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Isomorphous Substitution and the Generation of Catalytic Activity in VPI-5

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VPI-5 and substituted derivatives containing silicon or magnesium have been synthesized, analyzed, and tested for their catalytic activity. By means of ^{29}Si solid-state NMR, it could be shown that SAPO–VPI-5 prepared with polyphosphoric acid as a phosphorus source exhibits both "silica patches" and isolated silicon atoms incorporated in the framework. Brønsted acid sites in SAPO- and MAPO–VPI-5 could be detected by means of infrared spectroscopy in combination with pyridine adsorption. The isomorphously substituted VPI-5 samples were active in the hydroconversion of *n*-heptane, giving both cracking and isomerization products. The highest activity and the highest yield in iso-heptane, however, were observed with AlPO–VPI-5 as a catalyst. The catalytic activity could be ascribed to the presence of unreacted alumina. Upon treatment with an EDTA solution the Al/P atomic ratio decreased from 1.29 to 1.07, and the purified AlPO–VPI-5 showed considerably reduced catalytic activity.

INTRODUCTION

VPI-5, which belongs to the family of synthetic aluminophosphate-based molecular sieves was first reported in 1988 by Davis and his co-workers (*1–3*). Davis realized that VPI-5 exhibits a unique structure with 18-membered ring pores, which could be related to the Smith net no. 81(1) (*4*, *5*). The synthesis of VPI-5 involves the use of organic templates although the crystalline product is almost template-free. However, Davis *et al.* noted the similarity between the X-ray diffraction pattern of VPI-5 and that of an aluminophosphate denoted as H1, which is prepared in an organic-free medium (*1*). H1 had been identified by d'Yvoire as a novel compound in a mixture of hydrates (*6*). The template-free synthesis of H1 of high purity was achieved by Duncan *et al.*, and it appeared that VPI-5 is structurally identical with H1 (*7*).

Recently, a highly sophisticated structure determination by McCusker *et al.* (*8*) revealed that the pores of VPI-5 are filled with a highly ordered, hydrogen-bonded triple helix of water molecules acting as an inorganic template. The resulting structure model, predicting three tetrahedral P-sites and three Al-sites (one octahedral, two tetrahedral), is fully consistent with the ^{31}P and ^{27}Al NMR spectra of hydrated VPI-5 and explains the spectral changes observed upon heating (*9*). However, it might also explain why the generation of Brønsted acid sites is so difficult. A negatively charged framework and, in particular, the presence of charge-compensating cations would cause perturbations in the hydrogen-bonded water structure.

In order to overcome this problem, Martens *et al.* (*10*) suggested the use of organic templates which remain in the pores of (SAPO–)VPI-5, acting as proton acceptors at Brønsted acid sites. It was reported that a VPI-5 containing some silicon and occluded amine exhibited (low) activity in the isomerization of decane. Regrettably, the chemical

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composition was not reported, and the IR data presented give no evidence of bridging Brønsted hydroxyls in the catalyst.

A further problem arising from activation of VPI-5 concerns its low thermal stability. It is well known that VPI-5 undergoes an irreversible phase transformation towards AlPO-8 at relatively low temperatures, albeit that the various authors (*11–20*) give different, sometimes contradictory recommendations concerning prewashing, predrying, heating rates, etc., in order to minimize the extent of phase transformation. However, even at a low extent of AlPO-8 formation the adsorption capacity can be severely affected due to the presence of stacking faults (*13*, *14*).

In the present study we will focus on the generation of acidity in VPI-5. Samples obtained by means of direct syntheses and post synthesis modifications have been investigated with respect to isomorphous framework substitution and the formation of acid sites. Our results show that isomorphous substitution in VPI-5 is possible although the number of the acid sites formed is very low. The catalytic activity of the AlPO-form of VPI-5 in the isomerization of *n*-heptane, however, can be considerably higher than that of an acidic SAPO-form due to the presence of unreacted alumina. Removal of this catalytically active contamination by means of treatment with an aqueous EDTA solution yields highly crystalline VPI-5 of low activity.

