

Methanol to olefin conversion catalysts

Zhongmin Liu* and Juan Liang

The past year has seen remarkable advances both in methanol to olefin process development and in understanding the catalysts and reactions involved. The methanol to olefin process is now on the way to being commercialized locally with economic advantages in comparison with other natural gas utilization technologies and conventional naphtha cracking processes. Using a specially designed procedure, a catalyst for the selective synthesis of ethylene from methanol has been reliably reproduced. The relationships between catalyst properties and reaction performances are clearer than ever before.

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Abbreviations

GTL	natural gas to liquids
GTO	natural gas to olefin
LNG	liquefied natural gas
MTO	methanol to olefin
SAPO	silicoaluminophosphate

Introduction

Natural gas has become an abundant fuel and chemical feedstock. As the technology for methanol production from natural gas is widely used and well-established, the conversion of methanol to olefins tends to be an interesting and promising way of converting methane to chemicals. Solid acids can effectively catalyze this reaction to form hydrocarbons [1,2]. However, the selective production of light olefins, especially ethylene and propylene, is a challenge to catalysis. In the past decade, most of the literature has discussed the use of zeolite ZSM-5 as the appropriate catalyst [3], it possesses a 10-ring interconnected channel system and yields aromatics as by-products. Recently, catalyst researchers have focused on small pore silicoaluminophosphate (SAPO) molecular sieves [4,5], mainly on SAPO-34 [6–8], which gives a narrow range product distribution from C₁ to C₅ hydrocarbons. The present progress in research and development shows a great possibility for the commercialization of a MTO (methanol to olefin) process in the near future [9**]. This review will focus on the remarkable advances since 1997 in catalyst and process research, and on the advances in the understanding of catalysts and reaction mechanisms.

Methanol to olefin process development

The past year has seen remarkable advances in MTO process development. Vora *et al.* [9**,10**] reported pilot

plant results of the MTO reaction and the comparative economic estimations of the process. The test was carried out in a fluidized bed reaction system. The material balance data show that, in the case of high-ethylene production, the yield of ethylene is 19.98% and that of propylene is 12.99%. Comparison with other natural gas conversion and utilization technologies, such as natural gas to liquids (GTL) and liquefied natural gas (LNG), the process of natural gas to olefin (GTO) *via* MTO is significantly more attractive. To produce 500,000 MTA (metric tons annually) ethylene in equivalent GTL and LNG plants, the simple payback period is 5.1 years for GTO technology, 7.7 years for GTL, 7.9 years for LNG and 11.8 years for the naphtha cracking process, respectively. The economics were from a Middle East location using a natural gas price of 0.75 \$/MM Btu (million British thermal units) with a naphtha feed value of 150 \$/MT (metric tons). The natural gas to olefin technology is also more attractive than conventional naphtha cracking for ethylene and propylene production. The commercially manufactured catalyst contains SAPO-34 molecular sieve as the active component. Another pilot plant test was reported by Liu *et al.* [11**] using dimethyl ether as the feedstock, which is similar to a MTO reaction. The reaction was carried out in a fluidized bed reaction system (reactor diameter 100 mm) with continuous regeneration of the catalyst. The catalyst contains molecular sieve SAPO-34 synthesized using triethylamine as a templating agent. The cost is reduced by ~20% of the method using tetraethyl ammonium hydroxide as the templating agent. The material balance results show that the corresponding yield of ethylene and propylene from methanol are 20.38% and 13.35%, respectively.

