**Effect of framework topology of SAPO catalysts on selectivity and deactivation
profile in the MTO reaction**

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Abstract

The catalytic performance in MTO reaction was studied on four 8-ring silicoaluminophosphate (SAPO) molecular sieves with different framework topologies and cavity-windows of various dimensions: SAPO-35 (**LEV**), SAPO-56 (**AFX**), STA-7 (**SAV**) and SAPO-42 (**LTA**). The four catalysts were compared with the widely investigated SAPO-34 (**CHA**) and showed remarkable differences in life-time and products selectivity. In particular, the STA-7 catalyst gave higher selectivity to C3-C4 olefins while similar methanol conversion capacity compared to a SAPO-34 catalyst with similar crystal size and acidity. Organic species retained in the cavities of partially deactivated catalysts were analyzed at different time-on-stream. The changes in composition of trapped compounds were correlated with that of the effluent products in order to elucidate the reaction mechanism and the deactivation pathway. The differences in effluent product distribution and trapped coke species suggest that framework topology has a great influence not only on the stability of the materials but also on the products distribution.

Keywords

8R silicoaluminophosphate, methanol to olefins, selectivity, deactivation

Graphical Abstract

Highlights

- Small differences in size and shape of 8R strongly affect deactivation rate of SAPO
- Wider 8-ring and medium-sized cage of STA-7 favor high methanol conversion capacity
- Light branched alkanes can block narrow pores causing fast deactivation of SAPO-35
- Larger 8R openings of STA-7 and SAPO-42 enhance production of C4+ hydrocarbons
- Large cages in SAPO-56 boost the fast formation of heavy polyaromatic hydrocarbons

1. Introduction

The conversion of methanol to hydrocarbons (MTH) over acid zeolites or zeotype materials has been investigated for several decades as a promising process to produce gasoline, light olefins or aromatics from carbon sources other than petroleum, and has been receiving increasing attention in the last ten years [1-7]. Although at present the low oil prices are delaying the commercial production of petrochemicals from methanol, the foreseen exhaustion of oil as well as policies on diversification of strategic resources make these processes highly attractive due to the different sources methanol can be produced from: coal, natural gas, biomass or even CO₂ [8-12]. To make these processes industrially competitive in comparison with the production of hydrocarbons from petroleum, it is necessary to employ a catalyst that provides a high selectivity to the desired compounds. Depending on the kind of target product, zeolitic materials with different compositions and framework topologies are more effective as catalysts in the MTH processes. Zeolitic catalysts with medium pore size (10R) topologies tend to produce higher molecular weight compounds (C₅-C₇), while small pore (8R) topologies are more selective to light olefins up to four carbon atoms. H-ZSM-5 zeolite was used as catalyst to transform methanol into gasoline in a plant, built in New Zealand in the mid-1980s, that was planned to produce 600,000 tons of gasoline every year by the methanol to gasoline (MTG) process. The following drop in oil price caused that only the methanol production facility continued operating. Nevertheless, later on, the methanol to olefins (MTO) process attracted more interest to manufacture ethylene and propylene from methanol via the UOP/Hydro MTO technology using microporous silicoaluminophosphate SAPO-34 as catalyst [5, 13-15]. The small pore windows (3.8 Å diameter) of SAPO-34 (CHA framework code) restrict the diffusion of heavy or branched hydrocarbons, directing the selectivity toward light olefins by real product

selectivity. Another parameter that has a marked effect on selectivity is the acid strength of the catalyst. SAPO molecular sieves show mild acid strength, generating less paraffinic compounds than the isostructural zeolites, which possess stronger acid sites and, therefore, promote hydride transfer reactions that lead to formation of aromatics and alkanes [16].

The high selectivity that SAPO-34 displays to light olefins (ethylene and propylene) is caused both by the mild acidity of the catalyst and by the porous structure of the material itself. SAPO-34 possesses relatively large chabazite cavities with small 8R entrances [17], so high molecular weight compounds can be formed inside the cages but only small and linear hydrocarbons can diffuse through the windows, inhibiting the diffusion of aromatic hydrocarbons out into the product effluent. The main drawback of this catalyst is its rapid deactivation under reaction conditions. The complex mechanism of the MTO reaction and the deactivation kinetics of SAPO catalysts have been widely studied [6, 18-21]. The dual-cycle hydrocarbon-pool mechanism is accepted for the MTO process [16]. This mechanism describes methanol transformation as an autocatalytic reaction in which both alkene and aromatic intermediates are involved in two inter-related cycles of methylation and cracking or dealkylation reactions that lead to the production of light alkenes. In these cycles, methylation steps would involve both oxygenates present in the mixture of methanol, dimethyl ether and water formed in a first fast step of methanol dehydration. Several studies have been performed in order to elucidate the origin of the first C-C bonding formation. Some of the mechanisms proposed a direct route in which methanol or dimethyl ether molecules are combined to form hydrocarbons [1, 22] whereas in other studies it is stated that the reaction rate for these direct routes can be considered negligible compared to reaction of methanol with hydrocarbons or higher alcohols impurities present in the feeding or on the catalyst

during the initial induction period [23, 24]. However, it has been also experimentally verified that surface methoxy species are formed by the adsorption of methanol molecules on the Brønsted acid sites [22]. The coupling of those species with the two oxygenate reactants might lead to the formation of hydrocarbon species [25, 26]. In a very recent contribution, spectroscopic evidences are provided for the direct formation of the first C-C bond in SAPO-34 catalyst during the transformation of methanol to olefins by the detection of surface-bound acetate as reaction intermediate and methyl acetate as the first product with a C-C bond [27].

The deactivation of the zeolitic catalyst under reaction conditions has been also widely investigated lately. It has been proposed that the reaction between methanol and hydrocarbon pool species as well as the combination of hydrocarbon species themselves would lead to the formation of large aromatics and heavy or branched hydrocarbons [23, 28, 29]. These molecules cannot diffuse through the porous structure and form carbonaceous deposits that may block the pore openings, hindering the access of methanol and other molecules to the active acid sites and obstructing the diffusion of the reaction products. The type of molecules formed inside the catalyst is dependent on the specific mechanistic route of the reaction, which is influenced by the space confinement in the cavities of the catalyst. Applying a different approach, methanol has been proposed to be the main source of catalyst deactivation, considering that coke formation in zeolitic catalysts is originated by formaldehyde molecules coming from the hydrogen transfer reaction between two methanol molecules [30, 31].

Although SAPO-34 is one of the most studied silicoaluminophosphate catalysts in the MTO process, there are other related materials that could act as acid catalysts in this process [32-41]. It is known that the catalytic performance is strongly dependent on the physicochemical properties of the catalyst employed [15, 35, 42-44], but also small

differences in the framework topology of the zeotypes may result in different catalytic behavior [45]. Since nowadays one of the main challenges in the research on the MTO process is directing the selectivity towards specific olefins depending on the industry demand, it is of great interest to elucidate the influence of the topology of the zeolitic material chosen as catalyst on the selectivity towards different olefinic hydrocarbons.

To this aim, we have synthesized four small-pore silicoaluminophosphate materials, SAPO-35, SAPO-56, STA-7 and SAPO-42, with related frameworks but some key differences in their topologies (Fig.1, Table 1) [17], and tested them as catalysts in the MTO process.

Figure 1. Models of the cages accessible through 8-ring windows in SAPO-56 (A), SAPO-35 (B), SAPO-42 (C) and STA-7 (D) frameworks (built from crystallographic information files collected in [17]) and CPK models of the highlighted 8-ring windows showing pore apertures (in Å) delimited by oxygen atoms.

Table 1. Pore structure and dimensions of the SAPO catalysts.

Sample	Framework code	Channel Dimensionality	8-Ring Dimensions (Å)	$d_{\max}^a$ (Å)
SAPO-35	LEV	2	3.6x4.8	7.10
SAPO-56	AFX	3	3.4x3.6	7.76
STA-7	SAV	3	3.8x3.8 ; 3.9x3.9	8.82
SAPO-42	LTA	3	4.1x4.1	11.05
SAPO-34	CHA	3	3.8x3.8	7.37

^a Maximum diameter of a sphere that can be included in the SAPO cages.