METHODS

Synthesis and Modification

To synthesize VPI-5 without gel ageing, polyphosphoric acid was added to a slurry of pseudoboehmite (Catapal B) in water. Tetrabutylammonium hydroxide was combined with this aluminophosphate precursor mixture, and the final gel was homogenized and charged into an autoclave. Crystallization was allowed to take place during 24 h at 130°C with stirring. Si- (or Mg-) containing VPI-5 was prepared in the same way with addition of the appropriate silicon (or magnesium) sources. The products were filtered, thoroughly washed with hot water and dried at 60°C. Further details are summarized in Table 1.

Dealumination experiments with EDTA were performed with highly crystalline samples of AlPO–VPI-5. A suspension consisting of 10 g VPI-5 in 100 ml 0.3 mol Na-EDTA/l was refluxed for 1 h, and the solid was subsequently filtered off. After repeating the procedure, the sample was washed and dried.

Analyses

All samples prepared during this study were characterized by means of elemental analysis and X-ray diffraction (XRD) using Cu $K\alpha$ radiation. ^{31}P and ^{29}Si MAS NMR measurements were performed at 121.5 MHz and 59.6 MHz, respectively, applying single pulse excitations with high-power proton decoupling. Pulse angles were 75° and the relaxation delay was typically 15 s. The samples were spun at the magic angle at a rate of 3–5 kHz using dry nitrogen as spin gas. Infrared spectra were taken from self-supporting wafers after *in situ* drying at 500°C *in vacuo*. Pyridine adsorption was performed by contacting with pyridine vapor at 150°C for 15 min. Subsequently, physisorbed pyridine was removed by pumping off at 150°C for 15 min.

Hydro-isomerization of n-Heptane

The catalysts for the hydroconversion of n-heptane were prepared by pore volume impregnation of VPI-5 with an aqueous $Pt(NH_3)_4Cl_2$ solution, yielding Pt loadings of 0.5% by mass. After careful dehydration the samples were oxidized in dried air at 450°C, applying two-step heating at low heating rates (1°C/min). *In situ* reduction was performed in a flow of hydrogen at 30 bar pressure and at 400°C.

The catalytic experiments were performed in a multitube unit with six fixed-bed reactors. Five samples and a reference catalyst shaped as 40–80 mesh particles were tested in parallel under identical condi-

TABLE 1

Synthesis and Characterization of VPI-5 Samples under Study

Sample	Gel composition [Mol]						Si source	Product composition [Mol]					XRD analysis
	Al_2O_3	P_2O_5	SiO_2	MgO	R	H_2O		Al_2O_3	P_2O_5	SiO_2	MgO	R	
AlPO1	1	1	—	—	1	50	—	1.29	1	—	—	0.004	VPI-5
AlPO2	ex AlPO1 after EDTA treatments						—	1.07	1	—	—	—	VPI-5
SAPO1[a]	1	1	0.5	—	1	50	Aerosil	1.24	1	0.17	—	0.008	VPI-5 (trace amorphous)
SAPO2	1	1	0.5	—	1	50	Silicasol	1.09	1	0.15	—	0.01	VPI-5
SAPO3	1	1	0.5	—	1	50	Silicagel	1.1	1	0.16	—	0.01	VPI-5
SAPO4	1	1	0.5	—	1	50	Aerosil	1.07	1	0.17	—	0.02	VPI-5
MAPO1[b]	1	1	—	0.3	1	50	—	1.05	1	—	0.08	0.009	VPI-5

Note. R = Tetrabutylammonium hydroxide.

[a] Sample prepared with monophosphoric acid as a phosphorus source involving twofold pre-aging of the reaction gel.

[b] Sample prepared with magnesium acetate as an Mg source.

tions. The tests were run at a pressure of 30 bar, a WHSV of 1 g(g · h)$^{-1}$, and a H_2/*n*-heptane molar ratio of 4. The reaction temperature was typically 340°C.