SAPO molecular sieve catalysts

The small pore limitations of SAPO molecular sieves result in a rather high ethylene selectivity [5,12,13,14*]. However, it is for the same reason that it is difficult to apply conventional modification methods, such as ion-exchange and impregnation, to change the properties of the catalyst. Modification in the synthesis of the molecular sieve seems to be critical for improvement of catalytic performance. Remarkable results were observed using Ni-SAPO-34 [15], on which an ethylene selectivity of 88% was found at 450°C with 100% methanol conversion and without coke formation. This catalyst was not easy to reproduce [16] because the selectivity is very sensitive to those properties which depend on the preparation procedure. Inui and Kung [17**] reported a reliable procedure for the synthesis of Ni-SAPO-34, and investigated the factors involved in its preparation. The authors point out that the order of mixing of the starting materials is important to obtain a homogeneous gel mixture. The sequence of the addition of seed crystallites, milling for a time, treatment with ultrasonic waves and the application of a rapid crystallization method

[7] seem necessary to obtain a satisfactory catalyst. The catalysts have particles 0.8–0.9 μm in size and a sharp size distribution, with low acid density on both the internal and external surface, with a 86% selectivity to ethylene at 425°C. A linear relationship between internal acid density and the selectivity to ethylene was observed, thus one may expect to obtain more selective formation of ethylene by controlling the internal acid density to less than 4 $\mu\text{mol}/\text{m}^2$. The authors demonstrated that for most samples Ni is at least partly incorporated into the framework in the tetrahedral coordination state. The remaining part of Ni is in the octahedral coordination state. The amount of Ni incorporated in SAPO-34 is surprisingly very small ($\text{Si}/\text{Ni} \approx 100$). So it is interesting to argue what the exact effect of Ni is on the catalyst properties and on reaction performance.

Lischke *et al.* [18[•]] reported that the best results with respect to the formation of lower olefins are achieved over NiAPO-5 among various MeAPO-5 (Me = Co, Mn, Mg, Zn, Ni, Cr, Zr) catalysts. Selectivity of lower olefins increased gradually by raising the content of Ni. The assumed reason was due to the low density of acid sites of higher acidic strength and to the presence of only small portions of strong acid Lewis sites. Relatively higher conversion and selectivity towards C_2+ hydrocarbons were also found on the $\text{Ni}_{0.05}\text{Al}_{0.95}\text{PO}_4$ catalyst in comparison with other MeAlPO_4 (M = Cr, Mn, Fe, Co) catalysts [19[•]]. Tsoncheva *et al.* [20[•]] observed that the methanol to hydrocarbon reaction on CoSAPO is sensitive to the presence of isomorphously substituted cobalt and the generated strong acid centers.

It is worthy to note the observations of Djieugoue *et al.* [21[•]] on the reducibility, location and adsorbate interactions of Ni(I) in Ni(II)-exchanged SAPO-34 by electron spin resonance (ESR) and electron spin echo modulation (ESEM) techniques. After dehydration above 573K, Ni(II) was reduced to Ni(I). A similar phenomenon was also observed on a Cu(II)-exchanged SAPO-17 molecular sieve [22[•]]. A redox property of CoAPO-34 and CoSAPO-34 was observed by Moen *et al.* [23[•]] and Rajic *et al.* [24[•]]. Adsorption of methanol into a hydrogen-reduced sample forms two Ni(I)-methanol complexes that are suggested to be located at two different sites in the chabazite structure [21[•]]. At a higher reaction temperature, migration of Ni to a cation position is possible, and there is indeed some hydrogen in the product. The Ni in Ni-SAPO-34 possibly has another effect besides changing acid properties of the catalyst when under real reaction conditions.

Popova *et al.* [25[•]] suggested that the ratio between Brønsted and Lewis acid sites may also be important for ethylene selectivity and catalyst stability as well as the other structure related factors. They observed that the source of silicon and aluminum in the synthesis SAPO-34 has effects on the catalytic performance in a MTO reaction [26^{••}]. Although all the samples exhibited similar activities and selectivities, the samples synthesized from organic

precursors deactivated more rapidly accompanied with high methane formation. There have also been some advances in the synthesis method of zeolites [27[•]] and SAPO molecular sieves [24[•],28[•]]. The test of these methods to MTO catalyst and reaction will be interesting.

