JOURNAL OF CATALYSIS **115**, 291–300 (1989)

Catalytic Properties of Postsynthesis Phosphorus-Modified H–ZSM5 Zeolites

HANNELORE VINEK, GERD RUMPLMAYR, AND JOHANNES A. LERCHER[1]

Institut für Physikalische Chemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Vienna, Austria

Received April 13, 1987; revised June 20, 1988

A series of postsynthesis modified ZSM5 zeolites was prepared using orthophosphoric acid, trimethylphosphine, and trimethylphosphite. The density of strong and weak Brønsted acid sites was determined by the temperature-programmed desorption of pyridine. The ultimate effect of the phosphorus treatment was the removal of the strong Brønsted acid sites. The density of the weak Brønsted acid sites was found to increase after treatment with phosphoric acid and trimethylphosphite, whereas it was found to be unchanged after trimethylphosphine treatment. The turnover frequency in *n*-hexane cracking was constant for a given type of acid site with all samples investigated. The energy of activation increased with the increasing density of weak Brønsted acid sites indicating that the H^+ participated in the rate-determining step. For alkylation of toluene with methanol, nearly constant energies of activation were observed over all samples investigated, indicating no influence of the Brønsted acid site upon the rate-determining step. The decrease in activity is attributed to a decreased surface concentration of the reacting species in the rate-determining step or to a substantial decrease in the transition entropy from the reactants to the activated complex. © 1989 Academic Press, Inc.

INTRODUCTION

Modifications of ZSM5 zeolites with phosphorus compounds have been the subject of a considerable number of investigations during the past ten years (e.g., (*1–7*)). As a result, detailed information on their catalytic behavior with respect to reactions of alcohols and to alkylation is available. Most of these studies focus on one or two particular modifications that seem close to those described in the patent of Kaeding and Butter (*1*). We have broadened this approach by choosing three typical phosphorus modification agents (orthophosphoric acid, trimethylphosphine (TMP), and trimethylphosphite (TMPT), all mentioned in the patent of Kaeding and Butter (*1*)) and increasing the amount deposited until we saw no further changes in the catalytic and acid–base properties.

Védrine *et al.* (*5*) and Nunan *et al.* (*7*) concluded from their studies of phosphorus-modified ZSM5 zeolites that primarily the acid sites at the outer surface which increased the relative fraction of strong Brønsted acid sites in the channels are affected, while the results of Kaeding and Butter (*8*) and of Chandawar *et al.* (*6*) suggest a uniform distribution of the modifying agent. At low loadings, the phosphorus compound was concluded to block the sites for reactions that are not subject to shape selectivity control. It was assumed that this is achieved, e.g., by reaction of a proton of the zeolite with one of the functional groups attached to the phosphorus atom, thus creating a cation, which can bind to a bridged oxygen between a silicon or aluminum T atom (*1, 5, 9, 10*). If such a cation contains organic functional groups those may be removed by activating the sample in oxygen at about 773 K.

In previous papers we have reported the effects of increasing amounts of phosphoric acid (*9, 10*) and trimethylphosphine (*11*) deposited on the acid–base properties of H–ZSM5. It was found that the density of

---

[1] To whom correspondence should be addressed.

0021-9517/89 $3.00
Copyright © 1989 by Academic Press, Inc.
All rights of reproduction in any form reserved.

strong acid sites decreased with increasing amounts of phosphorus loaded. The density of weak acid sites increased for phosphorus acid-modified samples and remained constant for the TMP-modified samples. For the phosphorus acid-modified samples we interpreted this to be due to increasing concentrations of POH groups of phosphorus species that cover the bridged hydroxyl groups (*1, 5, 9, 10*) and for the TMP-modified samples to the decreasing density of strong Brønsted acid sites caused by strong adsorption of trimethylphosphine on the bridged hydroxyl groups.

In this paper we describe the catalytic activity and selectivity for *n*-hexane cracking and for alkylation of toluene by methanol as a function of the concentration of the weak and strong acid sites of several phosphorus acid-, TMP-, and TMPT-modified samples. The detailed attribution of the nature of the acid sites (especially the weak Brønsted acid sites) and the mechanism of postsynthesis phosphorus modification will be the subject of another report (*12*).