RESULTS AND DISCUSSION

Composition

Jahn *et al.* (*21*) reported that the time-consuming pre-aging of the reaction gel can be omitted if the synthesis of VPI-5 is performed with DPA (di-*n*-propylamine) as a template and polyphosphoric acid instead of monophosphoric acid. We observed the same beneficial effect of polyphosphoric acid in combination with other templates. Moreover, the use of polyphosphoric acid facilitates the formation of pure VPI-5 in the presence of silica and, in particular, metal ions such as Mg^{2+}. These additives normally tend to favour the formation of undesired phases such as H3.

Chemical analyses revealed Al/P atomic ratios > 1 for all products whereas at least in the case of AlPO- and MAPO–VPI-5 the ratios should be equal to or less than unity (Table 1). It appears, however, after a close look at the open literature, that VPI-5 with the ideal Al/P ratio of 1 does not exist. Typically, ratios between 1.05 and 1.3 are reported. It is interesting to note that the same holds for other AlPO structures which are synthesized with pseudo-boehmite as an alumina source. In our opinion, these "high" Al/P ratios results from the presence of XRD-amorphous, unreacted alumina rather than from defects in the framework due to missing phosphorus atoms.

^{29}Si NMR Results

All samples of SAPO–VPI-5 selected for this study have silicon contents between 2.6 and 3.1% by mass. The corresponding ^{29}Sr MAS NMR spectra are depicted in Fig. 1. Spectrum (a) stems from the only sample in this series that has been synthesized with monophosphoric acid as a phosphorus source (SAPO1). This spectrum exhibits two broad humps of which the one around −110 ppm is characteristic of amorphous silica. We ascribe the signal around −50 ppm to silicon alkoxide species, which could be formed upon reaction of the Aerosil with the template or degradation products thereof. SAPO4 was also synthesized with Aerosil as a silica source and gives a similar signal around −50 ppm (spectrum d). Broad spectra of this type with signals at low field can also be obtained from SAPOs synthesized with the highly reactive aluminium isopropylate as an alumina source (*22*). In such cases, the hydrolysis products of the aluminium isopropylate can react with the silica source. We assume that our sample "SAPO1" is not a SAPO-form of VPI-5 but rather a mixture of AlPO–VPI-5 and amorphous, partially alkylated silica.

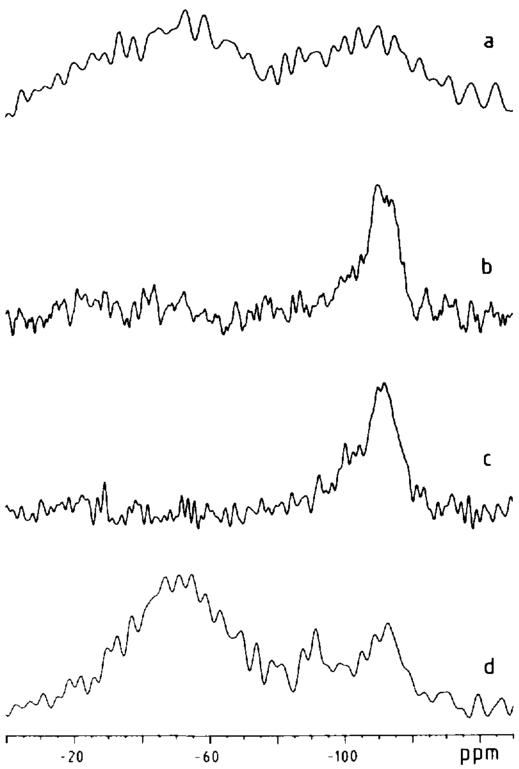

FIG. 1. ^{29}Si MAS NMR spectra of silicon-containing VPI-5: (a) SAPO1, (b) SAPO2, (c) SAPO3, and (d) SAPO4.