Acid sites

The acidic properties of SAPO molecular sieves are closely related with the silicon incorporation into the framework [29]. Smith *et al.* [30,31[•]] revealed that there are two distinct acid sites in the SAPO-34 unit cell: one in the eight-ring channel and the other in the six-ring. Understanding the crystallization mechanism and detailed distribution of silicon and aluminum in the framework is essential for catalyst research. Some interesting results focusing on the incorporation of silicon into the framework have been reported [32–34]. Sastre *et al.* [35^{••},36^{••}] reported the lattice simulation results of silicon incorporation into an AlPO_4 framework. They found that the single silicon incorporation process appears to be independent of the framework type, and ‘dispersed silicon’ is more stable than the distribution that has large areas of an ‘aluminosilicate phase’. If the silicon content is such that island formation is promoted, the acidic character will become strongly dependent on the topology of the material. Acidity directly relates to the concentration of the Si island. Large proportions of silicon-rich regions were found in mesoporous SAPOs [37[•]]. Experimental results [38^{••}] from a crystallization research of SAPO-34 indicate that silicon precursors directly take part in the formation of the crystal nucleus as well as in the growth of the crystal grains, giving the Si(4Al) structure at the initial stage (<2.5 h). At this stage ~90% of the total silicon entered the crystals with a relative crystallinity greater than 80%. Si(3Al), Si(2Al), Si(1Al) and Si(0Al) appeared only at a later stage, which implies the substitution of the Si atoms for the phosphorus and aluminum pair. The above results may explain the advantage of fast crystallization for enhanced catalyst performance.

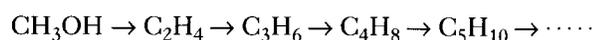
Reaction mechanisms

The conversion of methanol to olefins involves the formation of C–C bonds. Understanding the reaction mechanism is important for the development of a high efficiency catalyst. Two features of the reaction are clear: methanol equilibrates with dimethyl ether and water, and there is an induction period before the onset of extensive hydrocarbon synthesis. Methanol adsorption on the surface of the catalyst should be the first step for reaction. Salehirad and Anderson [39^{••}] studied the adsorption complexes on H-ZSM-5 and H-SAPO-34 by a solid state NMR technique. The results reveal that at low loading (up to one methanol per acid site) the methanol adsorbed in two-hydrogen bonded configurations. At higher coverage, methanol may cluster with the involvement of one methoxonium ion. Hunger and Horvath [40[•]] found that behavior of SiOH groups in zeolite Hbeta is different from that in ZSM-5 and HY zeolites in the adsorption of methanol. This suggests that, besides acid properties, the

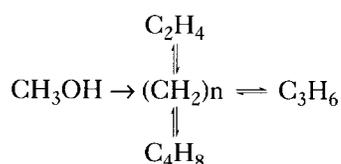
framework structure of zeolites also has an effect on the adsorption or activation of methanol. NMR has proven to be a particularly useful technique in the study of SAPO molecular sieves [8,32], the adsorption of methanol [39^{••},40[•]] and catalytic reactions [41[•],42].

Many and varied mechanisms have been proposed for the methanol to hydrocarbon reaction [43]. From a simplistic view, there are two main mechanism types for olefin formation in the methanol conversion reaction, which may be simply represented by the following schemes:

1. A consecutive-type mechanism: ethylene will be first formed in the reaction.



2. A hydrocarbon pool-type mechanism. Dahl and Kolboe [44,45] proposed that olefin synthesis occurs through a carbonaceous species of unknown stoichiometry, possibly a carbonium ion. This species is assumed to be alkylated by methanol or dimethyl ether until it eliminates an olefin and restarts the catalytic cycle.



The present results from pulse-quench catalytic reactor studies [46[•]] and an isotopic tracer method [14[•]] tend to support the carbon-pool mechanism. Lischke *et al.* [18[•]] suggested that all three lower olefins are formed simultaneously by C–C bonding, and an additional stepwise build-up occurs in the consecutive reaction sequence as the reaction proceeds.