EXPERIMENTAL

Catalysts and Reagents

The ZSM5 zeolite (Union Carbide, Linde Division, New York, Lot No. 8496-68) contained 99.35 mol% SiO_2, 0.59 mol% Al_2O_3, and 0.06 mol% Na_2O. To prepare the H_3PO_4-modified zeolites (ZSM5P), 10 g of the starting material was suspended in 100 ml distilled water and the desired amount of H_3PO_4 was added. This suspension was refluxed for 2 h and then the water was evaporated under reduced pressure. The remainder was dried at 373 K and calcined at 773 K for 1 h in air. The resulting catalysts contained 1, 2, and 5 wt% H_3PO_4, denoted ZSM5P1, ZSM5P2, and ZSM5P5, respectively. Trimethylphosphine-modified samples were prepared by adsorption–calcination cycles. The starting material was calcined at 873 K under vacuum (10^{-1} Pa) for 1 h. Then 900 Pa of TMP was admitted for 15 min into the reactor, which was evacuated subsequently for 15 min at ambient temperature. Then the sample was calcined in air at 573 K for 12 h. The treatment was repeated up to three times and the samples are denoted ZSM5TMP1, ZSM5TMP2, and ZSM5TMP3, respectively. The modification of H–ZSM5 with trimethylphosphite was made according to the example given in Ref. (*1*). Ten grams H–ZSM5 was dried in flowing N_2 for 1 h. Subsequently the sample was suspended in 50 ml *n*-octane and 4 ml TMPT and refluxed for 14 h. The suspension was filtered and the remainder was washed with methylene chloride and *n*-pentane. Then the sample was dried at 400 K for 1 h and at 500 K for 2 h in flowing N_2 and finally calcined at 773 K for 17 h in air.

Pyridine, *n*-hexane, toluene, and methanol were obtained from Merck (Uvasol grade). All gases used had at least 99.995 vol% purity.

Temperature-Programmed Desorption (TPD)

TPD was carried out under vacuum (below 10^{-2} Pa) using a temperature increment of 10 K min^{-1} between 400 and 1000 K. The reactor was a continuously pumped quartz glass tube, connected to a Balzers 311 quadrupole mass spectrometer, which was controlled by a Digital MINC computer. For details of the experimental setup, see Ref. (*13*). The sample (50 mg) was calcined *in situ* at 873 K for 1 h, cooled to ambient temperature, and contacted with 3 kPa of pyridine for 15 min. It was found that higher exposures did not lead to increased amounts of base adsorbed. Then the sample was evacuated at 423 K for 40 min prior to TPD.

In order to quantify the results the opening of the leak valve to the mass spectrometer and the amount of catalyst were kept constant during all experiments. Thus the signal of the mass spectrometer due to pyridine was proportional to the partial pressure of pyridine above the catalyst, which is directly proportional to the rate of desorption of pyridine, because high and con-

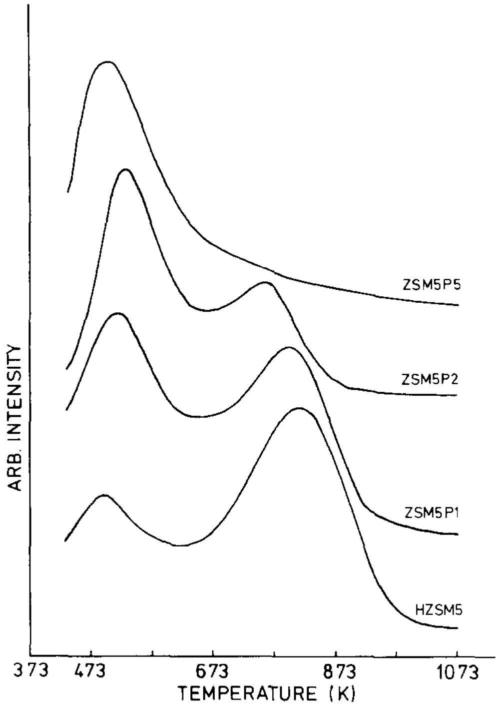

FIG. 1. TPD traces of pyridine from ZSM5P samples.

stant pumping speed was realized. The integral of the rates was therefore proportional to the total amount of pyridine desorbing from one adsorption state. From the concentration of tetrahedral aluminum atoms and hence the concentration of strong Brønsted acid sites in the starting sample all TPD maxima could be quantified. The reproducibility of this method was better than 3%.

