

THE SELECTIVITY CHANGES IN 1-HEXENE ISOMERIZATION AND ITS RELATION TO ACID PROPERTIES OF Pd/SAPO-11, SAPO-11, HZSM-5, AND H-MORDENITE CATALYSTS

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Abstract—The activity and selectivity patterns for 1-hexene isomerization have been compared in the temperature range of 150-450°C for four different kinds of acidic zeolites (H-mordenite, HZSM-5, SAPO-11 and Pd/SAPO-11) differing both in acid properties and geometric structure. At lower reaction temperatures (150-175°C) the predominant reaction pathway was double bond shift (DBS) and was not influenced by the type of catalyst. At higher temperatures significant shifts in selectivity were observed from DBS to cracking (C) or skeletal rearrangement (SR) depending on the type of catalyst.

Temperature programmed desorption (TPD) patterns of chemisorbed NH_3 were also determined. Three different peaks were found for the most of TPD patterns. The first peak might be associated with Lewis acid-site, and the other two peaks at higher temperatures might be associated with Brønsted acid-sites. It was found that significant loss of strong Brønsted acidity upon Pd loading on SAPO-11. A selectivity correlation at 350°C showed strong dependence of DBS and cracking on total acidity. The reaction seems well suited for investigation of the interrelation between pore structure and surface acidity in terms of these selectivity factors.

INTRODUCTION

Olefin isomerization, specially a selective shift of double bonds in olefins, with moderately acidic catalysts has been the main route to the synthesis of β and γ isomers, which are used as starting materials in synthesis of alcohols, aldehydes, ketones and acids [1,2]. Therefore, considerable amount of research interests have been placed on the reaction itself as well as on the effective acidic and basic catalyst: the isomerization of 1-butene, 1-pentene, and 1-hexene have been investigated on silicagel dosed with $\text{Al}(\text{NO}_3)_3$ [3], alumina [4], silica-alumina and zeolites [5,6], and recently on HZSM-5 [7]. So far, the main emphasis of studies are placed on the double bond shift (DBS) to trans/cis-2-enes, and trans/cis-3-enes at moderate temperature range (below 200-250°C) [8,9].

Less attention has been given to skeletal rearrangement (SR) and cracking/polymerization (C + P) selectivities at higher reaction temperatures (200-450°C). It is not well understood, and has not been reported at all on silico-aluminophosphate molecular sieves (specially, SAPO-11) as a 1-hexene isomerization catalyst at higher temperatures, focusing on the inter-

change among DBS, SR and (C + P) selectivities.

The main objective of present study is to establish the activity behaviors of Pd loaded and unloaded SAPO-11, and to compare such results with corresponding behaviors of HZSM-5 and H-mordenite. The families of phosphorous-containing zeolites commonly known as ALPO and SAPO were reported several years ago [10]. These materials are microporous and can exhibit pore structures that range from those similar to Y-zeolite (interconnected cage), to mordenite (single parallel pores), to ZSM-5 (two interconnected networks), however the phosphorous content significantly modifies the acidity of the zeolite [11,12]. The ideal ALPO-n consists of tetrahedra of oxygen surrounding aluminum and phosphorous such that $\text{Al/P} = 1$ [8], thus the framework is neutral. To create ion exchange capacity a portion of the Al and/or P is substituted [9]; in the case of SAPO-n this substitution is by Si either for phosphorous or an aluminophosphate pair [10]. Depending upon which substitution mechanism prevails, the structure of SAPO-n will vary; for example for $\text{Si} + \text{P} = \text{Al}$ the resultant material has the structure of faujasite (SAPO-37), while SAPO-11 contains one-dimensional channels of elliptical cross-section of char-

acteristic dimension ~ 0.6 nm. In principle, any of the SAPO-n can be converted to the corresponding acid form and utilized as solid acid catalysts [9-11]. From an overall point of view, then, the SAPO-n series could have catalytic applications as a medium acidity material with possible advantages to be obtained from the pore structure and with an acidity that perhaps can be adjusted in level over a relatively wide range. Applications of this sort have been reported for para-xylene production and for methanol conversion to olefins [12-16]. In the former case incorporation of P into ZSM-5 resulted in an increase in strength of acid sites (probably Lewis sites) that leads to increase in para selectivity [12, 14].

The possible modification of acidic properties leads to the second major objective here which is to examine the types of surface acidity of SAPO-11 (using TPD of ammonia as a probe) in comparison with corresponding properties of HZSM-5 and H-mordenite, and in view of the relative activities for 1-hexene isomerization.