SAPO-35 (framework code **LEV**) is isostructural with the natural zeolite levyne, which is made up of levyne cages connected through six-rings and double six-rings. Every levyne cage is accessible through three 8R windows with dimensions of 3.6x4.8 Å. These windows are connected with the 8R openings of the nearest levyne cages generating a two-dimensional channel system in which cavities are interconnected only in the 110 plane. The maximum diameter of a sphere that can be hosted inside SAPO-35 cages is 7.10 Å. SAPO-56 (**AFX** framework type) contains double six-rings arranged to form a 3D pore system with two type of cages, a smaller gmelinite (*gme*) cavity and a larger *aft* cavity, with 8R openings with dimensions of 3.6x3.4 Å. The maximum diameter of a sphere that can be included in the *aft* cages is 7.76 Å, but it should be taken into account that, due to the elongated shape of these cages, a sphere is not the most realistic way to evaluate the internal volume. STA-7 (**SAV** type material) is also a 3D zeotype which structure consists of an arrangement of two distinct channel systems. One channel is composed of cages stacked along the c axis and linked via planar 8R (3.9 Å in free diameter). These cages are also connected through four elliptical 8R openings (3.8 Å in free diameter) to the second channel system, made up of smaller interconnecting spaces. The maximum diameter of a sphere that can be included in

STA-7 cages is 8.82 Å. SAPO-42 (**LTA** topology) possesses *lta* cages that can host a sphere of 11.05 Å in diameter and are accessible through six 8R openings of 4.1 Å in free diameter, forming a 3D pore system. Every *lta* cage is connected to eight sodalite cages that possess only 6R openings which small free diameter makes sodalite cages not accessible to molecules like nitrogen or methanol. Compared to the cavities of SAPO-34 [17], the reference MTO catalyst, those in SAPO-35 are smaller, while the ones in STA-7 and SAPO-42 are larger and those in SAPO-56 are not only larger but also more elongated. Regarding the pore openings, STA-7 has pores of a comparable size to the ones of SAPO-34 whereas the pores present in SAPO-56 are smaller and the ones in SAPO-42, larger. On the other hand, SAPO-35 has elongated windows with a long axis longer than the SAPO-34 window diameter and a narrower short axis [17].

The aim of this study is to relate the catalytic behavior of the selected SAPO materials, in terms of catalyst lifetime and selectivity towards different products, with the framework topology of each catalyst. It is known that controlling some key physicochemical properties as acidity, crystal size or textural properties can improve catalyst stability under reaction conditions and also modulate selectivity. Therefore, the synthesis conditions used were selected to obtain SAPO samples having physicochemical properties as similar as possible, trying to isolate the effect caused by the topology on the catalytic behavior of the SAPO samples.

2. Experimental

2.1. Synthesis of the catalysts

Crystalline SAPO materials with different topologies were prepared by hydrothermal synthesis. The composition of the gels and the experimental conditions of the synthesis (temperature and crystallization times) were adjusted in order to obtain pure SAPO

phases with the desired framework topologies and physicochemical properties as similar as possible. In particular, the compositions of the synthesis gels were selected according to our previous experience to obtain solids with similar Si to Al+P ratio. The selected conditions and gel compositions are collected in Table 2. In all the cases, samples were crystallized using teflon-lined stainless steel autoclaves with an internal capacity of 40 cm³, and the obtained solids were collected by centrifugation, washed with ethanol and water and dried at 338 K overnight. Prior to catalyst testing and characterization, the organic template and the water trapped within the micropores of the as-synthesized solids were removed by calcination at 823 K.

Table 2. Molar composition of gels and hydrothermal synthesis conditions used to prepare SAPO materials.

Sample	Gel composition	Temperature (K)	Time (h)
SAPO-35	1Al ₂ O ₃ : 1P ₂ O ₅ : 0.6SiO ₂ : 1.5HMI: 55H ₂ O	473	24
SAPO-56	0.8Al ₂ O ₃ : 1P ₂ O ₅ : 0.6SiO ₂ : 2TMHD: 40H ₂ O	473	96
STA-7	1Al ₂ O ₃ : 0.75P ₂ O ₅ : 0.4SiO ₂ : 0.25TEAOH: 0.125Cyclam: 40H ₂ O	463	48
SAPO-42	1Al ₂ O ₃ : 1P ₂ O ₅ : 0.6SiO ₂ : 0.066TMAOH: 1.74 DEA: 0.34HF: 92H ₂ O	423	168

2.1.1. SAPO-35

Silicoaluminophosphate SAPO-35 was prepared from a synthesis gel in which the reactants were combined in the proportions detailed in Table 2. According to the procedure followed [46-48], aluminum hydroxide hydrate (Sigma-Aldrich) was dispersed in deionized water (33% of the total weight of water required) in a beaker, and a 34 wt% aqueous solution of orthophosphoric acid (Sigma-Aldrich, 85%) was added

slowly to the suspension. The mixture was stirred for two hours before adding the fumed silica (Aerosil 200, Degussa) and the remaining amount of water. After around 30 minutes, the total amount of hexamethyleneimine (HMI, Sigma-Aldrich, 99%) required was added dropwise with vigorous stirring until getting a homogeneous gel.

2.1.2. SAPO-56

SAPO-56 was synthesized using a standard method [49]. N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHD, Sigma-Aldrich, 99%) was used as template. Orthophosphoric acid (Sigma-Aldrich, 85%), pseudoboehmite (PURAL SB-1, Sasol) and fumed silica (Aerosil 200, Degussa) were combined in the same order reported previously (water, acid, alumina, silica and, finally, amine) and stirred together 1.5 hours before submitting the obtained gel to hydrothermal crystallization.

2.1.3. STA-7

STA-7 was prepared following the synthesis procedure proposed by M. Castro et al. [50], adapting the experimental procedure in order to prepare a material with the desired properties. H₃PO₄ (Sigma-Aldrich, 85%), Al(OH)₃ (Sigma-Aldrich) and SiO₂ (Aerosil 200, Degussa) were chosen as sources for phosphorous, aluminum and silicon, respectively. 1,4,8,11-tetraazacyclotetradecane (cyclam, Sigma-Aldrich, 98%) and tetraethylammonium hydroxide (TEAOH, Sigma-Aldrich, 35% aqueous solution) were used as co-templates to obtain pure STA-7. The synthesis gel was prepared with the molar composition indicated in Table 2, combining the reactants in the following order: water, acid, aluminum hydroxide, silica, cyclam and TEAOH. Prior to crystallization, the obtained mixture was stirred for 1 hour to gain a homogeneous gel.

2.1.4. SAPO-42

The synthesis procedure to obtain SAPO-42 was adapted from that reported in ref. [51]. Tetramethylammonium hydroxide (TMAOH, Sigma-Aldrich, 25% aqueous solution) and diethanolamine (DEA, Alfa Products, 98%) were employed as co-templates. The precursor compounds were pseudoboehmite (PURAL SB-1, Sasol), fumed silica (Aerosil 200, Degussa) and orthophosphoric acid (Sigma-Aldrich, 85%). Fluoride ions were introduced as hydrofluoric acid (Sigma-Aldrich, 48%). In a first step, in two different beakers, mixtures A and B were prepared. Mixture A contained 50% of the total water, orthophosphoric acid, alumina and silica, mixed in this order. Mixture B was composed of the remaining 50% of water, TMAOH, DEA and HF. Both mixtures were stirred for one hour before mixture B was added dropwise over mixture A. The synthesis mixture was stirred for 2 more hours until the gel became homogenous. A rotating oven was used for the hydrothermal synthesis in order to obtain SAPO-42 with high crystallinity.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of as-synthesized and calcined samples were recorded with a PANalytical X'Pert Pro diffractometer using $\text{CuK}\alpha$ radiation with a nickel filter. Textural data (both pore volume and surface area) of fresh and partially deactivated catalysts were determined by nitrogen adsorption-desorption measurements using a Micromeritics ASAP 2010 apparatus. Prior to measurements, parent samples were degassed at 623 K under vacuum for at least 20 h. In the case of catalysts obtained from the quenching experiments (partially deactivated samples), the pretreatment was carried out at 473 K under vacuum for 4 h, to prevent removal of the hydrocarbons retained inside the crystals. Crystal size and morphology were analyzed by scanning