Deactivation

It is known that coke formation cannot be avoided in the methanol to olefin reaction, and this will deactivate the catalyst. However, relatively fewer studies have been done on deactivation in the past year. Inui and Kung [17^{••}] observed that the amount of coke deposited largely depends on the acid density on the external surface of Ni-SAPO-34 crystals. This is due to fewer space-restrictions of external surface acid sites to the growth of bulk aromatic coke. As dimethyl ether is a key MTO reaction intermediate, Chen *et al.* [47[•]] studied the deactivation of SAPO-34 in the dimethyl ether to olefin reaction. Based on the assumption that the coke was randomly deposited inside the crystals, a kinetic model was developed with good consistency with experimental data to account for the effective diffusion and deactivation. Further research on coking mechanisms and its relation to catalyst properties is important for the development of a high efficiency catalyst.

Conclusions

The past year has seen remarkable advances both in methanol to olefin process development and in understanding catalysts and the reactions involved. The methanol to olefin process is now on the way to being commercialized with economic advantage in comparison with other natural gas utilization technology and the conventional naphtha cracking process. The catalyst for the selective synthesis of ethylene from methanol can be reliably reproduced by a specially designed procedure. A low internal acid density seems to favor ethylene selectivity. Methanol adsorption and mechanism studies suggest that the reaction may proceed by a carbon-pool mechanism. Further understanding of the relationship between catalyst preparation and performance needs research on the crystallization and silicon incorporation mechanism of small pore silicoaluminophosphate molecular sieves. Any application of *in situ* techniques to characterize a catalyst, reactions and deactivation will bring advances to this field. Quantum-chemistry simulations [48[•]] can also be helpful in MTO reaction and catalyst research.

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

- of special interest
 - of outstanding interest
1. Chang CD: **Hydrocarbons from methanol**. *Catal Rev Sci Eng* 1983, **25**:1-118.
 2. Chang CD: **Methanol conversion to light olefins**. *Catal Rev Sci Eng* 1984, **25**:323-345.
 3. Inui T: **High potential of novel zeolitic materials as catalysts for solving energy and environmental problems**. In *Proceedings in Zeolite and Microporous Materials*. Edited by Chon H, Ihm S-K, Uh YS. Amsterdam: Elsevier; 1997:1441-1468. [Studies in Surface Science and Catalysis, vol 105.]
 4. Lok BM, Messina CA, Patton RL, Gajek RT, Cannan TR, Flanigen EM: **Silicoaluminophosphate molecular sieves: another new class of microporous crystalline inorganic solids**. *J Am Chem Soc* 1984, **106**:6092-6093.
 5. Chen J, Wright PA, Natarajan S, Thomas JM: **Understanding the Brønsted acidity of SAPO-5, SAPO-17, SAPO-18 and their catalytic performance for methanol conversion to hydrocarbons**. In *Zeolites and Related Microporous Materials: State of the Art 1994*. Edited by Weitkamp J, Karger HG, Pfeifer H, Holderich W. Amsterdam: Elsevier Science BV; 1994:1731-1738. [Studies in Surface Science and Catalysis, vol 84.]
 6. Liang J, Li HY, Zhao SQ, Guo WG, Wang RH, Li MZ: **Characteristics and performances of SAPO-34 catalyst for methanol-to-olefin conversion**. *Appl Catal* 1990, **64**:31-40.
 7. Inui T, Matsuda H, Okaniwa H, Miyamoto A: **Preparation of silicoaluminophosphate by the rapid crystallization method and their catalytic performance in MTO**. *Appl Catal* 1990, **58**:155-163.
 8. Watanabe Y, Koiwai A, Takeuchi H, Hyodo S: **Multinuclear NMR studies on the thermal stability of SAPO-34**. *J Catal* 1993, **143**:430-436.
 9. Vora BV, Marker T, Barger PT, Nilsen HR, Kvisle S, Fuglerud T: **Economic route for natural gas conversion to ethylene and propylene**. *Stud Surf Sci Catal* 1997, **107**:87-98.
- The results of pilot plant test and process analysis show that MTO is economic for ethylene and propylene production from natural gas. One can see that the technology of MTO will be a stage for practical application.
10. Vora BV, Marker T, Arnold EC, Nilsen H, Kvisle S, Fuglerud T: **Conversion of natural gas to ethylene and propylene: the most-profitable option**. In *Natural Gas Conversion V*. Edited by

Parmaliana A. Amsterdam: Elsevier Science BV; 1998:955-960. [Studies in Surface Science and Catalysis, vol 119.]