EXPERIMENTAL

1. Catalysts

A commercial SAPO-11 was employed [17]; the empirical composition of this is $(\text{Si}_{0.06}\text{Al}_{0.49}\text{P}_{0.45})\text{O}_2$, with Si/Al about 0.12, and the structure is equivalent to that of ALPO-11 with elliptical, one-dimensional channels of ca. 0.6×0.4 nm nominal diameter and volume of $0.18 \text{ cm}^3/\text{g}$. The HZSM-5 employed [17] has a Si/Al molar ratio of 38, with Na/Al of 0.045 (0.08 wt% Na). H-mordenite employed was Norton 900H.

For preparation of the Pd/SAPO-11 the acid form was generated in flowing O_2 , 600°C , 1h and then impregnated with aqueous $[\text{Pd}(\text{NH}_3)_4(\text{NO}_2)_2]$ following method 2 of [13]. After impregnation the material was dried at 125°C overnight and calcined at 550°C , 6 h, then stored in air. The loading of Pd was 2.0 ± 0.1 wt%.

2. Activity measurements

A conventional fixed bed flow reactor system was employed for reaction measurements. In various experiments this was in operation at integral conversion, with a normal catalyst charge of 0.25 g. 1-Hexene was introduced into a feed system vaporizer via a controlled rate syringe pump into either H_2 or He flow giving a saturated hexene-He mixture at 25°C . Hexene/ H_2 ratios were varied from 0-40 in later experiments. Typical feed flow rates were $40 \text{ cm}^3/\text{min}$ at 20°C yielding space velocities ca. $200 \text{ cm}^3/\text{g cat-min}$. Product was sampled directly downstream of the reactant into a Hewlett-Packard 5730A GC, with separation in a

Table 1. Reaction rates for 1-hexene on various catalysts at 150, 250, 350 and 450°C

T($^\circ\text{C}$)	Steady state rate of consumption* (mmol/gcat-h)		
	SAPO-11	HZSM-5	H-Mordenite
150	8.33	7.70	9.34
250	5.47	10.80	7.68
350	7.40	14.52	—
450	10.72	14.81	5.10

*Catalyst weight = 250 mg; space velocity = $175 \text{ cm}^3/\text{gcat-min}$; (He/1-hexene) = 20

Supelco 0.19% picric acid on 80/100 mesh Carboxpack-C column, 2 m, at 190°C . In all reaction experiments the pretreatment sequence was He purging, 0.5 h, O_2 at 400°C , 1 h ($20 \text{ cm}^3/\text{min}$), He purging, 0.5 h, H_2 at 300°C , 3 h ($30 \text{ cm}^3/\text{min}$), and final He purging at reaction temperature, 0.5 h.

3. Temperature programmed desorption

The apparatus employed was typical flow system [18] automated temperature control (Omega Engineering Model CN2001J) and data acquisition system. Normally 0.20 g of catalyst was used with ultra high purity He as a carrier gas. Peak detection was via a Gow Mac Model 30S thermal conductivity cell with He reference. Before a run the sample was purged with He, 550°C , 14 h ($10 \text{ cm}^3/\text{min}$), then cooled to room temperature and outgassed via mechanical pump for 2 h. Ammonia saturation was carried out at room temperature, followed by a He flush for 0.5 h for the desorption of physisorbed NH_3 . TPD was then carried out at a linear heating rate of $10^\circ\text{C}/\text{min}$ with carrier He flow at $30 \text{ cm}^3/\text{min}$.

RESULTS AND DISCUSSION

1. Activity for 1-hexene isomerization

Table 1 is a summary of steady state reaction rates for 1-hexene consumption over SAPO-11, HZSM-5 and H-mordenite in the range of 150 - 450°C . On a per-gram basis it is seen that HZSM-5 is the most active, particularly for temperatures $>250^\circ\text{C}$. However, as will be seen, the main products are cracked/polymerized olefins in this case. At the lowest reaction temperature of 150°C all three catalysts demonstrate approximately the same activity, and there is an apparent linear decrease in activity with temperature for H-mordenite, and an apparent minimum in activity for the SAPO-11 in the vicinity of 250°C . The corresponding product distributions are shown in Fig. 1a, b, c for SAPO-11, HZSM-5 and H-mordenite, respectively. At low tem-

