

Selective alkylation of benzene with isopropyl alcohol over H₃PO₄-ZSM-5 catalyst

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Abstract: A comparative study of the reaction parameters involving the vapour phase isopropylation of benzene with isopropyl alcohol (IPA) over H-ZSM-5 and P-ZSM-5 catalysts was conducted to evaluate the performance of these two catalysts for the industrially important cumene synthesis. Evaluation of catalysts for isopropylation of benzene reaction using isopropyl alcohol as alkylating agent was carried out in a continuous, down-flow, fixed-bed reactor at atmospheric pressure in the temperature range 423-673 K. The influence of SiO₂/Al₂O₃ ratio (60-170) of the zeolite, P content, reaction parameters such as reaction temperature, molar ratio of benzene and isopropyl alcohol, space velocity, and time on stream was studied. Maximum conversion of benzene (12%) was observed at 523 K over 11.0 wt.% P-ZSM-5 (TOS = 3 h). The reaction selectivity on 11.0 wt.% P-ZSM-5-60 (SiO₂/Al₂O₃ = 60) was higher (> 97%; TOS = 6 h) than that of the most active H-ZSM-5 catalyst (74%) at the same temperature. Cumene selectivity over 11.0 wt.% P-ZSM-5-60 was found to stay over 70% with increase in time on stream (up to 16 h) when the feed used contained an IPA/benzene molar ratio 1:8.

Keywords: Benzene; Cumene; Isopropylation; ZSM-5; Heterogeneous.

Introduction

Cumene is an important petrochemical material mainly used for the production of phenol and acetone. In recent years, the worldwide cumene production has been increased because of the fact that more than 90% of phenol production is met by cumene only. Traditionally, it was manufactured by alkylation of benzene with propene using AlCl₃ [1] or phosphoric acid supported on silica [2].

The main drawbacks of these processes were corrosion, the disposal of spent harmful catalysts, formation of some diisopropylbenzenes and chlorinated products. In contrast to 'open' surfaces of solid acids (AlCl₃, H₃PO₄ on silica) on which only cumene and some diisopropylbenzenes and chlorinated products are formed, the alkylation of benzene in ZSM-5 zeolites results in the formation of undesired n-propylbenzene. Čejka and his coworkers [3] presented mechanistic evidence for formation of such an undesired by-product. Mitsui [4] has developed a cumene process in which propene used as benzene alkylating agent was obtained from acetone reduction to isopropyl alcohol and subsequent dehydration. Direct alkylation of benzene with IPA would result in a

more cost effective solution, but the expected negative effects on catalyst performances and lifetime due to the presence of the high water quantities generated in the reaction mixture have to be faced [5-7]. Recently, Das and his coworkers reported a sulfated ZrO₂-TiO₂ catalyst for the isopropylation of benzene with isopropyl alcohol [8].

The objective of the work described here was to investigate the catalytic behavior of the P-ZSM-5 catalysts with different SiO₂/Al₂O₃ ratios and P contents in the commercially important isopropylation of benzene reaction. The catalytic activity of the best catalyst was studied as a function of different reaction parameters. With the best catalyst, excellent selectivity to cumene was obtained. Furthermore, the catalyst can be easily regenerated by thermal treatment without any appreciable decrease in the activity, and the selectivity towards cumene.

Experimental

Materials and Methods

Na-ZSM-5 with different SiO₂/Al₂O₃ ratios was used as the support. These supports with SiO₂/Al₂O₃ ratios of 60-170 were synthesized as described in [9,10]. Materials were well crystallized according to scanning electron micrographs. Crystallite shapes were spherical, about 300 nm in size. Elemental analysis for

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SiO₂/Al₂O₃ ratio in the prepared samples was performed by inductively coupled plasma emission spectroscopy (ICP) [9].

A series of catalysts with varying P contents were prepared by impregnating calculated amounts of H₃PO₄ dissolved in deionized water on Na-ZSM-5 supports. The impregnated catalysts were dried at 110 °C for 12 h and then calcined in air at 500 °C for 6 h. All the impregnated catalysts were pressed into wafers, crushed and sieved to 20-40 mesh before use. The catalysts obtained are identified hereafter by n% P-ZSM-5, followed by the ratio of the SiO₂/Al₂O₃. For instance, 11.0% P-ZSM-5-60 indicates a catalyst with 11.0 wt.% of P, on a support with SiO₂/Al₂O₃ = 60.

Powder X-ray diffraction patterns were recorded on a Phillips diffractometer with Cu K α radiation (40 kV, 30 mA) over a 2 θ range from 5 to 45 degrees. The equipment was connected to a DACO-MP microprocessor using a Diffract-AT software. Single point BET surface area was measured on a Micromeritics Digisorb 2600 system at liquid N₂ temperature using N₂ as adsorbate.