By economic comparison of GTL, LNG and naphtha-cracking options with GTO, the conclusion is that a natural gas to olefins via methanol is the most-profitable option. For the production of 500,000 MTA ethylene from equivalent GTL and LNG plants, the simple payback period is 5.1 years for GTO technology, 7.7 years for GTL, 7.9 years for LNG, and 11.8 years for the naphtha cracking process. The economics were based on a Middle East location and the same product values were used.

11. Liu ZM, Cai GY, Sun CL, He CQ, Chang YJ, Yang LX, Shi RM, Liang J:
 • **Research progress and pilot plant test on SDTO process.** In *Natural Gas Conversion V*. Edited by Parmaliana A. Amsterdam: Elsevier Science BV; 1998:895-900. [Studies in Surface Science and Catalysis, vol 119.]

A brief summary of a pilot plant test. In the SDTO process, the secondary reaction (dimethyl ether to olefin) is similar to MTO. The catalyst can also be used for MTO. The SAPO-34 was synthesized by a triethylamine templating method, which is more economical than using tetraethyl ammonium hydroxide as the templating agent. The yield of ethylene and propylene from methanol are 20.38% and 13.35%, respectively. This is an important step in the practical use of this technology.

12. Inui T: **Structure-reactivity relationship in methanol to olefin conversion on various microporous crystalline catalysts.** In *Structure-Activity and Selectivity Relationship in Heterogeneous Catalysis*. Edited by Grasselli RK, Sleight AW. Amsterdam: Elsevier Science BV; 1991:233-242.
13. Nawaz S, Kolboe S, Kvisle S, Lillerud K-P, Sticker M, Øren HM: **Selectivity and deactivation profiles of zeolite type material in the MTO process.** In *Natural Gas Conversion*. Edited by Holmen A. Amsterdam: Elsevier Science BV; 1991:421-427.
14. Iglesia E, Wang T, Yu SY: **Chain growth of methanol on SAPO-34 and H-ZSM5.** In *Natural Gas Conversion V*. Edited by Parmaliana A. Amsterdam: Elsevier Science BV; 1998:527-532. [Studies in Surface Science and Catalysis, vol 119.]

By kinetic and isotropic tracer methods, the chain growth in a MTO reaction was confirmed to occur via methylation of adsorbed intermediates with CH_3OH , and alkenes desorbed via β -scission steps. The different product selectivity between HZSM-5 and SAPO-34 was observed to be due to their difference in diffusion constraints. Small SAPO-34 crystals with few external acid sites will lead to maximum ethene selectivity. The results will be helpful in MTO catalyst research.

15. Inui T, Phatanasri S, Matsuda H: **Highly selective synthesis of ethene from methanol on the novel nickel-containing silicoaluminophosphate catalyst.** *J Chem Soc Chem Commun* 1990:205-206.
16. van Niekerk MJ, Fletcher JCQ, O'Connor CT: **Effect of catalyst modification on the conversion of methanol to light olefins over SAPO-34.** *Appl Catal* 1996, **138**:135-145.
17. Inui T, Kung M: **Reliable procedure for the synthesis of Ni SAPO-34 as a high selective catalyst for methanol to ethylene conversion.** *Appl Catal A* 1997, **164**:211-223.