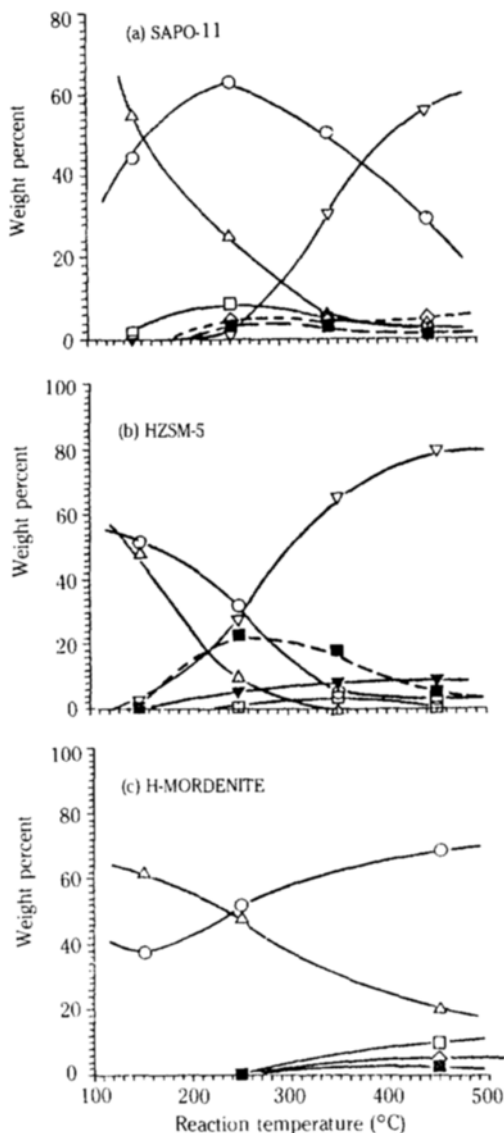


Fig. 1. Product distribution vs. reaction temperature for 1-hexene reactions on various zeolites.

○ 1-Hexene unreacted
 △ Cis/trans-2-hexene
 ◇ Cis/trans-3-hexene
 □ Monomethyl pentenes
 ■ Dimethyl butenes
 ▽ Cracked C₃-C₅ olefins
 ▼ Polymerized/cracked C₇-C₁₂ olefins
 (He/1-Hexene) = 20; Catalyst weight = 250 mg in all experiments.

peratures the major product is cis/trans-2-hexene regardless of the catalyst, with selectivities as high as 99%. Only negligible amounts of 3-hexene were found

Table 2. [(cis + trans)-2H]/[(cis + trans)-3H] at steady state

Catalyst	[(c + t)-2H]/[(c + t)-3H]			
	150°C	250°C	350°C	450°C
SAPO-11	> 10	6	1.4	0.8
HZSM-5	> 10	2.4	—	—
H-Mordenite	> 10	> 10	—	4.2
Equilibrium	—	2.65 ^a	—	—

^aFrom reference [19].

compared to 2-hexene (Selectivity is defined as wt% of its product divided by total wt% of 1-hexene reacted).

Certainly a major feature of these activity/selectivity results is the apparent minimum in activity for SAPO-11. We attribute this to a balance between double bond shift and cracking on this material. The amount of DBS declines rapidly with temperature in the range below 300°C, and the amount of cracked products is still small at 250°C, as shown in Fig. 1a. Increase in temperature behind ca. 300°C yields a large increase in cracking and, essentially, the disappearance of the DBS. It should also be noted from Fig. 1a that the amount of skeletal rearrangement, will not large, has a maximum at 250°C. The HZSM-5 also shows selectivity for skeletal rearrangement in the same temperature range Fig. 1b which suggests a possible role of pore dimension (~0.6 nm) in this conversion, but one notes also that cracking is well established at this temperature, reflective of the stronger acidity of the HZSM-5, as might be expected. Major products from SAPO-11 and HZSM-5 at higher temperatures above 350°C come from cracking with substantial contributions in the C₃-C₅ range. H-mordenite (~1.5 nm) even this range remains primarily a DBS catalyst, with the selectivity decreasing with increasing temperature (Fig. 5c) and only a small amount of skeletal isomerization at the highest temperature investigated, 450°C. Additional detail on DBS activity is provided by examining the (cis + trans)-2-hexene ratio to the corresponding figure for 3-hexene as shown in Table 2. On SAPO-11 the (2-hexene/3-hexene) ratio decreases strongly with temperature, approaching unity at 450°C. In fact, the amount of 3-hexene product remains constant at about 3-4 wt% of product and the decrease in the ratio is due to decrease in the 2-hexene via cracking (not to 3-hexene from hydrogen shift). Both SAPO-11 and H-mordenite are well above the equilibrium value [19]. While HZSM-5 is close to it.