As compared to spectrum (a), the other spectra in Fig. 1 exhibit relatively narrow signals between −90 and −120 ppm, which points to incorporation of silicon into the framework. The dominant resonances around −112 ppm stem from Si(4Si) units. Such units, if part of the framework, are typical of "silica patches" which do not give rise to Brønsted acidity (*22*). The "borderlines" of such silica patches consist of various silicon species with different nearest neighbors, which give resonances in the range between ca. −95 and −110 ppm. Comparison of spectra (b), (c), and (d) in Fig. 1 reveals that the amount of species in the "borderline" changes relative to the amount of Si(4Si) species. We conclude that the samples contain silica patches of different sizes.

Brønsted acidity in SAPOs is associated with the occurrence of Si(4Al) units in the framework, which are identified by a ^{29}Si NMR signal between −90 and −95 ppm. Among the samples under study only SAPO3 and SAPO4 (Fig. 1) give a distinct signal within this range. Taking the relative intensity of the signal between −90 and −95 ppm into account it can be assumed that the acidity of the samples increases in the order (SAPO1 $\leq$) SAPO2 < SAPO3 < SAPO4.

Infrared Analysis

IR spectra of the region of OH-stretching vibrations (Fig. 2) show the characteristic bands of Al–OH (3795 cm^{-1}) and P–OH (3675 cm^{-1}) groups. Samples prepared in the presence of a silicon source give an additional strong band at 3740 cm^{-1}, which is typical of Si–OH groups. Interestingly, signals stemming from bridging OH groups of Brønsted acid type cannot be observed.

A difference spectrum of the hydroxyl re-

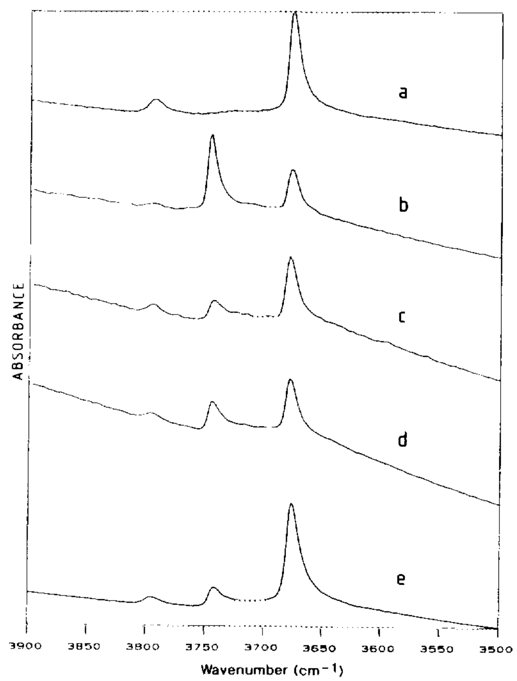

FIG. 2. Infrared spectra of hydroxyl groups on AlPO- and SAPO-VPI-5: (a) AlPO1, (b) SAPO1, (c) SAPO2, (d) SAPO3, and (e) SAPO4.

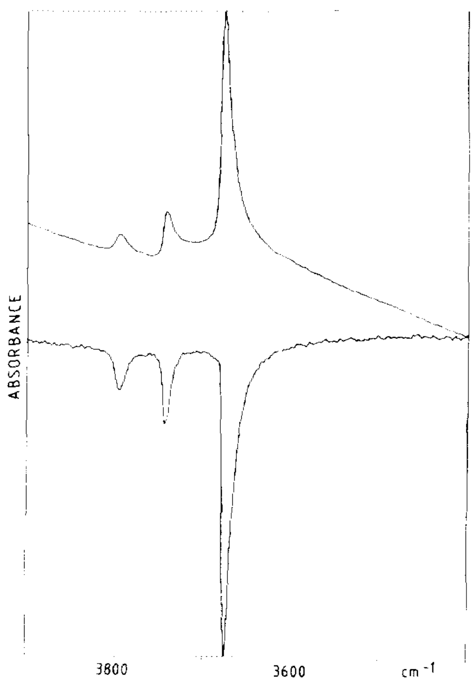

FIG. 3. Infrared spectra of hydroxyl groups on SAPO4: (top) normal spectrum and (bottom) difference spectrum after adsorption of pyridine.