The selectivity of catalyst, SAPO-34 is sensitive to its properties, and thus its preparation procedure. A high value of up to 88% ethylene selectivity in the MTO reaction is a remarkable and attractive result. A detailed investigation of the preparation factors and reproducibility of the catalyst will give interesting information on the relations of synthesis procedure, acid properties and catalytic performances. The order of mixing of the starting materials is important to obtain a homogeneous gel mixture. The followed addition of seed crystallites, milling for a time, treatment with ultrasonic waves and the application of a rapid crystallization method seem necessary to obtain a satisfactory catalyst. There seems a linear relationship between the acid density of internal surface and the selectivity to ethylene. These observations are important for understanding the acidity for MTO reaction.

18. Lischke G, Parltitz B, Lohse U, Schreier E, Fricke R: **Acidity and catalytic properties of MeAPO-5 molecular sieves.** *Appl Catal A* 1998, **166**:351-361.

The best MTO results to ethylene selectivity are observed with NiAPO-5. Selectivity of lower olefins can be increased gradually by raising the content of Ni. It was thought that this was caused by the low density of acid sites of higher acidic strength and by the presence of only small proportions of strong acid Lewis sites. In the case of less diffusion limitation, it is clearer to understand the metal effect than in NiSAPO-34.

19. Mishra T, Parida KM, Rao SB: **Transition metal promoted AlPO₄ catalyst 2. The catalytic activity of $\text{M}_{0.05}\text{Al}_{0.95}\text{PO}_4$ for alcohol conversion and cumene cracking/dehydrogenation reactions.** *Appl Catal A* 1998, **166**:115-122.

A relatively higher conversion and selectivity towards C_2+ hydrocarbons was found for a $\text{Ni}_{0.05}\text{Al}_{0.95}\text{PO}_4$ catalyst in comparison with other MeAlPO_4

(M = Cr, Mn, Fe, Co) catalysts, which is in agreement with the results from other researchers [18*]. This suggests that Ni may have a special promotion effect on the MTO reaction.

20. Tsoncheva T, Dimitrova R, Minchev C: **Methanol conversion as a test for framework cobalt elucidation in CoAPSO molecular sieve.** *Appl Catal A* 1998, **171**:241-245.

The methanol reaction is sensitive to the framework and extra-framework position of Co in the CoAPSO molecular sieve, which can be a probe to reveal the effect of metals in SAPO molecular sieves.

21. Djieugoue Marie-Ange, Prakash AM, Kevan L: **Electron spin resonance and electron spin echo modulation studies on reducibility, location, and adsorbate interactions of Ni(II) in Ni(II)-exchanged SAPO-34.** *J Am Chem Soc* 1998, **120**:4386-4391.

After dehydration of Ni(II)-SAPO-34 at 573K as well as γ -irradiation at 77K, the reduced Ni(II) is observed. Adsorption of methanol into reduced NiH-SAPO-34 forms two Ni(II)-methanol complexes that are suggested to be located at two different sites in the chabazite structure. This clearly shows that ion-exchanged Ni possesses a metallic as well as acidic properties.

22. Prakash AM, Kevan L: **Cupric ion location and adsorbate interactions in Cu(II) exchanged ironite-like SAPO-17 molecular sieve.** *Langmuir* 1997, **13**:5341-5348.

From this paper we can see what the effect of exchanged Cu(II) is on the adsorption of water, methanol and ethylene. When CD_3OH is adsorbed on CuH-SAPO-17, the complex contains two methanol molecules coordinating directly with the metal ion. This is different from the case when the metal is incorporated into framework.

23. Moen A, Nicholson DG, Renning M, Lambie GM, Lee J-F, Emerich H:
 • **X-ray adsorption spectroscopic study at the cobalt K-edge on the calcination and reduction of the microporous cobalt silicoaluminophosphate catalyst CoSAPO-34.** *J Chem Soc Faraday Trans* 1997, **93**:4071-4077.

Calcination leads to some extent the oxidation of framework Co(II) to Co(III), thereby leading to the view that the material is a redox catalyst. This redox property will have different effects on the MTO reaction from that of an acid property.