Catalytic Measurements

Cracking and alkylation experiments were carried out in continuous flow mode. *n*-Hexane was fed with a rate of 7×10^{-3} mol h^{-1} and a partial pressure of 15.9 kPa. The feed rates of toluene and methanol were 5.34×10^{-2} mol h^{-1}; the partial pressures were 26.6 kPa. In both experiments the total pressure was 1 bar using He as make-up gas. The amount of catalyst was between 50 and 150 mg. For *n*-hexane cracking the effluent was kept at 400 K and injected into the GC column (Chromosorb 102) via a six-port valve. A Hewlett–Packard 5840A gas chromatograph with FID was used. For alkylation experiments the effluent was sampled at the reactor exit with a syringe and injected into the GC (Perkin–Elmer F11, FID, column: 5% SP1200/5% Bentone 34). Both sets of catalytic data were analyzed by the differential method and conversions were below 5%.

RESULTS

Figures 1 and 2 show compiled plots of the rates of desorption of pyridine from H_3PO_4-, TMP-, and TMPT-modified samples. Three maxima have been found which are denoted α, γ^*, and γ in the following. The temperatures of the maxima were 373 K (α), 500 K (γ^*), and around 800 K (γ). By comparison with the corresponding IR adsorbate spectra the TPD desorption maxima were attributed to pyridine from weak Lewis acid sites (physisorption), weak Brønsted acid sites, and strong Brønsted acid sites, respectively (*9–12*). For quantification, we removed weakly adsorbed pyridine by evacuation at 373 K prior to TPD.

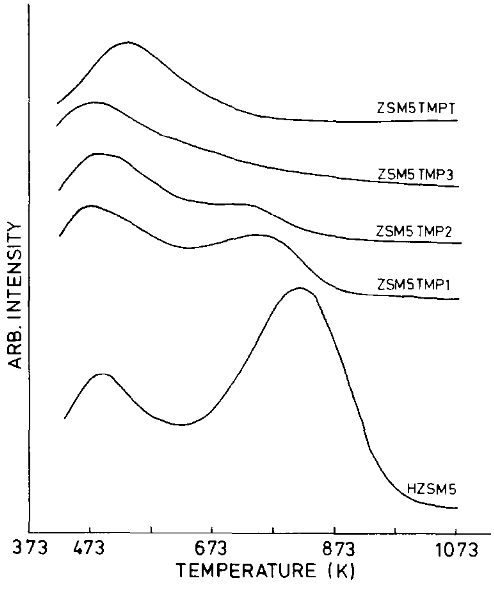

FIG. 2. TPD traces of pyridine from ZSM5TMP and ZSM5TMPT samples.

TABLE 1

Notional Surface Area and Quantification of the Acid Sites

Sample	Notional surface area [m^2 g^{-1}]	Molecules desorbing in γ [g^{-1}]	Molecules desorbing in γ^* [g^{-1}]
H–ZSM5	300	1.098×10^{20}	1.367×10^{19}
ZSM5P1	304	6.988×10^{19}	4.708×10^{19}
ZSM5P2	310	3.646×10^{19}	6.988×10^{19}
ZSM5P5	265	0	8.564×10^{19}
ZSM5TMP1	283	2.102×10^{19}	2.286×10^{19}
ZSM5TMP2	274	6.130×10^{18}	2.354×10^{19}
ZSM5TMP3	273	0	2.27×10^{19}
ZSM5TMPT	278	0	9.405×10^{19}

The following discussion will focus only on pyridine molecules desorbing in the γ^* and γ peaks. In contrast to the opinion expressed by Topsøe *et al.* (*14*), we demonstrated (*10–12*) that pyridine could be used for characterization of the acid sites of ZSM5 and that it was a probe equivalent to, if not better than, NH_3 for quantification of the sites.

Pyridine TPD from unmodified H–ZSM5 showed both the γ and the γ^* peaks, the former being significantly more intense than the latter. With increasing amounts of H_3PO_4 deposited the γ^* peak increased in intensity, while the γ peak decreased. The γ peak was not present in H_3PO_4 samples with 5 wt% H_3PO_4 deposited. The intensity of the γ peak also decreased with increasing concentrations of TMP deposited. The γ^* peak and hence the concentration of pyridine molecules desorbing from weak Brønsted acid sites did not change. With ZSM5TMPT the γ peak was absent and the peak was substantially larger than that with H–ZSM5. The quantifications of the areas under the TPD peaks are compiled in Table 1.

Cracking of n-Hexane

Areal yields, turnover frequencies, and the energy of activation are collected in Table 2. By modification with any of the phosphorus compounds the areal yields decreased from 10^{15} to 10^{12} molecules s^{-1} m^{-2}. Thus, for samples that did not exhibit a γ peak (ZSM5P5, ZSM5TMP3, and ZSM5TMPT) the same activity was found. The somewhat higher selectivity to C_4 hydrocarbons suggests that some of the cracking products stem from larger molecules that had been formed by oligomerization.