gion taken after adsorption of pyridine (Fig. 3) demonstrates that all types of OH groups are involved in the interaction with pyridine molecules. The wavenumbers of the pyridine bands, on the other hand, indicate the presence of adsorption complexes formed with Lewis sites, while specific bands stemming from pyridine adsorption at the weakly acidic terminal OH groups are not observed (Fig. 4). SAPO-samples 3 and 4 (spectra (d) and (e)), however, show additional, very weak bands due to pyridinium ions formed at Brønsted sites (1545 cm^{-1}). A ranking of the VPI-5 samples according to the intensity of this band yields an acidity sequence (SAPO1 $\leq$ SAPO2 $\leq$ SAPO3 $<$ SAPO4) as found previously by ^{29}Si MAS NMR. In view of the weakness of the band at 1545 cm^{-1}, however, it should be concluded that even the most acidic SAPO-VPI-5 exhibits many fewer Brønsted sites than a typical SAPO of, e.g., structure type 5, 11, or 34. Probably, this very low concentration of Brønsted sites in SAPO-VPI-5 is the reason why the corresponding stretching vibrations cannot be observed directly in the IR spectra of the hydroxyl region.

The MAPO variant of VPI-5 synthesized in the presence of magnesium ions shows similar IR characteristics to the SAPO forms: there is no specific band due to bridging hydroxyls, but the adsorption of pyridine reveals the presence of a very small amount of Brønsted sites (Figs. 5 and 6). It is worth noting that the band stemming from Al-OH groups appears to be considerably less intense than in the case of AlPO- and SAPO-VPI-5. This observation is in line with the relatively low Al/P ratio established for this sample.

EDTA forms strong complexes with aluminium ions. It is known that EDTA can be used to dealuminate zeolites or dissolve unreacted non-framework alumina. The ap-

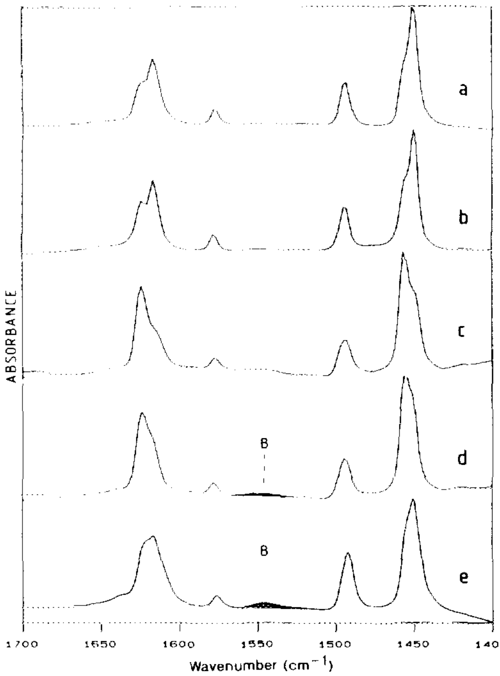

FIG. 4. Infrared spectra of pyridine adsorbed on AlPO- and SAPO-VPI-5: (a) AlPO1, (b) SAPO1, (c) SAPO2, (d) SAPO3, and (e) SAPO4.