electron microscopy (SEM) using a Hitachi TM-1000 microscope operating at 15 kV. The total organic content of the partially deactivated samples was studied by thermogravimetric analysis (TGA) using a Perkin-Elmer TGA7 instrument. TGA analyses were carried out at a heating rate of 20 K/min from 303 to 1173 K, under air flow. Elemental analyses for Al, P and Si were done for calcined samples by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin-Elmer 3300DV spectrometer. ^{29}Si CP/MAS NMR spectra were recorded at room temperature using a Bruker AV 400-WB spectrometer operating at 79.5 MHz, with a 4 mm probe spinning at 10 kHz. A $\pi/2$ pulse of 3 μs , contact time of 6 μs and recycle delay of 5 s was used. The chemical shifts were referenced to tetramethylsilane (TMS). Ammonia temperature programmed desorption measurements (NH_3 -TPD) were performed using a Micromeritics Autochem II chemisorption analysis equipment. In a typical procedure, 100 mg of sample pellets (20-40 mesh) were pre-treated at 827 K for 1 h in helium flow (25 mL/min) and then cooled to the adsorption temperature (450 K). A gas mixture of 5.0 vol% NH_3 in He was then allowed to flow over the sample for 4 h at a rate of 15 mL/min. Afterwards a 25 mL/min helium flow was passed over the sample while maintaining the temperature at 450 K for 30 min to remove weakly adsorbed NH_3 , and finally the temperature was increased to 823 K at a rate of 10 K/min. Characterization of acid sites was carried out by Fourier-transform infrared (FTIR) spectroscopy of adsorbed acetonitrile. Spectra were registered in the mid-infrared region (400-4000 cm^{-1}) in the transmission mode at 4 cm^{-1} resolution using a Thermo Nicolet Nexus 670 spectrometer provided with a MCT detector. Samples were prepared as self-supporting wafers (thickness ca. 7.0 mg/cm^2) and treated under vacuum at 723 K for 2 h. The pre-treated sample wafers were cooled down to room temperature, kept in contact with a 14

mbar pulse of CD₃CN (Aldrich, 99.8% at. D) for 20 min and finally the IR cell was evacuated for 10 min at room temperature.

2.3. Catalytic testing

All the catalytic tests were performed at atmospheric pressure and 673 K in a fixed bed tubular quartz reactor with 6 mm inner diameter. The temperature probe was located in the lower part of the catalyst bed enclosed with a quartz sheath. Before each test, samples were pretreated *in situ* under oxygen flow at 823 K for one hour, in order to remove water and any trace of organic material adsorbed in the SAPO pores. Methanol was fed to the reactor by passing a He flow of 10 mL/min through a saturator at 293 K resulting in a methanol partial pressure of 130 mbar. The catalyst mass employed for each test was 50-300 mg (pellets of 250-420 µm in size), obtaining a WHSV in the range 0.35-2.05 h⁻¹.

The reactor effluent stream was analyzed by on-line GC analysis with an Agilent 6890N gas chromatograph with a FID detector and automatic sampling, using an Agilent HP-PLOT Q capillary column (15 m, 0.320 mm i.d. and film thickness of 20 µm).

2.4. Analysis of coked catalysts

Organic species trapped in the channels of spent catalysts were analyzed following a dissolution and extraction procedure. Typically, 15 mg of used catalyst were transferred to a Teflon vial and dissolved with 1 mL of hydrofluoric acid (15%). The organic molecules released were extracted from this solution with 1 mL of dichloromethane containing m-chlorotoluene (2.5 µL/L) as internal standard. The organic extract was analyzed using a GC-MS (Agilent 5975MS) equipped with a J&W DB-5ms column (60 m, 0.25 mm i.d. and film thickness of 0.25 µm). The individual compounds were

identified from their fragmentation patterns using the mass spectral library of the NIST98 database. A similar procedure was followed to analyze the volatile compounds retained inside SAPO-35 crystals. 15mg of deactivated catalyst were dissolved with 1 mL of hydrofluoric acid (15%) in a vial closed with a septum. Once dissolved the catalyst, the volatile compounds were collected with a syringe and directly injected in the GC-MS equipment for their characterization.

3. Results and discussion

3.1. Characterization of the catalysts

Powder XRD patterns of the four 8R SAPO materials prepared are shown in Fig. 2.

Figure 2. Powder XRD patterns (black lines) of the calcined SAPO materials and simulated patterns (grey lines) of the corresponding AFX, LEV, LTA and SAV framework types computed from structural data reported in [17].

These patterns are in good agreement with simulated patterns generated from structural data collected in [17] for framework types LTA (aluminosilicate, zeolite A), SAV (magnesium aluminophosphate, Mg-STA-7), AFX (aluminophosphate, AIPO-56) and LEV (aluminosilicate, zeolite levynite). The small shifts that can be observed in the diffraction peaks of the experimental patterns respect to their simulated counterparts, especially in the case of aluminosilicate reference materials, can be attributed to small differences in unit cell size, that can be caused by the different chemical composition of the framework. Indeed, the diffraction patterns of the synthesized samples closely match those previously reported for SAPO-42 [51] SAPO-56 [49] and SAPO-35 [48] materials, confirming that pure crystalline phases are obtained in the synthesis conditions shown in Table 2. In the case of STA-7, comparison with the XRD pattern reported in [50] suggests that this sample might contain a minor impurity phase.

Crystal size has been proven to be a key parameter that affects the catalytic performance of SAPO materials in the MTO process, as crystal size reduction down to the nanometer scale can lead to a marked delay of catalyst deactivation [42, 43]. Therefore, scanning electron microscopy has been used to determine crystal size and morphological features of the catalysts. SEM images (Fig. 3) show that SAPO-35 crystals exhibit the characteristic rhombohedral habit and both SAPO-42 and STA-7 samples possess cubic crystals, with sizes in the range of tenths of microns. On the other hand, SAPO-56 crystals appear as hexagonal plates with side ca. 20-30 μm long and ca. 2-5 μm thickness. Although the SAPO crystals show significant morphological differences, all catalysts possess relatively large crystals with a rather similar size. It is known from previous studies on other SAPO materials that decreasing crystal size from tenths to few μm does not cause a remarkable effect on the catalytic behavior of the material, and that at least one order of magnitude further crystal size reduction is required to boost the

diffusion of products, resulting in the enhancement of the catalyst life time [52]. It can therefore be considered that eventual differences in deactivation profiles among the catalysts will not be dominated by differences in crystal size.

Figure 3. SEM images of the calcined SAPO materials.

Textural properties of calcined SAPO materials were determined by nitrogen adsorption–desorption at 77 K. All the samples exhibit type I isotherms (according to the IUPAC classification) [53, 54], typical of microporous materials, with an additional nitrogen uptake at high relative pressure, which is present in all samples except SAPO-56 and is due to filling of interparticle spaces in the meso-/macropore size range (Fig. 4). From these isotherms, high micropore surface area and pore volume are calculated for all samples (Table 3), with only a small contribution of non-microporous (external) surface area, in agreement with the relatively large size of the crystals. The isotherm of SAPO-42, however, shows a high volume of nitrogen adsorbed at pressures close to

saturation, which can be attributed to adsorption into meso-/macropore spaces between particles. Sample SAPO-42 also shows lower surface area and micropore volume than the other three samples. The lower adsorption capacity of this material is caused by the inability of nitrogen to access the sodalite cages due to steric factors, as the free diameter of the 6R windows of sodalite cages (2.2 Å) is smaller than the kinetic diameter of nitrogen molecules (2.67 Å). Thus, only the micropore surface corresponding to *lta* cages can be determined when nitrogen is used as adsorbate.

Figure 4. N₂ adsorption-desorption isotherms of calcined SAPO samples. Solid symbols correspond to adsorption and empty symbols, to desorption.

Table 3. Textural properties of calcined SAPO materials.