The apparent energy of activation increased from approximately 80 kJ mol^{-1} for H–ZSM5 to 180 kJ mol^{-1} for the phosphorus-modified samples. Note that ZSM5P5 and ZSM5TMP3 had approximately the same apparent energies of activation, whereas that of ZSM5TMPT was somewhat lower (150 kJ mol^{-1}).

Alkylation of Toluene with Methanol

The areal yields, the apparent energies of activation, and the product selectivities are

TABLE 2

Cracking of *n*-Hexane

Sample	Areal yield [mol s^{-1} m^{-2}]	Turnover frequency [mol s^{-1} $H^{+\,-1}$]	Energy of activation [kJ mol^{-1}]
ZSM5	1.07×10^{15}	2.92×10^{-3}	79
ZSM5P1	6.9×10^{14}	3.00×10^{-3}	110
ZSM5P2	3.15×10^{14}	2.68×10^{-3}	120
ZSM5P5	2.7×10^{12}	—	171
ZSM5TMP1	2.15×10^{14}	2.89×10^{-3}	115
ZSM5TMP2	8.9×10^{12}	3.98×10^{-4}	130
ZSM5TMP3	2.8×10^{12}	—	172
ZSM5TMPT	1.6×10^{12}	—	151

TABLE 3

Alkylation of Toluene with Methanol

Sample	Areal yield, 773 K [mol s^{-1} m^{2}]	Energy of activation [kJ mol^{-1}]	Xylene distribution (773 K, mol%) *p*/*m*/*o*	*p*-Selectivity[a] 773 K
H-ZSM5	2.44×10^{15}	61.5	66/24/10	55.8
ZSM5P1	1.77×10^{15}	64.0	71/19/10	62.3
ZSM5P2	1.20×10^{15}	58.0	76/16/ 8	68.8
ZSM5P5	1.20×10^{14}	34.0	100/ 0/ 0	100
ZSM5TMP1	1.87×10^{15}	71.6	84/10/ 6	79.2
ZSM5TMP2	1.28×10^{15}	69.9	88/ 7/ 5	84.4
ZSM5TMP3	1.66×10^{15}	69.9	81/11/ 8	75.3
ZSM5TMPT	7.10×10^{14}	49.7	75/12/13	67.5

[a] Sel = $(y - y_e)/(100 - y_e) \cdot 100$, where y_e is the mole percent at equilibrium and y is the mole percent observed.

listed in Table 3. Impregnation with H_3PO_4 led to a sharp decrease (one order of magnitude) in the areal yield compared to the unmodified H-ZSM5. However, only an approximately 30–50% decrease in the activity was found with TMP-modified samples. While the selectivity to *p*-xylene increased to 100% by deposition of 5 wt% H_3PO_4, it increased only to approximately 95% by TMP and TMPT treatment and remained approximately constant independent of the phosphorus loading. The energy of activation was about 60–70 kJ mol^{-1} for alkylation over all samples investigated, except for ZSM5P5 and ZSM5TMPT where the apparent activation energies were 34 and 50 kJ mol^{-1}, respectively. This may indicate a change in mechanism or the influence of diffusional constraints.

As indicated in the literature (*2*, *15*) the selectivity to *p*-xylene decreased with increasing conversion and increased (for a given conversion) with temperature (see, e.g., Fig. 3). For a given conversion and temperature the selectivity to *p*-xylene always increased symbatically with the phosphorus concentration on the catalyst. It should be especially noted, however, that the activity and selectivity of the zeolites are not mutually dependent. The catalytic activity of ZSMTMP2 is slightly higher than that of ZSM5P2 and it showed significantly higher selectivity for the formation of *p*-xylene.

DISCUSSION

The Concentration and Strength of Acid Sites

To describe the effects of postsynthesis treatment of zeolites (in particular of H-ZSM5) with phosphorus compounds several authors (*2*, *5*, *9*, *10*) advanced a model

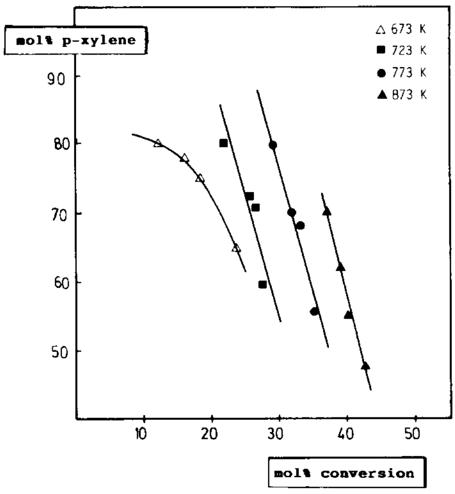

FIG. 3. Alkylation of toluene with methanol over ZSM5TMP samples.