With the exception being the trade-off between double bond shift and cracking on SAPO-11, clearly

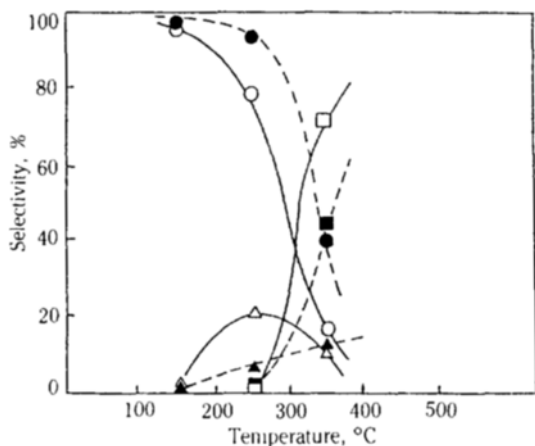


Fig. 2. Comparison of selectivities on SAPO-11 and Pd/SAPO-11.

- Double bond shift
- △▲ Skeletal rearrangement
- Cracking
- Open symbols → SAPO-11
- Closed symbols → Pd/SAPO-11

chemical in origine, most of the selectivity factors noted above can be understood in terms of pore structures of the different materials. The relatively large diameter and parallel configuration of the pores in H-mordenite permit comparatively free access to the 1- or 2-hexene and result in high selectivity for double bond shift (0.71) even at 450°C. This is accompanied by only a small amount of cracking/polymerization (selectivity of 0.04 at the same temperature) and, since DBS decreases with temperature, the overall conversion of 1-hexene also goes down. The more restrictive and/or complex structures of SAPO-11 and HZSM-5 lead to considerable amounts of cracked products at higher temperatures. Selectivity for cracked products was 0.71 at 350°C and increased to 0.84 at 450°C on SAPO-11. For HZSM-5 there is a sharp decrease in DBS selectivity already in the vicinity of 250°C (selectivity DBS = 0.17) and highest selectivity for cracking products, approximately constant at 0.92 for temperatures greater than 350°C.

2. Reaction on Pd/SAPO-11

As discussed earlier, a 2 wt% Pd on SAPO-11 catalyst was prepared using the zeolite as originally supplied as the starting material. Metals such as Pd are also effective for the double bond migration in olefins [20]; the double bond is opened on the metal site and hydrogen added; upon subsequent dehydrogenation the position of the double bond is shift. This metal-catalyzed reaction has been well-investigated [21] and is, of course, separate from the action of the acid func-

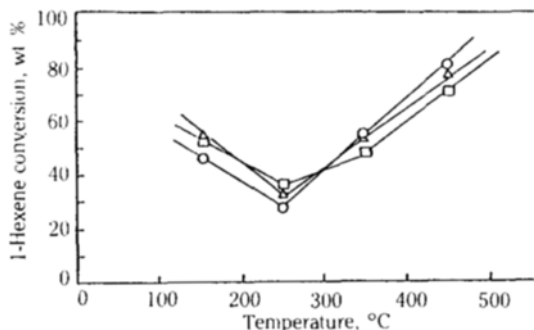


Fig. 3. Effect of $H_2/1$ -hexene feed ratio R on 1-hexene conversion over SAPO-11.

- $R = 0$
- △ $R = 20$
- $R = 40$

tion. The difference in the selectivity changes between Pd loaded and unloaded SAPO-11 catalysts could be compared in Fig. 2. It is apparent that the selectivity of DBS is much enhanced up to 250°C (the apparent minimum in 1-hexene reactivity disappears) and that there is also significant decrease in cracked products at high temperatures up to 400°C. There was significantly lower selectivity for skeletal rearrangement on Pd/SAPO-11 at temperatures below 350°C, so the contribution of Pd is seen primarily in double bond migration on the bifunctional catalyst.

The activity vs. time-on-stream behavior for Pd/SAPO-11 was comparable to SAPO-11 for temperatures up to 400°C, with good activity maintenance after approximately 15 min reaction time. However, at 450°C the Pd/SAPO-11 deactivated rapidly to a very low activity level. Evidence for significant coke formation at this level was afforded by visual inspection, but no formal analysis of coke content was undertaken.