Sample	Surface area (m ² /g)		Pore volume (cm ³ /g)	
	S _{BET}	S _{ext}	V _{micro}	V _{ext}
SAPO-35	527	21	0.22	0.05
SAPO-56	691	23	0.29	0.05
STA-7	587	29	0.24	0.08
SAPO-42	343	39	0.13	0.23

The chemical composition of calcined SAPO materials was determined by ICP-OES. As shown in Table 4, all samples possess similar content of Si, Al and P. It can be noticed that the composition of the solids is different from that of the corresponding synthesis gels and that it was necessary to use different composition of the synthesis gels for each SAPO structure in order to obtain solids with the same composition.

Table 4. Chemical composition of the SAPO materials, total acidity determined by NH₃-TPD and concentration of Lewis and Brønsted acid sites determined by FTIR of adsorbed CD₃CN.

Sample	Si/(Si+P+Al) ratio in the synthesis gel	Molar composition of the solid	Total acidity (mmol NH ₃ /g)	Lewis sites (mmol CD ₃ CN/g)	Brønsted sites (mmol CD ₃ CN/g)
SAPO-35	0.13	Si _{0.15} Al _{0.47} P _{0.38} O ₂	0.6	0.19	0.79
SAPO-56	0.16	Si _{0.15} Al _{0.51} P _{0.34} O ₂	0.8	0.44	0.92
STA-7	0.10	Si _{0.16} Al _{0.47} P _{0.37} O ₂	0.4	0.10	0.62
SAPO-42	0.13	Si _{0.15} Al _{0.49} P _{0.36} O ₂	0.3	0.01	0.03

Although the four samples possess similar silicon content, acid properties of SAPO materials depend not only on their silicon content but also on its distribution within the silicoaluminophosphate framework. The framework of microporous aluminophosphates is built up of Al and P atoms tetrahedrally coordinated to oxygen atoms, with AlO₄ and PO₄ tetrahedra linked to each other through the corner sharing of the four oxygen atoms in a strictly alternating arrangement. SAPO materials are obtained by isomorphous substitution of Al and P by Si. It is well known that incorporation of Si can follow different mechanisms, so it is possible to generate multiple silicon environments within the SAPO framework. When a silicon atom is incorporated in a phosphorous position (so-called substitution mechanism SM2), a Si(4Al) environment is created (a SiO₄ tetrahedron linked to four AlO₄ tetrahedra). This substitution of pentavalent P by

tetravalent Si generates one net negative charge per Si atom incorporated in the framework. If this negative charge is compensated by a proton, a Si-OH-Al bridging hydroxyl is formed that acts as Brønsted acid site. But Si can be also incorporated into the framework via substitution mechanism 3 (SM3), in which the incorporation of Si occurs by a simultaneous substitution of a pair of adjacent Al and P atoms by two Si atoms [55, 56]. As a trivalent Al and a pentavalent P are substituted by two tetravalent Si atoms, this substitution mechanism preserves the charge neutrality of the framework and, therefore, the incorporation of these Si atoms does not imply the creation of any Brønsted acid site. The actual incorporation of Si into the AlPO framework occurs either by mechanism SM2 alone or by a combination of mechanisms SM2 and SM3 in such a way that formation of the unstable Si-O-P bonds is prevented. Thus, the concentration of Brønsted acid sites in the SAPO material depends on the total Si content but also on the relative contribution of mechanisms SM2 and SM3. The combined SM2+SM3 mechanism leads to the formation of silicon-rich areas (so-called silicon islands) in which different silicon environments exist, namely Si(0Al), Si(1Al), Si(2Al) and Si(3Al), that is, every SiO₄ tetrahedron can be linked to n AlO₄ tetrahedra and 4-n SiO₄ tetrahedra (with n = 0-3). It has been proposed that the strength of the acid sites present in the border of Si islands is higher than that of the acid sites originated by isolated Si species (Si(4Al) sites) [57, 58]. Therefore, it can be concluded that, for a given Si content, the larger the contribution of mechanism SM3 respect to SM2, the lower the number of acid sites and the higher the average acid strength of the SAPO material.

²⁹Si CP/MAS NMR spectroscopy was used to identify the different silicon environments present in the calcined samples. The spectra (Fig. 5, left) can be interpreted as the result of the overlapping of various distinct resonances in the range

-85 to -110 ppm. These signals are attributed to the different Si(nAl) environments, as the ^{29}Si NMR signal exhibits an upfield shift that increases as the number of AlO_4 tetrahedra (n) linked to the silicon atom decreases and, accordingly, the number of SiO_4 neighboring tetrahedra, i.e. 4-n, increases.

Figure 5. ^{29}Si CP/MAS NMR spectra, shifted vertically for clarity (left) and ammonia TPD profiles (right) of the SAPO catalysts.

The spectrum of SAPO-56, displays a main signal centered at ca. -90 ppm, which is assigned to silicon atoms surrounded by four aluminum atoms in the second coordination sphere ($\text{Si}(4\text{Al})$ species). This result indicates that most of the Si atoms in this sample are isolated species. In the case of SAPO-35, there is also a main signal centered at the chemical shift assigned to $\text{Si}(4\text{Al})$ environment, but the spectrum shows some tailing at high field that indicates that there is also a small contribution of other signals corresponding to Si atoms linked to both SiO_4 and AlO_4 tetrahedra. On the other hand, the spectra of samples STA-7 and SAPO-42 show higher intensity in the -95 to -110 ppm region, indicating a large contribution of $\text{Si}(3\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(1\text{Al})$ and $\text{Si}(0\text{Al})$ species. These results evidence the presence of silicon islands and, therefore, higher

aggregation of silicon, in these later samples. As mentioned before, the Si incorporation mechanism might be dependent on the framework topology, and maybe it is not possible to force a similar silicon incorporation path for the different samples prepared, because of their cavity shape and the type of templates employed in each case as well as the experimental conditions required to obtain the desired topology controlling other properties as the size of the crystals or the textural properties.

Although the four SAPO samples possess similar silicon content, the NMR results reveal significant differences in Si distribution among them. It is therefore expected that they also exhibit different acidity, as a higher aggregation of Si also implies a higher contribution of the SM3 substitution mechanism, which does not lead to the creation of acid sites, and should result in lower acid sites concentration. NH₃-TPD analysis was used to determine the amount and relative strength of the acid sites. The total concentration of acid sites, determined as the area under the TPD plots (Fig. 5, right), is reported in Table 4. It can be found that total acidity decreases in the order SAPO-56 > SAPO-35 > STA-7 > SAPO-42. These results are in good qualitative agreement with ²⁹Si CP/MAS NMR results, which showed that the degree of Si aggregation increases in the same order as total acidity decreases. Besides, the ammonia desorption temperature can be related to the acid sites strength. The TPD profiles show for all samples a low temperature desorption band centered at ca. 525 K, while an additional desorption at higher temperature (above 600 K) is found for samples SAPO-56, SAPO-35 and STA-7 but is absent in the TPD profile of sample SAPO-42. These results would suggest that sample SAPO-42 possesses mainly one type of acid sites with low acidity, while samples SAPO-56, SAPO-35 and STA-7 possess a second type of acid sites with higher strength. This seems to disagree with the NMR results that showed that SAPO-42 possesses the highest proportion of Si atoms in the border of silicon islands, which are

expected to generate stronger Brønsted acid sites than isolated Si atoms. However, the high basic strength of ammonia might mask the differences in strength of acid sites associated to Si atoms in different environments, and, on the other hand, the TPD profiles might also include desorption of ammonia adsorbed on Lewis acid sites.

In order to gain deeper insight on the acidity of the SAPO samples, they were characterized by FTIR spectroscopy using acetonitrile as basic probe. FTIR spectra of degassed neat samples (Fig. 6 left, full lines) show weak bands at ca. 3743 and 3677 cm^{-1} , corresponding to terminal Si-OH and P-OH groups, respectively, and several strong bands in the 3640-3570 cm^{-1} wavenumber range, characteristic of the O-H stretching of Si-OH-Al bridging hydroxyl groups in SAPO materials. Samples STA-7 and SAPO-56 show two strong overlapping bands centered at ca. 3620-3625 and 3595 cm^{-1} . The spectrum of SAPO-35 shows these two bands slightly shifted to higher wavenumbers (3630 and 3605 cm^{-1}) and a third band at ca. 3580 cm^{-1} , which have been attributed to Si-OH-Al bridging groups in different framework locations [59]. It is remarkable that sample SAPO-42 show narrower and much weaker $\nu(\text{OH})$ bands (note that the spectrum has been multiplied by a factor of 5). This result suggests that SAPO-42 possesses a much lower concentration of bridging hydroxyl groups, in line with the higher aggregation of Si evidenced from its ^{29}Si NMR spectrum and the lower concentration of acid sites determined by NH_3 -TPD. Nevertheless, it cannot be ruled out that the extinction coefficient of these bands might be different among these SAPO samples.