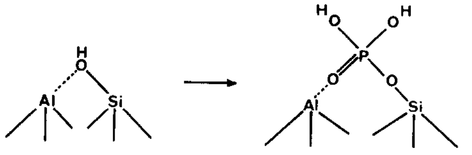

FIG. 4. Proposed model for phosphorus modification of strong Brønsted acid sites.

that is shown in Fig. 4. We shall not discuss whether the phosphate group is present in the form depicted here or is rotated around one P–O axis as suggested in Refs. (*2*, *5*). Formally, the OH^- group is replaced by the $H_2PO_4^-$ group. The substitution of the Brønsted acidic hydroxyl group by the $H_2PO_4^-$ group implies three consequences for the strength and density of the Brønsted acid sites, as follows.

(i) Strong Brønsted acid sites are converted into weak Brønsted acid sites. The resulting terminal hydroxyl groups always have a lower acid strength than the bridged hydroxyl groups (*16*, *17*).

(ii) The number of acid sites increases.

(iii) Because OH^- and $H_2PO_4^-$ groups have approximately the same intermediate electronegativity according to Sanderson (*18*), the substitution should not change the polar character of the surface and hence the acid strength of the remaining unsubstituted hydroxyl groups.

For H_3PO_4 (*9*, *10*)- and trimethylphosphite (*1*)-treated H–ZSM5 these criteria have been reported to be qualitatively fulfilled and are also reflected in the TPD of pyridine (Fig. 1). In contrast to the increase in the density of the weak Brønsted acid sites of H–ZSM5 by H_3PO_4 and trimethylphosphite treatment, the number of pyridine molecules that desorbed from weak Brønsted acid sites (γ^* TPD peak) did not change after postsynthesis modification with trimethylphosphine (see Fig. 2). As we described in detail in Ref. (*11*), the methyl groups attached to phosphorus could not be oxidized and therefore TMP acted as an electron pair donor molecule blocking the strong Brønsted acid sites by adsorption.

The same temperature of the maximum of the rate of desorption of pyridine from weak Brønsted acid sites suggests that after all postsynthesis treatments the strengths of these acid sites were the same. The variation of the concentration of the acid sites as a function of the preparation procedure suggests that the model of the nature of the phosphorus modification outlined above cannot be generalized. Certainly, POH groups cannot be responsible for the weak Brønsted acid sites found in the unmodified H–ZSM5 and the TMP-modified samples. Because of the same temperature of the maximum of the TPD of pyridine from these sites, we suggest that the weak Brønsted acid sites at least on H–ZSM5 and on ZSM5TMP samples are AlOH groups on extra-lattice alumina regenerated by dealumination during calcination steps or SiOH groups of hydroxyl nests formed by the same process. Investigations to confirm this proposal are described in Ref. (*12*).

Cracking of n-Hexane

The decrease in the catalytic activity for cracking of *n*-hexane and the increase in the energy of activation for that process as a consequence of postsynthesis treatment of H–ZSM5 with phosphorus compounds suggest a decrease in the strength and/or the density of active sites by postsynthesis treatment of H–ZSM5 with phosphorus compounds. The change in energy of activation indicates that Brønsted sites participate in the rate-determining step. (The assumption that the rate-determining step of cracking of alkanes is the generation of carbenium ions (e.g., Ref. (*19*)) is compatible with our results.) Consequently, two catalysts showing the same energies of activation should have about the same strengths of Brønsted acid sites acting as active sites. This was confirmed, because all samples that had only weak Brønsted acid sites exhibited an apparent energy of activation of