24. Rajic N, Ristic A, Tuel A, Kaucic V: **A CoAPO-34 derived from a triclinic precursor prepared in the presence of HF.** *Zeolites* 1997, **18**:115-118.

CoAPO-34 prepared in the presence of HF exhibits higher stability than a non-fluoride system. Cobalt(II) substitutes exclusively for the tetrahedral aluminum. Calcination of the as-synthesized material results in the oxidation of Co(II) to Co(III). Interesting results are: firstly, the material will have both redox and acid properties; and secondly, the application of the synthesis method to MTO catalysts.

25. Popova M, Minchev C, Kanazirev V: **Effect of the different modifications of AlPO-5 molecular sieve on its acidity and catalytic properties in methanol conversion to hydrocarbons.** *React Kinet Catal Lett* 1998, **63**:379-384.

It has been demonstrated that an appropriate Brønsted to Lewis acid ratio is essential for ethene selectivity and catalyst stability. It is beneficial to understand the relationship between acidity and catalytic performance.

26. Popova M, Minchev C, Kanazirev V: **Methanol conversion to light alkenes over SAPO-34 molecular sieve synthesized using various sources of silicon and aluminium.** *Appl Catal A* 1998, **169**:227-235.

The article demonstrated that all samples from various sources have similar activities and selectivities. However, the samples have different acidity and different deactivation behaviors. To know the reasons for these observations is important for both catalyst research and development.

27. Slangen PM, Jansen JC, van Bekkum H: **Induction heating: a novel tool for zeolite synthesis.** *Zeolites* 1997, **18**:63-66.

The use of induction heating as an alternating magnetic field to generate heat was shown to be effective for zeolite synthesis. It would be interesting to apply the new technique to the synthesis of MTO catalysts.

28. Venkatakshri N, Hegde SG, Rajamohanam PR, Sivasanker S:
 • **Synthesis of SAPO-35 in non-aqueous gels.** *J Chem Soc Faraday Trans* 1997, **93**:3411-3415.

This is first successful synthesis of SAPO-35 in non-aqueous gels. Si mainly replaces the P atoms in AlPO-35 giving rise to three different Brønsted acid bridging hydroxy groups. The absence of Si islands in the structure implies that there are no strong acid sites. The application of this new method to the synthesis of MTO catalyst will be interesting.

29. Barthomeuf D: **Topological model for the compared acidity of SAPOs and SIAL zeolites.** *Zeolites* 1994, **14**:394-401.

30. Smith L, Cheetham AK, Morris RE, Marchese L, Thomas JM, Wright PA, Chen J: **On the nature of water bounded to a solid acid catalyst.** *Science* 1996, **271**:799-802.

31. Smith LJ, Davidson A, Cheetham AK: **A neutron diffraction and infrared spectroscopy study of the acid form of the aluminosilicate zeolite, chabazite (H-SSZ-13).** *Catal Lett* 1997, **49**:143-146.

A remarkable work reveals the existence of two distinct acid sites in SiAl chabazite, which is slightly different to the case in SAPO-34. This is helpful for a deep insight into the acid sites.

32. Löffler E, Zibrowius B, Hunger M: **Multinuclear MAS n.m.r. and i.r. spectroscopic study of silicon incorporation into SAPO-5, SAPO-31, and SAPO-34 molecular sieves.** *Zeolites* 1992, **12**:167-174.
33. Vomscheid R, Briend M, Peltre MJ, Man PP, Barthomeuf D: **The role of the template in directing the Si distribution in SAPO zeolites.** *J Phys Chem* 1994, **98**:9614-9618.
34. Ashtekar S, Chilukuri SVV, Chakraborty DK: **Small-pore molecular sieve SAPO-34 and SAPO-44 with chabazite structure: a study of silicon incorporation.** *J Phys Chem* 1994, **98**:4878-4883.