Figure 6. Left: FTIR spectra of SAPO samples after pre-treatment (full lines) and after acetonitrile adsorption at room temperature (broken lines). Right: Difference FTIR spectra of adsorbed CD₃CN obtained by subtracting the spectrum recorded after pretreatment to the one recorded after adsorption of acetonitrile. a: SAPO-35, b: STA-7, c: SAPO-56, d: SAPO-42. Spectra have been normalized to a sample thickness of 7 mg/cm². Labels indicate the assignment of absorption bands to the antisymmetric and symmetric stretching of the methyl group of deuterated acetonitrile ($\nu_{as}(\text{CD}_3)$ and $\nu_s(\text{CD}_3)$, respectively) and the CN stretching of acetonitrile adsorbed on Lewis (L) and Brønsted (B) acid sites.

Upon adsorption of deuterated acetonitrile at room temperature, the bands in the 3640-3570 cm⁻¹ region were almost completely removed in samples SAPO-35, STA-7 and SAPO-56 (Fig. 6 left, broken lines). This depletion of hydroxyl bands is caused by the interaction of protons with the nitrogen lone pair of the CN group of the weakly basic acetonitrile, which evidences the acidic nature of these hydroxyls. In the case of sample

SAPO-42, adsorption of acetonitrile produced a decrease of only 25-30% of the intensity of the bands at 3630 and 3585 cm^{-1} , indicating that a large fraction of the bridging hydroxyls are not accessible to acetonitrile. Therefore, it can be concluded that part of the bridging hydroxyls are located inside the sodalite cages, which are inaccessible to acetonitrile as it cannot diffuse through their narrow 6R windows. Thus, in contrast to ammonia, which small kinetic diameter (2.6 Å) allows it to enter the sodalite cages and interact with all acid sites [60, 61], acetonitrile would probe only those acid sites accessible through 8R windows or larger pore apertures. This result is significant from the point of view of the evaluation of catalytic activity of these materials in the MTO reaction, as acetonitrile would allow to determine the actual content of acid sites that can be reached by methanol that, like acetonitrile, is unable to enter sodalite cages.

The adsorption of acetonitrile on acid sites gives rise also to the development of additional bands in the 2350-2100 cm^{-1} region, which can be observed as increased absorbance in the difference spectra (Fig. 6 right). Medium to strong IR bands corresponding to stretching of the CN group interacting with Lewis and Brønsted acid sites are found at ca. 2320 and 2290 cm^{-1} , respectively, and two weak bands appear at 2250 (shoulder) and 2112 cm^{-1} , assigned to stretching modes of the CD_3 group [62]. The asymmetric shape of the two $\nu(\text{CN})$ bands suggests that they are actually composed of several overlapping bands. As the adsorption of acetonitrile on acid sites produces a shift of its $\nu(\text{CN})$ band that depends on the acid strength [63], the spectra indicate that the samples possess acid sites, both Lewis and Brønsted, with different strengths. The concentration of acid sites titrated by acetonitrile (Table 4) was estimated from the integrated absorbance of the composite bands at ca. 2320 and 2290 cm^{-1} calculated using spectral deconvolution into Gaussian curves. The extinction coefficients were

taken as those determined by Wichterlová et al. for the CN stretch of acetonitrile linked to Brønsted and Lewis sites on ferrierite (2.05 and 3.6 cm/μmol, respectively) [62]. As shown in Table 4, the total amount of acid sites determined by adsorption of acetonitrile is around 50% higher than the value determined from NH₃-TPD in SAPO-35, SAPO-56 and STA-7. Even though this suggests that the extinction coefficients used are underestimated, data reported in Table 4 would be a reliable measurement to compare the relative concentration of acid sites among samples. These results show that SAPO-35 and SAPO-56 possess similar concentration of Brønsted sites, which is slightly higher than that of sample STA-7, and that all these samples contain also a significant proportion of Lewis sites, that reaches nearly one third of the total acid sites in the case of sample SAPO-56. For sample SAPO-42, the concentration of acid sites determined by acetonitrile is one order of magnitude smaller than that determined from NH₃-TPD, which highlights the fact that the vast majority of acid sites are not accessible to acetonitrile, as discussed above. As a consequence, the concentration of Brønsted sites determined by adsorption of acetonitrile is more than one order of magnitude smaller for sample SAPO-42 compared to the rest of the samples. Accordingly, the number of active sites actually available to convert methanol in the MTO reaction would be much smaller for sample SAPO-42 than for samples SAPO-35, SAPO-56 and STA-7.

3.2. Catalytic performance of SAPO materials with different topologies.

The catalytic performance of the different materials (SAPO-35, SAPO-56, STA-7 and SAPO-42) in the MTO reaction has been studied under the conditions detailed in the experimental section. Trying to understand the catalytic behavior of the materials, the retained organic molecules formed during the reaction have been analyzed at different times on stream (conversions), in order to have information about the reaction products and the retained molecules simultaneously. Moreover, aiming to adjust the obtained

data to a deactivation model, several tests were performed at different contact times. With this information, the influence of the dimensions of cages and channels on the type of intermediates formed during the reaction and their influence on the catalyst deactivation has been studied. All the selected SAPO zeotypes have similar 8R pore entrances that suppress the transfer of branched aliphatic and heavy aromatic hydrocarbons, thus increasing the selectivity towards light olefins even though large aromatic molecules are expected to be formed inside the cages of the SAPO catalyst in all the cases. The differences in size and shape of the cages may cause differences in the catalytic performance, deactivation rates and selectivities, since the dimension of the cage will determine the amount and kind of PolyMethylBenzenes (PolyMB) present as active intermediates and the PolyAromatic hydrocarbons (PAH) that can be further formed. The restriction caused by the volume of the cages may influence the formation of PolyMB and thus the selectivity of the process, but it can also influence the kind and amount of these PAH and, therefore, the deactivation of the SAPO samples.

3.2.1. Catalyst stability.

A first series of catalytic tests at different WHSV were carried out trying to adjust the experimental data obtained to a deactivation kinetic model [18] (Fig. 7). As expected, longer life times were obtained in all cases when the tests were performed with the lowest space velocity. Even though the tests were carried out with a quite low space velocity, the rapid deactivation suffered by the different samples under these conditions, provoked that the experimental plots (conversion vs. time on stream) presented a very low resolution. Considering the lowest space velocity (with the highest resolution over time) it can be observed that, in the case of SAPO-35, SAPO-56 and STA-7, there is an initial period of complete conversion after which a rapid deactivation occurs leading to conversion close to 0% (Fig.7). However, SAPO-42 sample plot is radically different.

In this case, there is not a first period with 100% of conversion, but a progressive loss of activity that ends in a nearly constant conversion rate of around 10%. If the initial conversion was 100%, then the deactivation pathway of SAPO-42 could be associated with the one in which the coke molecules are formed from products instead of from reactants [22]. However, the activity of the catalyst is too low to reach full initial conversion.

Figure 7. Conversion of oxygenates as a function of time on stream for the catalysts with the four different topologies at four different WHSV. Comparison of the life time and the deactivation. WSHV is indicated for each test.