3. Effect of hydrogen

A series of experiments was conducted over the same temperature range with (H_2 /hexene) in the feed from 0-40. For no H_2 in the feed, He was saturated with hexene at 20°C and a total flow of 40 cm^3/min (20°C) maintained; for hydrogen containing feeds the hydrogen rate was varied so as also to maintain total flow at 40 cm^3/min . Fig. 3 shows the resulting changes in overall conversion of 1-hexene as a function of (H_2 /hexene) feed ratios, R , over the temperature range for the unloaded SAPO-11. Again there is a minimum in conversion at 250°C, that is not substantially affected by the presence of hydrogen. In previous discussion it was pointed out that the main reaction path was shifted from DBS to SR or cracking with increasing temperature. Fig. 3 shows a crossover with respect to R as temperature increases, with the highest conversion

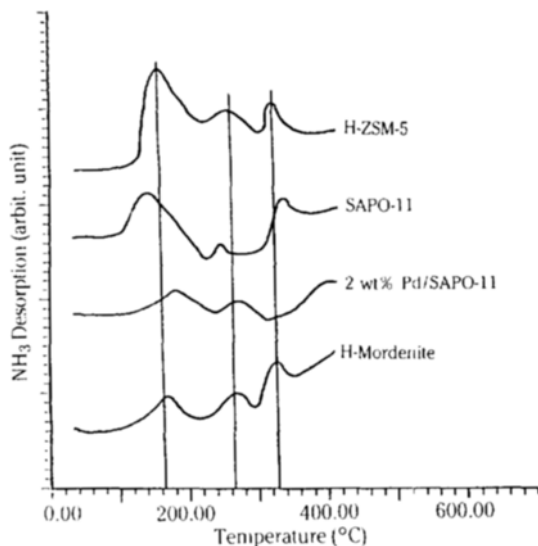


Fig. 4. NH_3 TPD patterns on HZSM-5, SAPO-11, H-mordenite and 2% Pd/SAPO-11.

at high R for temperatures above 300°C. There is, then, some hydrogen inhibition of DBS at lower temperatures, and promotion of cracking at higher temperatures. One would conclude that in SAPO-11 under these conditions there is possible some exchange of protons, increasing the acidity at higher temperature, producing the higher cracking activity.

4. Acidic properties from TPD

A number of sources have reported correlations of acid sites/acid strength for SAPO-n based on ammonia TPD spectra; however, there is considerable variation. Thompson and Wolf [8] found ZSM-5 and SAPO-34 to exhibit both low and high temperature desorption peaks, whereas SAPO-5 and -11 show only the low temperature peak at ca. 170°C. On the other hand, Tapp et al. [22] found two overlapping peaks at 240 and 340°C, possibly indicative of both Lewis and Brønsted sites on the SAPO-11. Further, they report only a single peak at 370°C for ZSM-5, while Thompson and Wolf found clearly separated peaks at 200 and 400°C. According to Halik and Lercher [19], TPD of ammonia from SAPO-11 gives maxima at 187-237, 267 and 307°C. In comparison with IR spectra, the low temperature peak was attributed to desorption from Lewis acid sites, while it was postulated that medium and high temperature peaks were the result of desorption from moderate and strong Brønsted sites, respectively.

The variety of these results would indicate that another try at TPD from SAPO-11 is warranted. In addition, we report here the corresponding results for the HZSM-5, H-mordenite and Pd/SAPO-11 used in the

Table 3. Relative areas of TPD peaks

Catalyst	Peak #1(A)	Peak #2(B)	Peak #3(C)	Total	A/(B+C) ^a
HZSM-5	1.73	0.56	0.42	2.71	1.77
SAPO-11	1.50	0.10	0.18	1.78	5.36
H-Mordenite	0.71	0.52	0.44	1.67	0.74
Pd/SAPO-11	0.53	0.46	0.03	1.02	1.08