Catalytic activity test

The catalytic activities of the samples were tested for isopropylation of benzene with isopropyl alcohol. The reaction was conducted at 423-673 K under atmospheric pressure in a flow pyrex reactor (i.d. 8 mm) with 0.5 g catalyst. A mixture of benzene and isopropyl alcohol with 8:1 ratio was passed into the reactor at WHSV = 2.5 h⁻¹ in term of isopropyl alcohol. The IPA was dissolved in benzene and the mixture was fed into the reactor with an infusion pump (GENIE, Kent Scientific Corporation). Before each run of the reaction, the catalyst was preheated at 673 K for 2 h in a flow of dry nitrogen (50 ml/min). Usually, the initial 30 min of the reaction was deduced from the reaction time-on-stream (TOS) since material balance during this initial period was poor. After this 30 min of reaction, products from the reactor were collected each hour in an ice/salt trap and were analyzed using a GC (Shimadzu model 14 A) equipped with a (15 m) capillary SE-30 column and a FID detector.

Results

Catalyst characterization

The XRD analysis of the P-ZSM-5 zeolites (Fig. 1) shows that by loading the zeolite with H₃PO₄ and during the calcinations processes, its crystallinity is lost to some extent, possibly by dealumination of the zeolite. This effect is more pronounced in the P-ZSM-5-60, whereas P-ZSM-5-170 shows highest stability.

Surface areas of the catalyst used in this work are on the expected lines and these values are higher for samples with higher silicon content. For instance, 11.0% P-ZSM-5-60 has a surface area of 120 m² g⁻¹, and 11.0% P-ZSM-5-170 has a surface area of 212 m² g⁻¹.

Acidity measurements

The surface acidities of the catalysts used in this work are given in Tables 1 and 2 as the amount of pyridine adsorbed at saturation (μ mol pyridine/g catalyst). We have done these measurements in an attempt to clarify the acid properties of the different catalysts used in this study. It is generally accepted that pyridine is adsorbed on both Brønsted and Lewis acid sites.

We have shown in this study that the H₃PO₄ loaded ZSM-5 catalyst is a more efficient catalyst in comparison with the H-ZSM-5 catalyst. The alkylation of aromatic hydrocarbons with alcohols is a reaction well-characterized as a Brønsted acid catalytic process. Therefore, the alkylation reaction generates water and the Lewis acid sites could be converted to Brønsted acid sites by adsorbing the generated water. However, we think that the H₃PO₄ plays an important role in destroying these new strong Brønsted acid sites. We will talk more about this point in the discussion section.

Table 1, shows the changes in the acidity of the samples in relation to temperature. As the temperature increased, the surface acidity dramatically decreased, since only the strongest acid sites were able to retain the adsorbed pyridine. Table 2, shows the acidity of the catalysts used as a function of the SiO₂/Al₂O₃ ratio which 11.0% P ZSM-5(60) has the highest acid density. Data of these tables shows that there are more Brønsted acid sites in comparison with Lewis acid sites, which are also supported by the IR spectra (Figures 2 and 3). The IR spectra show that the number of both Brønsted and Lewis sites decreased significantly at 573 and 673 K, but the decrease in Brønsted centers was greater.

Effect of the H₃PO₄ load

Improvement of P-ZSM-5 catalyst is made by optimizing the P load. The variation of P loads (4.7-18.9 wt. % P) has different effects on the activity and selectivity of the reaction. Maximum conversion of benzene appears on the catalyst with ca. 11.0 wt. % P, and interestingly, the cumene selectivity also increases with increasing the load up to the same load level for maximum catalyst activity. Therefore, for the comparison of the twenty catalysts prepared (with

different phosphoric acid loadings), the best reaction conditions, were obtained. The alkylation activity (benzene conversion) and selectivity to different products are presented in Table 3. For the zeolite with no phosphoric acid on it, we did not observe any alkylation activity (zero benzene conversion). When the ZSM-5-170 and ZSM-5-120 were loaded with 4.7 to 18.9% P, no benzene conversion was observed; although the isopropyl alcohol conversion was 100%. Therefore, it is clear that these catalysts acted like purely dehydration catalyst with propene and other oligomeric products with 100% selectivity. With increase in aluminum content of the zeolite, the catalyst showed benzene conversion, and the ZSM-5-60 in this regard was best. With increase in P loading

on the Na-ZSM-5-60 to 11.0% the alkylation activity increases, and surprisingly the cumene selectivity reaches its highest value (100%, based on the selectivity to alkylbenzenes). As can be seen from the data of Table 3, loading of P on the Na-ZSM-5-60 by higher and lower values than 11.0%, resulted in decrease in benzene conversion. From these data it seems that there should be a balance between the Brønsted and Lewis acid sites for alkylation of benzene with isopropyl alcohol. It is interesting to note that in the case of ZSM-5-170 and ZSM-5-120, 4.7-18.9 wt. % P loaded samples did not show any alkylation activity, although they contained some Brønsted and Lewis acid sites.