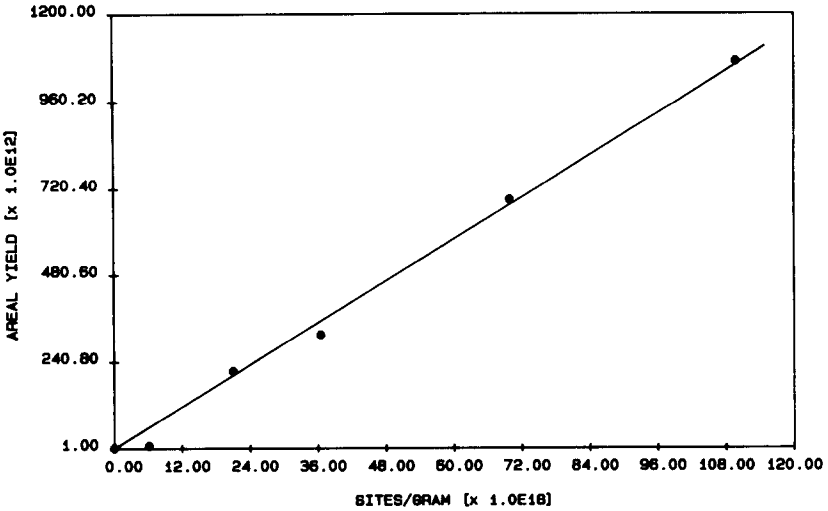

FIG. 5. Dependence of the activity for cracking of *n*-hexane upon the density of strong Brønsted acid sites.

172–178 kJ mol^{-1} suggesting equal strengths of these acid sites.

As suggested by the TPD of pyridine, only two types of catalytically active sites are present in our materials, namely strong and weak Brønsted acid sites. The acid strength of these sites does not change with postsynthesis treatment. The concentration of the sites, however, changes as a function of the conditions of the postsynthesis treatment with phosphorus compounds. Provided the strength of the sites does not change and diffusional effects do not play a significant role, the turnover frequencies (number of molecules reacted per site of a specific type and unit time) should be different for both types of sites, but should not be a function of postsynthesis treatment conditions.

If this holds true, the activity of a specific sample must be given by the sum of the turnover frequencies of both Brønsted acid sites multiplied by their concentration. The turnover frequencies of the two Brønsted acid sites were estimated by the activity of the unmodified H–ZSM5 and the ZSM5TMP3 samples. While H–ZSM5 has a large fraction of strong and a small fraction of weak Brønsted acid sites, ZSM5TMP3 has only weak Brønsted acid sites (about the same concentration of weak acid sites as H–ZSM5). Because the turnover frequency of the strong Brønsted acid sites is three orders of magnitude larger than that of the weak Brønsted acid sites, the activity is mainly governed by the concentration of strong Brønsted acid sites (see Table 2). Figure 5 exemplifies the good agreement between the experimental points and the calculated variation of activity (solid line) confirming the validity of our approach.

Alkylation of Toluene with Methanol

The effects of phosphorus postsynthesis treatment upon the catalytic properties for alkylation of toluene with methanol were quite different from those observed for cracking of *n*-hexane. The energy of activation was about 60–70 kJ mol^{-1} for all samples, except for ZSM5P5 and ZSM5TMPT, which exhibited 34 and 50 kJ mol^{-1}, respectively. For these two catalysts the low values of the energy of activation are likely to be indicative of diffusional control as we have found additional extra-crystalline material by SEM (*10*). Since we determined significant changes in the concentration of

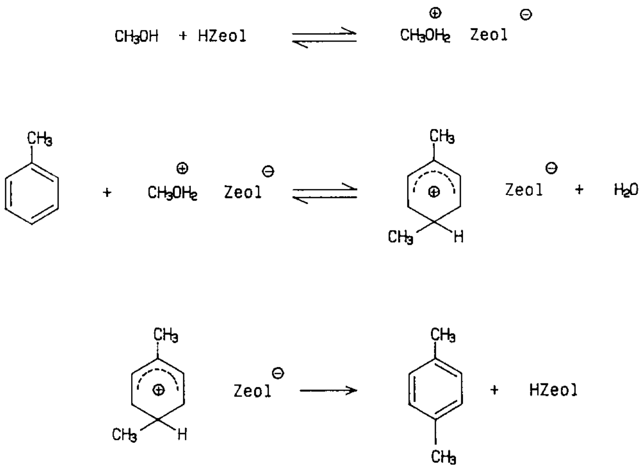

FIG. 6. Proposed mechanism for alkylation of toluene with methanol.

strong and weak Brønsted acid sites, which are not reflected in the energy of activation, we suggest that the rate-determining step does not involve the Brønsted acid site.