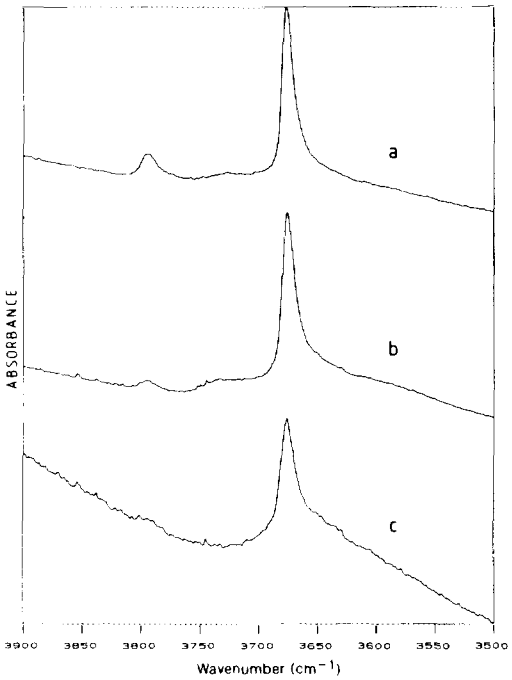

FIG. 5. Infrared spectra of hydroxyl groups on AlPO- and MAPO-VPI-5: (a) AlPO1, (b) AlPO2 (AlPO1 after treatment with EDTA), and (c) MAPO1.

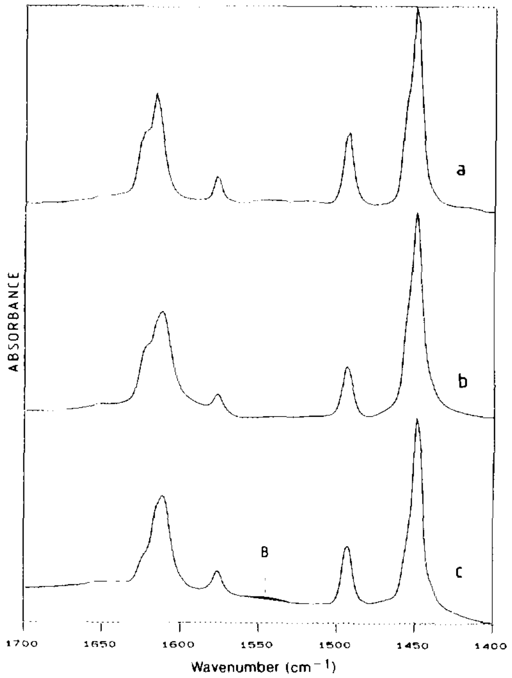

FIG. 6. Infrared spectra of pyridine adsorbed on AlPO- and MAPO-VPI-5: (a) AlPO1, (b) AlPO2 (AlPO1 after treatment with EDTA), and (c) MAPO1.

plication of an EDTA treatment to our samples of AlPO-VPI-5 resulted in a decrease in total aluminium content (Table 1), while the XRD-crystallinity appeared to improve slightly. The IR spectra in Figs. 5a and 5b indicate that the number of Al-OH groups relative to the number of P-OH groups is lower after dealumination with EDTA.

Hydroconversion of n-Heptane

The hydroconversion of *n*-heptane comprises cracking as well as isomerization reactions. In particular, the isomerization activity of a catalyst can be related to the presence of acid sites since cracking products can also be formed upon hydrogenolysis of the feed.

Our results summarized in Table 2 are very surprising. The highest conversions of *n*-heptane and the highest yields in iso-heptane (9%) could be achieved with AlPO-form of VPI-5. Martens *et al.* (*10*) reported isomer yields of about 20% for their most active SAPO-VPI-5 using *n*-decane as a feed. However, the space velocity of 0.4 h^{-1} applied by Martens *et al.* is much lower than

TABLE 2

Catalytic Performance of AlPO-, SAPO-, and MAPO-VPI-5 in the Hydroconversion of *n*-Heptane

Sample VPI-5	Conversion of $n-C_7$ (mass%)	Selectivity to $i-C_7$ (mass%)	Selectivity to $C_3 + C_4$ cracking prod. (mass%)
AlPO1	12.4	72.0	23
AlPO2	7.2	60.2	26
SAPO1	9.8	57.6	37
SAPO2	4.8	50.6	36
SAPO3	5.2	50.6	35
SAPO4	6.0	50.7	30
MAPO1	4.1	52.8	38