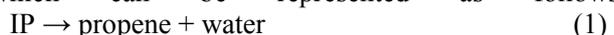
Table 1. Concentration of Brønsted (PyrH⁺) and of Lewis (PyrL) acid sites in the 11.0% P-ZSM-5(60) catalyst at different temperatures, after evacuation.

Catalyst	T (K)	PyrH ⁺ (μmol/g)	PyrL (μmol/g)
11.0% P-ZSM 5(60)	473	306	1.7
	573	60.5	4.8
	673	44.3	1.3

Table 2. Concentration of Brønsted (PyrH⁺) and of Lewis (PyrL) acid sites in 11.0% P-ZSM-5 catalysts at 473 K, after pyridine adsorption.

Catalyst	PyrH ⁺ (μmol/g)	PyrL (μmol/g)
11.0% P ZSM 5(60)	461.1	2.7
11.0% P-ZSM-5(80)	80.8	21.9
11.0% P-ZSM-5(120)	32.4	28.5
11.0% P-ZSM-5(170)	24.3	39.5

The isopropylation of benzene with 2-propanol is a multistep and sequential reaction, the main reactions of which can be represented as follows:



(isomerization of 1,4-

DIPB to 1,3-DIPB),



From the selectivity of different alkylated products, cumene was found to be the major component whereas 1,3,5-triisopropylbenzene as the minor product along with minor quantities of propene and other aliphatic products (for 11.0% P-ZSM-5-60, 1.3%). It may be suggested that the acid strength of 11.0% P-ZSM-5-60 could be ideal to favor reactions 2 and 4, which led to the higher cumene selectivity. The alkylation of benzene over acidic catalyst is an electrophilic

reaction. Therefore, among DIPBs, 1,3 and 1,4-DIPBs can be formed as a primary product preferentially via the isopropylation of IPB. However, in the present study DIPBs were formed only in trace amounts (less than 0.1 %) at the best reaction conditions (TOS = 3h) and TIPB was more predominant in discordance with earlier studies on the zeolites [28-31]. The probable reason for an decrease in the selectivity of IPB and an increase in the selectivity of TIPB may be due to the dealkylation of DIPB to form IPB as a major product (reaction (3) reverse) and DIPB was dealkylated to form propene and IPB, and that propene again alkylated DIPB to form TIPB as a major by product (reaction (5)).

Another significant observation was the no detectable formation of n-propylbenzene which usually appeared as a damaging byproduct. It should be mentioned that Kaeding and Holland [11] have reported considerable

amount of n-propylbenzene above reaction temperature of 523 K in alkylation of benzene with propene over H-ZSM-5 catalyst. However, Siffert and his coworkers cited that the formation of undesired n-propylbenzene can be suppressed on the dealuminated H-Beta zeolite [28]. Also, Lercher and his coworkers [32] have found that after treatment of H-ZSM-5 with H_3PO_4 the concentration of the Brønsted acid sites are decreased and the weakest acid sites are created by dealumination of H-ZSM-5. Wichterlová and Čejka [33] have also considered that the formation of n-propylbenzene is strongly dependent on the dimension and architecture of the channels of the molecular sieve. Formation of this product in the product stream is damaging to the cumene synthesis process.