^aRatio of areas $A/(B+C) \propto (\text{Lewis}/\text{Brønsted})$

reaction studies. Fig. 4 shows the basic TPD patterns obtained for the four materials with a He flush of 150 $\text{cm}^3/\text{g cat-min}$ (20°C) and a heating rate of 10°C/min. Although there are some variations among the individual materials, the maximum of the first desorption peak indeed is in the vicinity of 170°C, in accord with Thompson and Wolf, which we ascribe to Lewis acid sites following ref. [19]. One also sees clearly defined peaks at 240 and 330°C in this study, as reported by Tapp et al. [22], but better resolved. Qualitative trends may be estimated from relative intensities. Specifically, for the SAPO-11 samples the unloaded material has relatively weak intensity for the second peak and strong intensity for the third, while Pd/SAPO-11 shows medium intensity in the second peak and essentially no third peak. This suggests significant loss of strong Brønsted sites through the process of Pd loading. Similarly, it would appear that Lewis acid, weak Brønsted acid and strong Brønsted acid sites are relatively evenly distributed on the H-mordenite employed, while the HZSM-5 has a strong component of Lewis acidity.

More quantitative interpretation can be obtained on the basis of relative peak areas as shown in Table 3. If we interpret the total area as related to total acidity, HZSM-5 is easily the most acidic, with others following inline as shown. While there is not a substantial difference in Lewis acidity between HZSM-5 and SAPO-11 (Peak #1), the Brønsted function of the former is much stronger. This accords with Thompson and Wolf [8]; the decrease in Brønsted acidity is a function of very different Si/Al ratios, but is also a reflection of the modification by phosphorous in SAPO-11 [12, 14].

The ordering of acidity is consistent with the selectivity for formation of cracked olefins at temperatures greater than 300°C; on the other hand DBS selectivity, particularly at lower temperatures, is independent of total acidity. A representative result for higher temperature selectivity (350°C) is given in Fig. 5. The selectivity for structural rearrangement is obviously insensitive to acidity, however there is a strong correlation with the shift from DBS to cracking.

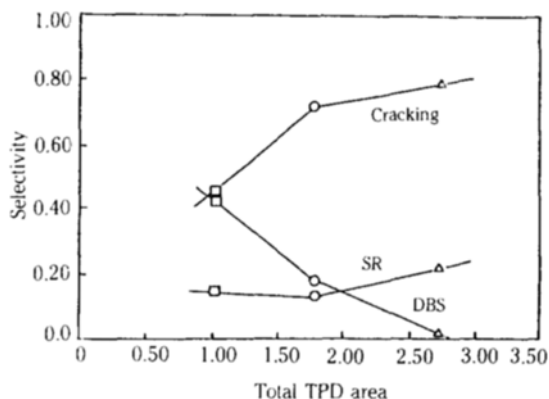


Fig. 5. Relationship of product selectivities to total acidity (TPD) at 350°C.

- Pd/SAPO-11
- SAPO-11
- △ HZSM-5

Close examination of the data of Table 3 shows that the trend of the first TPD peak is similar to that of total acidity, while the second and third peaks are not in consistent order. The correlation of DBS and cracking to this first (equivalent to Lewis acidity) peak only was found essentially linear. However, the simplest way to form carbonium ions is via olefin abstraction of a proton from a Brönsted site [23,24]. Thus it may be that the Lewis sites do not contribute directly to the formation of hexyl carbonium ions, but rather participate in conversion to Brönsted sites produced by water driven off at the higher temperatures. This, of course, increases with increasing temperature. It is for a reaction as complex as *n*-hexene conversion for such a wide range of materials, but at this point there seems no reason for further complexity.

CONCLUSIONS

There is high selectivity (over 99%) to DBS without regard to the type of catalyst at low reaction temperature (150°C). However, reaction temperature is increased from 250-450°C each of the materials develops a unique selectivity. H-mordenite persists with high DBS selectivity even at 450°C; HZSM-5 shows a significant change towards cracking/polymerization; SAPO-11 is intermediate between these two. Considering the wide range of pore size/structure involved it is reasonable to conclude that there is a strong influence of the geometrical factors of these catalysts at the higher reaction temperatures.

TPD of ammonia produced three peaks for all the catalysts, at roughly 170, 240 and 330°C. It can be

thought that the lowest temperature peak is representative of the Lewis acid sites of the catalyst, while the two peaks at higher temperatures represent weak and strong Brönsted acid sites. On this basis it is concluded that Pd/SAPO-11 has a significantly smaller Brönsted character than unloaded SAPO-11.

There is a strong correlation between the shift from DBS to cracking and total acidity. The correlation of SR reactions is not so well defined. Such evidence points to a conversion of Lewis acid sites into Brönsted sites at higher reaction temperatures, possibly through interaction with water.

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