As suggested by the mechanism proposed for homogeneously catalyzed liquid-phase alkylations (*20*), the role of the Brønsted acid site is to protonize the methanol molecule (see Fig. 6). Then, the rate-determining step may be the addition of the methyl carbenium ion or the desorption of the resulting xylene. The cleavage of the proton from the activated complex is unlikely to be rate determining, because in that case the reaction should be easier over weaker Brønsted acidic sites and this was not observed.

The areal activity decreased by a factor of 2 for samples modified with TMP, by a factor of 3 for samples modified with TMPT, and by one order of magnitude for samples modified with H_3PO_4. The activity of the samples which had no strong Brønsted acid sites can be ranked as ZSM5TMP3 > ZSM5TMPT > ZSM5P5. Note that the energy of activation and the notional surface area (accessible pore volume) decreased in that order indicating that diffusional constraints may cause additional decreases in activity for the latter two samples. No correlation between the activity and the density of the strong and/or weak Brønsted acid sites was found, in agreement with the results of Bezouhanova *et al.* (*21*) for H–ZSM5 with varying Si/Al ratios. Both results support the validity of the proposed reaction scheme outlined in Fig. 6.

Because the energy of activation remained constant, except for ZSM5P5 and ZSM5TMPT, the main cause for the decrease in activity after modification with phosphorus must be a decrease in the pre-exponential factor (large negative entropy change to the activated complex) or a decrease in the surface concentration of the reacting species of the rate-determining step. Although the present data do not allow us to differentiate between these two possibilities unequivocally, recent results with alkali-exchanged ZSM5 zeolites (*22*) and the independent variation of activity and selectivity support the latter proposal.

Within this context Ashton *et al.* (*23*) reported that severe steaming conditions decreased the toluene conversion. Following the arguments given above, the decrease in the concentration of strong acid sites caused by steaming should not cause the decrease in activity. The samples with low catalytic activity have, however, a significant fraction of extra-framework aluminum oxide, which causes a subtle decrease in the sorption capacity of the material. We think that a similar process caused the decrease in activity in our case. By means of MAS NMR measurements a Si/Al ratio of 300 was found for ZSM5P5 suggesting substantial dealumination during the modification with H_3PO_4 (*24*). Furthermore, platelets of condensation products of H_3PO_4 were observed by scanning electron microscopy (*10*) on ZSMP5 indicating a further possible cause for the decrease in accessible pore volume.

With respect to the increase in selectivity to *p*-xylene brought about by the modification with phosphorus compounds we stress the independence of activity and selectivity changes. Selectivity to *p*-xylene increased with the decreasing concentration of strong acid sites. Hence, the possible effect of the change of transition entropy cannot be correlated with more spatial constraints in the transition state.

High *p*-xylene selectivity may be caused by (i) a very slow rate of diffusion of *o*-xylene (coke deposits could enhance this effect (e.g., Ref. (*2*)), (ii) transition state selectivity favoring *p*-xylene (*25, 26*), and (iii) the conversion of *o*-xylene to other products (*25*). Haag and Olson (*27*) showed that the selectivity to *p*-xylene increased with increasing diffusion residence time for *o*-xylene, no matter how they treated the catalyst in order to increase the diffusional constraints. This is fully consistent with shape selectivity resulting from a classical diffusion/reaction mechanism as, for example, discussed by Weisz (*28*). On the other hand, according to Wei (*29*), in part, one could account for the increase in the *p*-xylene selectivity on the basis of the lower concentration of acid sites. If this holds true, the role of the phosphorus compounds may be to reduce (or remove) strong acid sites within the pores (catalytically active for xylene isomerization (*30*)). Note that the effects after postsynthesis treatment with phosphorus compounds are very similar to those observed after steaming H–ZSM5.

CONCLUSIONS

Postsynthesis treatment of H–ZSM5 with phosphoric acid, trimethylphosphine, and trimethylphosphite decreased the concentration of strong Brønsted acid sites. By increasing the extent of the treatment, samples with virtually no strong Brønsted acid sites could be prepared. The most subtle of the reagents was trimethylphosphine, which only blocked the strong Brønsted acid sites without affecting the concentration of the weak acid sites. The concentration of the latter sites was found to increase by H_3PO_4 and TMPT treatment.

The cracking of *n*-hexane was found to be a function of the concentration of strong and weak Brønsted acid sites. The results can be explained assuming constant turnover frequencies for strong (and weak) acid sites. This confirms our earlier (*9, 10*) conclusions that the strength of the unmodified sites is not affected by the postsynthesis treatments applied for this study.