From a direct comparison of the conversion vs. time on stream plots for the four samples tested it is easily observed that sample STA-7 has longer time life than SAPO-35 and SAPO-56. This different behavior could be related with their structural differences. According to the main topological differences of the four catalysts tested, it can be postulated that the rapid deactivation of SAPO-35 is likely to be caused by the fact that it has channels only in two directions, thus hindering the diffusion of the reaction products and making the framework much easier to be blocked by bulky molecules than SAPO-56 or STA-7. Surprisingly, from the experiments carried out at different space velocities, it is possible to notice that SAPO-56 is even less active as catalyst than SAPO-35. SAPO-56, with **AFX** structure, has the narrowest channels among the selected topologies, and also the largest cages (Fig.1). *Aft* cages present in SAPO-56 material are big enough to host very large molecules inside. The same occurs in SAPO-42 and STA-7 materials, but the difficulty of the products to diffuse through the narrow channels of SAPO-56 (which causes that they stay retained inside the catalyst evolving to heavier compounds) provokes that **AFX** framework suffers such an extremely rapid deactivation under reaction conditions. STA-7 catalyst, with slightly smaller cages compared to those in **AFX** framework but wider channels, shows the longest life time among the catalysts tested in this work. It can be proposed that the diffusion of products is easier in this material and, thus, the formation of bulky molecules in the cavities is less favored than in SAPO-56. This is in good agreement with previous studies in which the faster deactivation is correlated with a higher available space to form large aromatic molecules inside the catalyst structure [64]. At long contact times, the SAPO-42 curve is different from the other materials, so its stability is difficult to be compared based on the same parameters. As reported previously for various 10R-zeolites [65], methanol seems to be the main source for the

formation of the catalyst deactivating molecules in silicoalumophosphates with **AFX**, **LEV** and **SAV** topologies considering the shape of the deactivation curve. In the case of SAPO-42, the catalyst is clearly less active than the others. Tested at the same experimental conditions, it does not reach full initial conversion, so it is complicated to associate its behavior to a deactivation model. Considering the accessible amount of acid sites that this material has (Table 4), the lower activity of SAPO-42 in the reaction conditions can be associated to the low density of Brønsted sites, that are not enough to convert all the methanol feed into products. Actually, the turnover number calculations indicate that each center in SAPO-42 converts notably more methanol than the centers in the other materials (Table 5).

Table 5. Methanol cumulative conversion capacity* of the catalysts for the different WHSV tested and Turnover number (TON) calculated at 0.35 h⁻¹ WHSV.

Sample	WHSV (h ⁻¹)				TON**
	2.05	1.04	0.51	0.35	
SAPO-35	-	-	-	0.35	0.4
SAPO-56	-	-	-	0.32	0.3
STA-7	1.62	1.47	1.54	2.31	3.7
SAPO-42	0.54	0.55	0.66	1.30	43.3

*Conversion capacity is defined as the amount of methanol (grams) converted into products per gram of catalyst until complete deactivation. The conversion capacity of SAPO-42 at WHSV=0.35h⁻¹ is calculated from 100% to 10% of conversion.

**Turnover number considered as grams of methanol converted per mmol of accessible Brønsted acid sites.

Initially, these findings are not just connected to the topology, but also to the acidic properties. However, considering that all the materials were prepared aiming to have a comparable Si/Al ratio in the solid, it is interesting to see how the topological features are also playing a role in the formation of the acid centers of the SAPO materials, which

also has a clear effect on their catalytic performance in the MTO conversion. As it was described in Section 3.1, the acidic properties of each catalyst are strongly influenced by the shape and size of their cavities and the structure of the organic structure directing agent used in each case. Topological and acidic properties are, then, connected.

Considering the differences found in the shape of the deactivation curve, the catalysts can be studied more properly using the total methanol conversion capacity, that can be defined as the total weight of methanol converted to products per gram of catalyst until complete deactivation. Data of conversion capacities are collected in Table 5.

Conversion capacity of SAPO-35 and SAPO-56 samples can be only calculated accurately for the test carried out with at lowest space velocity because it is not possible to integrate the area under the conversion curves obtained with higher space velocities due to the small temporal resolution of the analysis. For STA-7 or SAPO-42, the conversion capacity increases as the space velocity decreases. The best result is obtained with STA-7 at $WHSV = 0.35 \text{ h}^{-1}$, which produces 2.31 grams of methanol per gram of catalyst. SAPO-35 and SAPO-56 render the lowest conversion capacities at $WHSV = 0.35 \text{ h}^{-1}$, whereas SAPO-42 presents intermediate values even though it has lower initial activity.

According to the model proposed by Janssens et al. [18], deactivation is directly proportional to the conversion of methanol. Considering the autocatalytic reaction, the time to 50% of conversion should be proportional to the contact time and this is so for STA-7 and SAPO-42 as it can be observed in Figure 8. In Janssens model it is considered that the slope of the linear fit describes the deactivation. The deactivation constant (a) can be calculated from the slope of linear plot, thus resulting in $a = 15.15$ for STA-7 and $a = 52.63$ for SAPO-42. The difference in the deactivation constant reflects the higher stability of STA-7. Moreover, this finding is in a good agreement

with the conversion capacity calculations (Table 5), confirming the faster deactivation of SAPO-42 in comparison with STA-7. As we pointed out before, this can be explained in terms of the effect that the topology has in the acidic properties of the materials. The diffusion in SAPO-42 is not hindered by the narrow diameter of the pores, as it happens in SAPO-56, but in the LTA topology the number of accessible centers is lower.

Figure 8: Measured catalysts lifetime at 50% of conversion vs contact time (W/F) for STA-7 and SAPO-42 (Correlation coefficient R for the linear fit is: R= 0.971 for STA-7 and R=0.999 for SAPO-42).

3.2.2. Product Selectivity.

The lowest space velocity (0.35 h^{-1}) was chosen to compare the selectivity to different products obtained with each catalyst, as well as to analyze the evolution with time on stream of the amount and type of the trapped organic species – referred as coke.

In all the cases the main effluent products of the reaction are short chain olefins, in the range C2-C4, as it is usual in 8R SAPO catalysts [66]. Over SAPO-35, SAPO-56 and STA-7, the main reaction products are ethylene and propylene, whereas C4 olefins are

the main reaction products over SAPO-42, displaying this catalyst as well a high selectivity to C6 hydrocarbons (Table 6). It has been previously reported that the selectivity to ethylene is higher for catalysts with smaller cages [67]. According to our results, the dimensions of the pore openings are also a key parameter controlling the product distribution. Even though it is also true in our case that the highest selectivity to ethylene is reached with the catalyst containing smallest cages (SAPO-35), SAPO-56, with large *afu* cages, also catalyzes the formation of an ethylene rich hydrocarbon mixture. On the other hand, looking at the production of C4 olefins, the selectivity obtained with SAPO-42, which has both large cages and windows, is clearly higher compared with that obtained using SAPO-56 as catalyst, being the windows of SAPO-56 rather smaller. The selectivity of C4 olefins is rather high when STA-7 is used as catalyst (19.3%), and not higher than 15% at any conversion level over SAPO-35. In this sense, it can be proposed that the production of butenes is favored when the material presents wider pores and so the selectivity decreases in the sequence SAPO-42>STA-7>SAPO-35>SAPO-56.

Table 6. Integral selectivities of the different effluent products obtained in the MTO reaction tests carried out at WHSV of 0.35 h⁻¹.

Sample	C2=	C3=	C4	CH ₄	C2	C3	C4	C5	C6	Aromatics	C3=/C2=	C4
			olefins				parafins					olef./C2=
SAPO-35	29.6	40.8	11.0	5.2	1.0	2.5	0.2	5.6	4.0	0.0	1.4	0.4
SAPO-56	28.0	30.4	13.7	3.8	1.7	19.9	0.2	1.4	1.0	0.0	1.1	0.5
STA-7	23.4	33.8	19.3	2.7	0.9	7.1	0.6	9.6	2.6	0.0	1.4	0.8
SAPO-42	9.1	22.3	26.8	3.2	0.4	1.0	5.5	13.2	16.6	2.0	2.4	2.9

Integral selectivities have been calculated as the cumulated yield of a given product over the whole reaction time referred to the total yield of all products detected

Selectivities to the different type of products detected in the effluent stream as a function of time-on-stream are plotted in Fig. 9 for tests carried out at WHSV = 0.35 h⁻¹.

698

699 **Figure 9:** Selectivity to products in the MTO reaction as a function of time-on-stream.