Note. Catalysts: VPI-5 + 0.5 %m/m Pt; 40–80 mesh; temperature = 340°C; pressure = 30 bar; WHSV = 1 $g(g \cdot h)^{-1}$; $H_2/n-C_7 = 4$.

in our experiments, and *n*-decane is more reactive than *n*-heptane. For the hydroisomerization over Pt/Ca–Y, Weitkamp reported a 20–30°C reactivity difference between *n*-decane and *n*-heptane (*23*). Taking this into account we assume that the hydroisomerization activity of our AlPO–VPI-5 is at least comparable to that of the most active SAPO–VPI-5 reported in the literature.

Our silicon- and magnesium-containing samples of VPI-5 are not only less active but also less selective than AlPO–VPI-5 since more cracking products are formed. Interestingly, dealumination with EDTA solution resulted in a loss of activity as compared to the parent material. This result, in particular, suggests that the active component in AlPO–VPI-5 is unreacted alumina. In fact, the catalytic activity of "nonacidic" AlPOs like AlPO-5 in acid-catalyzed reactions such as cracking, isomerization, and alkylation has been reported previously by many authors (*24–28*). Typically, the samples under investigation, if analysed, exhibited Al/P ratios larger than unity, indicating contamination by nonframework alumina species. We think that reactive alumina species, possibly interacting with terminal P–OH and Al–OH groups of the AlPO, can significantly contribute to the overall acidity, and that the effect on catalytic performance has been underestimated in previous studies.

It is also interesting to note that SAPO1, containing as much excess alumina as AlPO–VPI-5, gives the highest conversion among all SAPO samples. Since ^{29}Si MAS NMR indicates the presence of amorphous rather than incorporated silica, we tend to ascribe the catalytic activity again to the presence of unreacted alumina. The other SAPOs make considerably more cracking products at lower conversions of *n*-heptane. However, within this group the activity increases with increasing number of Brønsted acid sites as derived from NMR and IR analyses. The fact that the cracking products formed are predominantly C_3 and C_4 species (Table 2) clearly indicates that the reaction is acid-catalyzed, since hydrogenolysis would yield considerably more methane. We, therefore, assume that the few Brønsted sites generated upon isomorphous substitution contribute to both catalytic isomerization and cracking. The same may hold for the sample of MAPO–VPI-5, which shows a similar catalytic performance to the SAPO analogues.

The possibility of phase transformations during modification of VPI-5 and its application as a catalyst have been taken into account. The catalyst preparation involving pore volume impregnation, dehydration and oxidation did not affect the crystallinity of our samples. However, the spent catalysts were found to contain ca. 10% of material with the XRD characteristics of AlPO-8. It is likely that this partial phase transformation occurred prior to the testing during *in situ* reduction since this operation requires a second heating step with concomitant formation of water. While accepting that catalytic properties may be affected by such a structural change we would like to stress, however, that our catalysts, irrespective of the chemical composition, exhibited comparable stability. Thus, we can exclude that the differences in catalytic performance originate from different degrees of crystallinity.

CONCLUSIONS

Although the synthesis of VPI-5 could be facilitated greatly, especially with the use of polyphosphoric acid, and although silicon and magnesium can be incorporated such that Brønsted sites are formed, the low site densities achievable and the difficulties in handling VPI-5 are still a point of major concern.

The activity of SAPO- and MAPO–VPI-5 exhibiting Brønsted acidity is poor in view of the performance of nonsubstituted VPI-5. Our results suggest that unreacted alumina can confer on aluminophosphates sufficient activity to isomerize and crack saturated hydrocarbons. In the case of VPI-5, the contribution of nonframework alumina to the catalytic activity is even more significant than that of the few Brønsted sites generated upon isomorphous substitution.

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