In contrast, the activity for alkylation of toluene by methanol was found not to depend upon the concentration of Brønsted acid sites. The nearly constant energy of activation suggests that the rate-determining step does not involve a Brønsted acid site. We propose that the rate-determining step is the addition of a methylcarbenium ion to an adsorbed toluene molecule. The decrease in the rate of xylene formation was concluded to be due to the decreased surface concentration of the reacting species in the rate-determining step or to a large negative entropy change to the transition state caused by the increased spatial constraints in the channels. Because of the independent variation of activity and selectivity we conclude that it is the surface concentration rather than the change in the transition entropy which causes the decrease in activity.

ACKNOWLEDGMENTS

This work was supported by the FWF ("Fonds zur Förderung der Wissenschaftlichen Forschung") under Grant P5757. We are indebted to Professor Freude for the measurement of the Si/Al ratio of two samples by MAS NMR and to Professors Conner and Schwank for helpful discussions.

REFERENCES

1. Kaeding, W. W., and Butter, S. A., U.S. Patent 3,911,041 (1975).
2. Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B., and Butter, S. A., *J. Catal.* **67,** 159 (1981).
3. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **69,** 392 (1981).
4. Chen, N. Y., Kaeding, W. W., and Dwyer, F. G., *J. Amer. Chem. Soc.* **101,** 6783 (1979).
5. Védrine, J. C., Auroux, A., Dejaifve, P., Ducarme, V., Hoser, H., and Zhou, S., *J. Catal.* **73,** 147 (1982).
6. Chandawar, K. H., Kulkarni, S. B., and Ratnasamy, P., *Appl. Catal.* **4,** 287 (1982).
7. Nunan, J., Cronin, J., and Cunningham, J., *J. Catal.* **87,** 77 (1984).
8. Kaeding, W. W., and Butter, S. A., *J. Catal.* **61,** 155 (1980).
9. Lercher, J. A., Rumplmayr, G., and Noller, H., *Acta Phys. Chem.* **31,** 71 (1985).
10. Lercher, J. A., and Rumplmayr, G., *Appl. Catal.* **25,** 215 (1986).
11. Rumplmayr, G., and Lercher, J. A., submitted for publication.
12. Jentys, A., Rumplmayr, G., and Lercher, J. A., submitted for publication.
13. Latzel, J., and Kaes, G., *React. Kinet. Catal. Lett.* **9,** 183 (1978).
14. Topsoe, N. Y., Pedersen, K., and Derouane, E. G., *J. Catal.* **70,** 41 (1981).
15. Young, L. B., Butter, S. A., and Kaeding, W. W., *J. Catal.* **76,** 418 (1982).
16. Mortier, W. J., Sauer, J., Lercher, J. A., and Noller, H., *J. Phys. Chem.* **88,** 905 (1984).
17. Derouane, E. G., and Fripiat, J. G., *J. Phys. Chem.* **91,** 145 (1987).
18. Sanderson, R. T., "Chemical Bonds and Bond Energy." Academic Press, New York, 1971.
19. Gates, B. C., Katzer, J. R., and Schuit G. C. A., "Chemistry of Catalytic Processes." pp. 30 et seq. McGraw-Hill, New York, 1979.
20. Bethell, D., and Gold, V., "Carbonium Ions—An Introduction." pp. 178 et seq. Academic Press, London/New York, 1967.
21. Bezouhanova, C., Dimitrov, C., Nenova, V., Spassov, B., and Lechert, H., *Appl. Catal.* **21,** 149 (1986).
22. Vinek, H., Derewinsky, M., and Lercher, J. A., submitted for publication.
23. Ashton, A. G., Batmanian, S., Dwyer, J., Elliott, I. S., and Fitch, F. R., *J. Mol. Catal.* **34,** 73 (1986).
24. Freude, D., Rumplmayr, G., and Lercher, J. A., unpublished results.
25. Seddon, D., *J. Catal.* **98,** 1 (1986).
26. Ashton, A. G., Barri, S. A. I., and Dwyer, J., *Acta Phys. Chem.* **31,** 25 (1985).
27. Haag, W. O., and Olson, D. H., U.S. Patent 4,117,026.
28. Weisz, P. B., *Pure Appl. Chem.* **52,** 2091 (1980).
29. Wei, J., *J. Catal.* **76,** 433 (1982).
30. Babu, G. P., Hegde, S. G., Kulkarni, S. B., and Ratnasamy, P., *J. Catal.* **81,** 471 (1983).