700 Test conditions: $T = 673\text{K}$, $\text{WHSV} = 0.35 \text{ h}^{-1}$.

Selectivities changed with time on stream for SAPO-35, SAPO-56 and STA-7, whereas SAPO-42 displayed less conversion-dependent selectivities (Fig. 9). In the first three cases, the selectivity to methane, a product associated with the formation of aromatics and the deactivation of the catalyst [7], increases with time on stream. Also, it can be observed for the three catalysts that the production of ethylene is favored at low conversion rates. This observation has been reported before [68-70], and could be ascribed to the growing blockage of the pores in the materials at low conversion rates, hindering the diffusion of the heavier reaction products and enhancing the release of less bulky hydrocarbons, as ethylene.

Specific changes in product selectivities on SAPO-35 with time on stream are also noticeable. During the initial stage of the reaction, the selectivity curve of C5 compounds follows the opposite trend to that found for ethylene and propylene, so it can be postulated that olefins in this case are formed by cracking C5 compounds at high conversion levels [71]. This observation is quite clear at short reaction times, but after 30 minutes on stream the production of ethylene, propylene and C5 hydrocarbons seems to be independent (Fig.9).

The narrow 8R pores, prevent the production of aromatics keeping their selectivity low in all the cases. Nonetheless, propane is a secondary product formed by the condensation of propylene to form aromatics, so it can be used as an indicator of the formation of such molecules inside the SAPO catalysts. On SAPO-56, the selectivity towards propane is surprisingly high at short reaction time (Fig.9). As mentioned before, the large *aft* cages present in **AFX** framework are able to host really bulky molecules. The combination of large and long *aft* cages, that allow the formation of large aromatic molecules, and the narrow pores, that hinder the diffusion of reaction products, apparently leads the rapid formation of aromatics, thus increasing the

selectivity to propane. In the case of sample STA-7, due to the smaller cages and wider channels present in the **SAV** structure compared to those in **AFX**, the formation of aromatics is not so high and thus the selectivity to propane is lower. Small LEV cages in SAPO-35 prevent the formation of bulky aromatics and, thus, the selectivity to propane is lower in this case. Finally, looking at the product distribution obtained using SAPO-42 as catalyst, it is surprising to find a negligible selectivity to propane, considering the large cages in this material, comparable to those in SAPO-56 or STA-7. A plausible explanation to this lies in the high selectivity that this materials displays to C4 parafins. Taking into account the highest concentration of C4 olefins, the aromatic molecules trapped inside the catalyst might be formed from C4 olefins rather than from propylene in this case.

Another remarkable result shown by SAPO-42 is the considerable amount of heavier compounds (C5-C6 hydrocarbons) formed, which production remains quite stable with time on stream, as well as the total amount of short chain olefins (C2-C4). Additionally, after the first 200 min of reaction, butenes became the main reaction products over SAPO-42 instead of ethylene or propylene, in contrast to the behavior shown by SAPO-35, SAPO-56 and STA-7. These results could be attributed to the wider channels of SAPO-42 or might be also caused by a higher ratio of external acid sites, considering the higher external surface area of this material (Table 3).

3.2.3. Characterization of the retained species.

The aromatic and branched bulky molecules formed in the cavities of the silicoaluminophosphates cannot diffuse out of the cavities and are trapped inside, resulting in a fast coke formation. After testing, different colours are observed along the catalyst bed, indicating, as in previous work over ZSM-5 and other various zeolites, that

the amount of hydrocarbons generated along the catalyst bed was not homogeneous [23, 65, 72]. It was generally observed for all the catalysts studied that, at conversion close to 100%, the top layer displayed a darker color compared to the bottom layers that were light gray with the exception of SAPO-56 sample in which the bottom part of the catalyst bed was brown. After longer time on stream all the catalyst bed turned dark enough not to be able to distinguish differences in colours along the bed.

The analyses of the deactivated catalysts have been carried out on representative samples of solid taken after thoroughly mixing the catalyst bed obtained at selected reaction times. Some series of MTO reactions were carried out on each catalyst for different reaction times. The recovered solids were analyzed by TGA and N₂ adsorption. It has been previously suggested that deactivation in cage-like SAPO materials is more strongly dependent on the extensive build-up of PAH within the crystals than to the formation of external coke. Therefore, a part of the spent catalysts were acid digested, as explained in the experimental section, and the organic phase extracted from these partially deactivated materials was analyzed by GC-MS, in order to identify the organic compounds trapped inside the catalysts pores.

The GC-MS analyses of the different samples have been presented in Figure 10 detailing, for each case, the identification of the most relevant molecules.

It has been previously reported that the materials trapped in the catalysts are different depending on the size and shape of the size and shape of the cavities [41]. In our case, larger cages (that provide an empty space) along with narrow pores (than hinder the diffusion of reaction products) allow the fast formation polycyclic aromatics. This is only the case of large-cage SAPO-56 catalyst, in which the more intense and abundant peaks in the chromatograms are those corresponding to PAH compounds (Fig. 10).

Figure 10: GC-MS chromatograms of gradually deactivated SAPO catalysts showing the evolution of retained species with increasing reaction time. The peak corresponding to the internal standard m-chlorotoluene is marked with an asterisk.

The chromatograms show the presence of molecules formed by up to five aromatic rings even at very short reaction times. These bulky molecules detected in the GC-MS analysis can be trapped within the catalyst pores according to Monte Carlo simulations that demonstrate that the *aft* cages are large enough to host these species (Fig. 11). Unlike what occurred in the case of SAPO-56, the amount of inactive PAH molecules formed in STA-7 and SAPO-42 increases gradually with reaction time. Although large cages in STA-7 and SAPO-42 also allow the growth of large aromatic molecules, as in SAPO-56, their wider channels facilitate the diffusion of reaction products, leading to a slower formation of PAH compounds. In the chromatograms of STA-7, many different

molecules are found to be trapped in the material during the MTO reaction. Substantial amounts of PolyMB with 1 to 6 methyl groups that can be detected at any value of conversion; but just small amount of PAH can be detected at short reaction times, being their formation progressive. After methanol breakthrough, the distribution of the complex coke species does not changes significantly with a higher degree of deactivation. Monte Carlo calculations were also employed to demonstrate that the largest molecules detected in the GC-MS analyses can be hosted in STA-7 cages (Fig. 11).

Figure 11: Models of the bulkiest molecules identified by GC-MS analysis of organic species retained in spent catalysts SAPO-56 (top) and STA-7 (bottom) showing that they can fit inside the cages of these zeotypes.

The analyses of sample SAPO-35 confirms the important effect of the confinement, restricting the smaller cages the formation of heavy aromatics. In the chromatographs, a

substantial amount of methylated benzenes, containing from one to three methyl groups is detected. At the longest reaction times, there were also small peaks of naphthalene and methylnaphthalene (Fig. 10). However the deactivation of the catalyst is too rapid to be caused just by the small molecules found in the GC-MS analyses. As it could be possible that other bulky but more volatile molecules were responsible of the blockage of SAPO-35 pores, GC-MS analysis of the volatile fraction desorbed from the deactivated catalyst was carried out (Fig. 12).

Figure 12: GC-MS chromatograms of the volatile retained organic molecules in deactivated SAPO-35.

As it can be observed, in this analysis a large amount of branched alkanes were found in the deactivated SAPO-35. The small levyn cages provide a space constraint for growth of coke molecules, but the low number of 8-member ring openings in each cage (3 windows per cage) as well as the relatively poor connectivity of the pore structure of the material can facilitate the blockage by small branched molecules such as those detected in the CG-MS analysis.

The fast formation of heavy aromatics is related with a faster deactivation. In this sense, even though SAPO-56 has a three directional channel system, the deactivation is as rapid as in SAPO-35. As explained before, the presence of large cages combined with the small size of cage windows can be proposed as the main reason for this quick deactivation of SAPO-56. The limited diffusion could facilitate the rapid evolution of hydrocarbons to large molecules. Moreover, due to the large cages in SAPO-56, there is enough space to host large molecules, thus providing coke since short reaction times. This is in accordance with the observed selectivity towards propane at short reaction times, and can be attributed, as mentioned before, to the topology of the material.

Quantification of coke at different reaction times was carried out by TGA, by measuring the total amount of retained molecules that can be removed by combustion. Changes in the adsorption capacity due to the build-up of the retained organics pool were evaluated by N₂ adsorption-desorption measurements. Figure 13 shows the coke content in the gradually deactivated catalyst calculated from the mass losses detected by TGA and also changes in the micropore surface area calculated from the N₂ isotherms by using the t-plot method.

