due to increasing annual demand for propylene world wide and current highly energy intensive cryogenic distillation process practiced. In this context, development of adsorptive separation process has attracted attention of zeolite researchers. Thus, numerous attempts have been made to develop selective adsorbents for C3 separation. In the literature a number of adsorbent materials based on π-complexation have been reported [32, 33]. Typically, Ag+/Cu+-zeolites and silver/copper impregnated alumina/silica/clay supports have been extensively studied for light olefin paraffin separation [34–39]. However, regeneration and safety issues have still found to be major challenges for their commercial use. Furthermore, such systems are often prone to feed impurities such as water and acetylene [34–36]. Therefore, focused attempts are being made to develop promising adsorbents with high selectivity and easy regenerability. In this regard, molecular sieve adsorbents based on molecular gate effect, differential diffusion are envisaged to be ideal for light olefin separation [40, 41]. This has led to discoveries of new small pore molecular sieve frameworks such as all silica DD3R [37–39], ITQ-3 [37–39], ITQ-12 [40, 41], ITQ-32 [42], Si-CHA [37–39], and high silica ZSM-58 [37–39] which have opened up new avenues for exploring their sorption potential.

These molecular sieve frameworks offer leverage to design adsorbent formulation for C3 separation based on either molecular gate effect or differential diffusion concepts. Interestingly, higher diffusion rates for propylene have been noticed over CHA type framework (pore dimension: 3.8 × 4.2 Å) vis-à-vis propane molecules [37–39]. This is mainly due to smaller molecular size of olefin which favors diffusion of propylene over propane in CHA framework. Interestingly, ITQ-12 framework demonstrates molecular gate effect at 353 K for propane and could be an ideal choice for further development [41]. Similar effect is also shown by ITQ-32 framework for tras-2-butene at ambient conditions [43]. Other than these aforementioned efforts, attempts were made to explore framework potential of mesoporous solids *viz.* SBA-15 by tuning its textural parameters [44]. In view of the aforementioned developments, efforts need to be focused on development adsorptive/hybrid separation processes.

4 MTO process

Unstable crude oil prices, depleting refinery margins and economic constraints in recent past has renewed interest in Coal to liquid (CTL) and Gas to Liquid (GTL) processes. Although there are multiple options which can be practiced using syn gas produced via. coal gasification/gas reforming, economic drivers favour production of light olefins through methanol production from syn gas by employing methanol to olefin (MTO) process [45]. Excellent reviews related to catalyst and process options are available in the literature [46]. Typically, SAPO-34 (CHA topology) based catalyst is employed for this process either in fluidized bed or moving bed option [47, 48, 49, 50]. The main reason for such process options is often ascribed to rapid deactivation of SAPO-34 catalyst because of rapid coking thus resulting into short time on stream cycle. Thus, attempts have been made to either tailor the catalyst or crystallite size to improve the catalyst performance. In this context, University of Oslo attempted to tailor acidity of SAPO-34 framework through controlled substitution of Si in the presence of F^- media. This has resulted into successful crystallization of UiO-*n* framework with CHA topology

[51]. However, it may be noted that such attempts are yet to be proven for catalyst on stream life.

To the best of our knowledge, it is only recently a successful attempt is made to diagnose the real problem of SAPO-34 framework during MTO process. Accordingly, crystallization of SAPO-34 was investigated in great detail which revealed the co-crystallization of AEI (SAPO-18) along with CHA (SAPO-34) structure. Interestingly, both the structures belong to small pore zeolite family but differ slightly in pore dimensions (AEI: 3.8 × 3.8 Å; CHA: 3.8 × 4.2 Å) which is substantial to impart detrimental effect on catalyst performance (It may be noted that CHA framework is reported to be ideal for light olefin separation [37, 38, 39]). In view of this, successful attempt has been made to control the intergrowth of AEI structure during MTO catalyst preparation which has resulted into crystallization of EMM-2 framework [52]. The catalyst so prepared has demonstrated improved time on stream than those reported for earlier ones. Like wise, successful attempts have been reported recently in patent literature on synthesis of pure CHA framework [51].

5 Zeolite design for monoalkyl-aromatic production

Success of MCM-22 (MWW topology) for production of ethyl benzene (EBmax proprietary process) using ethylene and benzene feedstocks has added impetus to design novel zeolite synthesis methodologies to produce zeolite framework having similar or at least comparable catalytic potential to MCM-22 [53]. This has led into successful designing of UZM-*n* type zeolites by M/s UOP and flexible/rigid template coupled with high throughput (HT) syntheses approach by Corma et.al. [54] resuting into discovery of ITQ–30 molecular sieve.

The discovery of UZM-*n* is based on novel synthesis approach called ‘‘Charge Density Mismatch’’ (CDM) approach. Such approach allows control crystallization of desired molecular sieve framework by creating mismatch between electrostatic interactions of aluminosilicate reactive gel species with structure directing agent (SDA). Typically, these conditions are accomplished by creating an aluminosilicate reaction mixture (typically a clear gel) using a large SDA (low charge density) and a low Si/Al ratio (high charge density) which disfavors the zeolite crystallization. The crystallization of desired framework is then accomplished by manipulating charge density of reactive gel media through addition of secondary structure directing agent/s. Thus UOP has announced a new family of zeolites UZM-n (UZM-4, UZM-5, UZM-8, UZM-9, UZM-15 and UZM-17) [10, 11]. Among them, UZM-8 is found to have unique layered structure has a large number of acid sites at or near the external surface of the zeolite crystals and reported to be high selective for production of mono-alkyl-aromatics.

Like wise, ITQ-30 [54] is reported to have MWW topology and is reported to have similar catalytic potential as that of MCM-22.

6 Way forward

Based on above discussion, it is imperative that introduction of novel zeolytic frameworks could offer opportunity to develop new processes for production of desired products during oil refining and petrochemical operations. However, more focused synthesis and post synthesis efforts are essential to address following aspects:

- Structural stability of ITQ-13,-33,-21,-30 (Al-germeniumsilicate framework) under hydrothermal conditions at commercial level. For this purpose, attempts may be focused to (a) derive synthesis conditions for crystallization of the aforementioned frameworks with low germanium content, (b) investigate the effect of rare earth exchange on stabilization of germanium and aluminium framework hydrolysis (c) optimize template removal via. Solvent extraction route and post synthesis Al-incorporation route to achieve right balance between rare earth exchange and Al- and Ge- level.
- Identification of cheaper and specific templates for ITQ-12, -32, Si-CHA frameworks for development of light olefin separation process (current templates are expensive and difficult to prepare at bulk level).
- Establishment of desorption strategy for light olefin separation.
- Designing of mono-alkyl-aromatic production catalyst with (a) Ability to operate at lower benzene/olefin feed ratios (reduce benzene recycle) and (b) High tolerance to suspect feed poisons (Nitrogen and Sulfur).

Addressing such aspects, we believe, could definitely offer unique platform for zeolite researchers to exploit applicative potential to the maximum.

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