35. Sastre G, Lewis DW, Catlow CRA: **Modeling of silicon substitution in SAPO-5 and SAPO-34 molecular sieves.** *J Phys Chem* 1997, **101**:5249-5262.

The formation of larger islands is calculated to be energetically more favorable in SAPO-5 compared with SAPO-34, as observed experimentally. Estimates of deprotonation energies indicate that greater acidity exists at the edges of islands and there is a correlation between acidity and island size, indicating that the acidity of these systems is directly related to the concentration of Si islands. The discovery implies that silicon distribution is a main factor influencing acid strength distribution and catalytic performance. It is possible that SAPO-34 with good MTO performance needs a suitable silicon distribution in its structure.

36. Sastre G, Lewis DW, Catlow CRA: **Mechanism of silicon incorporation in aluminophosphate molecular sieves.** *J Mol Catal* 1997, **119**:349-356.

Single silicon incorporation appears to be independent of the framework type. The formation of silicon islands is a structure-dependent process. Dispersed silicon is more stable than a distribution that has large areas of an aluminosilicate phase. The excellent correlation between calculations and experimental data can be profitable in understanding the behavior of SAPO materials.

37. Chakraborty B, Pulikottil AC, Viswanathan B: **Physico-chemical and MAS NMR characterization of mesoporous SAPOs.** *Appl Catal A* 1998, **167**:173-181.

Silicon-rich regions are found in large proportions in mesoporous SAPOs, which is different from the case of microporous SAPOs. This suggests that silicon incorporation into the framework is related to structure type of molecular sieve.

38. Tan J, Liu ZM, He CQ, Liu XC, Han XW, Zai RS, Bao XH: **Study on the crystallization mechanism of SAPO-34.** *J Catal (Chinese)* 1998;436-441.

Changes of crystallinity, composition and properties of the as-synthesised samples were monitored by various techniques. Two crystallization stages were observed. In the initial stage (<2.5 hours), silicon precursors directly take part in the formation of the crystal nucleus as well as in the growth of the crystal grains giving the Si(4Al) structure. At this stage ~90% of total silicon entered the crystals with a relative crystallinity greater than 80%. Si(3Al), Si(2Al), Si(1Al) and Si(0Al) appeared only in the later stage. It is interesting to relate the property of a sample to the synthesis procedure.

39. Salehirad F, Anderson MW: **Solid state NMR studies of adsorption complex and surface methoxy groups on methanol-sorbed**

microporous materials. *J Catal* 1998, **177**:189-207.

A significant research on methanol adsorption over H-ZSM-5 and H-SAPO-34. Methanol adsorption is closely related to the properties of the acidic sites. The results of this research support the presence of two types of surface complex. It is interesting to compare these results with those for the adsorption of water by Smith [30].

40. Hunger M, Horvath T: **Sorption of methanol on zeolite Hbeta investigated by in situ MAS NMR spectroscopy.** *Catal Lett* 1997, **49**:95-100.

Although the aim of the article was not related to MTO reaction, the significant difference observed in the adsorption of methanol on HZSM-5, HY and Hbeta reveals that the zeolite structure has a strong effect on adsorption and/or activation of methanol molecule.

41. MacNamara E, Raftery D: **A high-resolution solid-state NMR probe for in-situ studies of heterogeneous catalysis under flowing conditions.** *J Catal* 1998, **175**:135-137.

An interesting design enables a real *in situ* study of a reaction. A similar characterization of a MTO reaction is expected.

42. Xu Y, Grey CP, Thomas JM, Cheetham AK: **An investigation into the conversion of methanol to hydrocarbons over a SAPO-34 catalyst using magic-angle-spinning NMR and gas chromatography.** *Catal Lett* 1990, **4**:251-260.

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The reaction mechanism of MTO is still far from clear. The *in situ* characterization of a reaction is expected to get information near real reaction conditions. The application of a pulse-quench catalytic reactor is an approach to *in situ* analysis. The results support the 'carbon pool' mechanism proposed by Dahl and Kolboe [44,45].

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