In all cases, a clear trend in the textural properties (micropore surface area) from fresh to completely deactivated catalysts can be observed. In general, the micropore surface area decreases when the time on stream increases due to the blockage of the channels of the SAPO materials caused by the deposition of large organic molecules. Specifically, this decrease is especially sharp in the case of SAPO-56 (Fig. 13), although it is necessary to point out that the total amount of organic compounds retained stabilizes at a relatively low value, around 4 mg per 100 mg of catalyst. It is commonly accepted that the amount of retained organic material increases with the deactivation of the catalyst. The total amount of coke in SAPO-35 is also rather low. As it was previously

845 mentioned, the organic compounds trapped inside lewyne cages are not heavy aromatics,
846 but light branched molecules bulky enough to block the framework of SAPO-35.

847

848 **Figure 13.** Quantification of the mass of retained organic molecules and measured
849 variations in the micropore surface area of gradually deactivated catalysts.

850

851 However, in the case of SAPO-56 no increase in the organic weight was detected after
852 30 minutes on stream. This is in the same line with the results reported by Bhawe and
853 coworkers [67], and could mean that a considerable amount of coke must be formed
854 during the first stages of reaction, as demonstrated by GC-MS and also by the high
855 selectivity to propane at short reaction times. The small amount of coke detected by
856 TGA suggests that the catalyst is not totally filled with organic molecules, as this would
857 imply that the registered weight loss were much higher. It is plausible that coke

molecules are formed mainly at the most external cages of the material, as its accumulation might cause the blocking of the access to the inner part of the crystals (in agreement with the measured sharp decrease in the micropore surface area accessible to nitrogen), thus generating a rapid deactivation that would effectively hinder the reaction in the inner part of the crystals, and hence generating a low mass of trapped hydrocarbons. Again, we can attribute this behavior to a combination of the size and shape of pores and cages, because for STA-7, which has also relatively large cages but wider channels, the micropore surface area of the sample is simultaneously reduced as the coke content increases when the time on stream increases (decreasing conversion). The total organic content in the completely deactivated sample is noticeably higher than in SAPO-56 and, in general, also higher than in all the other catalysts studied in our contribution. This suggests that the cages in STA-7 have the adequate size and shape to low the intrinsic energy barrier for the reaction to happen, as it has been calculated for SAPO-34 [73]. On the other hand, it can be postulated that the topology of STA-7 facilitates the diffusion, so the inner part of the crystals would also be active in the reaction and, therefore, it would also be filled with coke in the severely deactivated samples. The comparison between SAPO-56, SAPO-35 and STA-7 with SAPO-42, that also has large cavities, is hampered because nitrogen (as well as methanol) cannot enter the sodalite cages, resulting in a lower micropore surface area of the fresh SAPO-42 sample. This implies that the catalyst surface area per unit mass of catalyst initially available for reaction is also lower for SAPO-42. Nevertheless, after deactivation, SAPO-42 still retains a significant part (around one third) of its micropore surface accessible to nitrogen. It has been previously suggested that the deactivation of SAPO-42 sample can be attributed to reaction products rather than reactants. From Figure 13 it can be observed that there is a first increase in the coke formation up to 3.5 mg per 100

mg of catalyst during the first 200 minutes on stream, followed by a plateau in which the mass of retained organic molecules shows a very small increase. This profile suggests that the heavy aromatic molecules found in the gradually deactivated samples (Fig. 10) are not formed by the incorporation of new methanol molecules, which would increase the mass of organic species retained as it in the case of STA-7, but by reaction between these trapped products.

Other remarkable finding connected is the evolution of the micropore volume in the gradually deactivated SAPO-35 samples. As mentioned before, the formation of coke in SAPO-35 is rather low, but the rapid deactivation of this catalyst is reflected in the meaningful reduction of the micropore surface area after 30 minutes on stream. Even though the catalyst is totally deactivated after 70 minutes on stream, nitrogen adsorption measurements indicate that there is still a significant fraction of accessible micropores, so maybe the deactivation in this case is not just related with the blockage but also to the poisoning of the acid sites.

3.2.4. Catalytic performance in comparison with SAPO-34.

As it was previously mentioned, direct comparisons of stability, deactivation and products distribution of SAPO catalysts with different topologies can be complicated due to differences in physicochemical properties. Many previous studies reported that SAPO-34 performance in the MTO process strongly depends on the acidity, the size of the crystals and the textural properties of the samples. Therefore, a sample of SAPO-34 with physicochemical properties as similar as possible to the other four catalysts tested in this work was selected for a comparison of the stability and selectivity to C2-C4 products (sample labelled S-4 in reference [15]). A comparative plot of the catalytic activity of all the samples is presented in Figure 14.

Figure 14. Conversion as a function of time on stream over SAPO-35, SAPO-56, STA-7, SAPO-42 and SAPO-34 in the same experimental conditions: $T = 673\text{K}$, $\text{WHSV} = 0.35\text{ h}^{-1}$.

Although significant differences in the catalytic performance of the selected materials have been described in the previous sections, regarding their stability, catalysts can be ranked in three groups. On one hand, SAPO-35 and SAPO-56 deactivate very quickly after short reaction time. A second type of behavior is found for SAPO-34 and STA-7, which maintain higher rates of conversion for longer time on stream before showing a fast deactivation. Finally, the deactivation profile of SAPO-42 is different from the rest, showing a conversion decay with lower slope than SAPO-34 and STA-7, but with an initial activity clearly lower than that of the other materials.

Comparing the selectivities to the different light olefins obtained at full methanol conversion (Fig. 15), it can be easily noticed that the formation of bulkier molecules is favored in materials with wider pores. Thereby, the selectivity towards C4 olefins increases in the catalysts tested as the diameter of the 8R windows increases. It should

be remarked that our results show that STA-7 is a promising catalyst and, after an optimization of the physicochemical properties, could be a MTO catalyst as stable as the optimized SAPO-34, but with higher selectivity to propylene and butenes.

Figure 15. Integral selectivity to C2-C4 olefins in MTO process on SAPO-35, SAPO-56, STA-7, SAPO-42 and SAPO-34, in the same experimental conditions: $T = 673\text{K}$, $\text{WHSV} = 0.35\text{ h}^{-1}$.

4. Conclusions

The catalytic performance and deactivation of four different 8R silicoaluminophosphate materials have been studied for the MTO reaction at 673K. The effluent reaction products and the retained organic compounds were analyzed along time on stream. Noticeable differences in the catalytic behavior have been detected among the catalysts, depending on dimensions of the SAPO cages and size of 8R windows. All the catalysts displayed high selectivity to short chain olefins under reaction conditions, but those with wider pores (STA-7 and SAPO-42) showed higher selectivity to heavier

compounds as butenes or C5 and C6 hydrocarbons, which is attributed to the enhanced diffusion of these compounds.

Bulky aromatics were not found inside SAPO-35 structure. It has been found that branched alkanes were able to block the **LEV** framework, thus causing the deactivation of the material. Large cages of SAPO-56 allow the formation of heavy molecules inside the catalyst. On the other hand, narrow pores hinder the diffusion of reaction products facilitating their evolution to larger molecules, resulting in a rapid formation of heavy polyaromatic hydrocarbons in SAPO-56 cages and the subsequent release of propane. SAPO-42 is deactivated by products instead of by the growing of trapped compounds by incorporation of methanol molecules, so the deactivation curve is different from the typical profile observed in SAPO-34, and the product distribution is rather stable with the deactivation of the catalyst. Both polymethylbenzenes and polyaromatic hydrocarbons were found inside the SAPO-42 cages. Considering the high selectivity to hydrocarbons in the range C5-C6 displayed by SAPO-42, it does not appear as an interesting catalyst for MTO process.

Wider pores and medium-sized cages of STA-7 facilitate the diffusion of products delaying the deactivation of the catalyst and favoring the formation of butenes.

In summary, it is demonstrated that size and shape of both cavities and 8R windows influence the stability but also quite strongly the selectivity of SAPO catalysts in the MTO process.

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