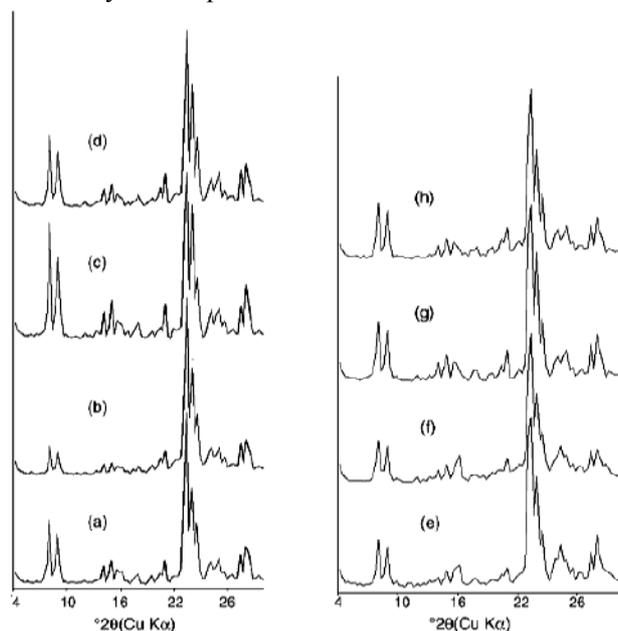


Fig 1: XRD spectra of ZSM-5 and H_3PO_4 /ZSM-5 (2.9 wt% P) with various Si/Al ratio: (a) ZSM-5-60, (b) H_3PO_4 /ZSM-5-60, (c) ZSM-5-80, (d) H_3PO_4 /ZSM-5-80, (e) ZSM-5-120, (f) H_3PO_4 /ZSM-5-120, (g) ZSM-5-170, and (h) H_3PO_4 /ZSM-5-170.

Influence of the reaction temperature

Temperature has a significant effect in the product distribution for isopropylation of benzene over 11.0% P-ZSM-5-60. The results are represented in Table 4, which is clear that with increase in reaction temperature the benzene conversion increases up to 523 K. Also, the cumene selectivity is increased with temperature and reaches to its maximum value of 97.3% (with TOS = 6 h) at 523 K, and at the same time the di- and especially triisopropylbenzene selectivity decreased. However, it has been reported that this

might be due to transalkylation of DIPBs and 1,3,5-triisopropylbenzene to form cumene [12]. Furthermore, at higher temperature (above 523 K) the cumene selectivity became fairly steady and conversion of benzene was decreased. These results indicate that dealkylation of DIPB (reaction (3) reverse) as well as alkylation of IPB (reaction (2) reverse) was observed at higher temperatures (above 523 K) and probably showed a thermodynamic equilibrium between conversion of benzene and selectivity to IPB and DIPB. Similar types of observation are reported in earlier literature [5,12,20]. As shown in Table 4, below 523 K the formation of DIPBs and triisopropylbenzene were observed in the product stream. But with increase in reaction temperature and reaching to the optimum temperature, not only the TIPB disappears but also 1,3- and 1,4-diisopropylbenzenes reach to their lowest amounts (Figure 3). 1,4-DIPB was predominant than 1,3-DIPB at lower temperatures (below 523 K); however 1,3-DIPB was predominant over 1,4-DIPB at higher temperatures (above 523 K). These changes may be due to the fact that the alkylation of IPB (reaction (3)); competes favorably with transalkylation of DIPB with benzene to IPB (reaction (4)). Thermodynamically stable 1,3-DIPB is more favorable than 1,4-DIPB isomers at temperatures above 523 °C. It is also observed by Waghmode et al. [20] that 1,4-DIPB isomerizes to 1,3-DIPB isomer above 498 K. However, in the present case and in agreement with the data reported by Das et al. [12], it should be mentioned that 1,3-DIPB is quite stable on 11.0% P-ZSM-5-60 catalyst up to 673 K and transformation of 1,4-diisopropylbenzene to 1,3-diisopropylbenzene (reaction (3)) or the disproportionation of IPB to benzene and DIPB (reaction (7)) is favorable. The final point that might be interesting to note is that by increasing the temperature from the optimum temperature (523 K) as mentioned before, 1,3-DIPB selectivity increases and cumene selectivity decreases. As this data shows, the greater the E_{act} , the greater the effect of a given change in temperature. Taking this into consideration, one could explain the higher apparent activation energy for isopropylation of benzene.

Influence of benzene: isopropyl alcohol molar ratio

The influence of benzene to isopropyl alcohol molar ratio in the feed on the conversion and product distribution was studied at 598 K. The results are represented in Table 5. For the ratio lower than 6, conversion of IPA was under 100 mol%. When the ratio of benzene/isopropanol decreases, the alkylation of benzene is reduced, while the oligomerization and

cracking reaction, which lead to the formation of small alkanes and alkenes as well as the formation of DIPBs and TIPB, are favored (Table 5). These results are in agreement with previously reported work [11]. However, oligomerization of propene is an important reaction over Brønsted acid sites and deactivates fast the dehydration sites owing to the formation of oligomers that causes the low conversion of IPA at low B/IPA molar ratio. For ratio higher than 3, conversion of IPA remained at about 100 mol%. The same type of observation was also reported by Sasidharan et al. [13] over NCL-1 large pore zeolite for isopropylation of benzene and by Reddy et al. [6] for isopropylation of toluene over H-beta zeolite. It is clear that the surface of the catalyst is moderately hydrophilic ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$) and it has more tendencies to absorb isopropyl alcohol compared to benzene. If we accept that the isopropylation of benzene with isopropyl alcohol is a multistep and sequential reaction network the main reactions of which are the conversion of isopropyl alcohol to propene, and alkylation of benzene with propene (propene was also detected at low B/IPA molar ratio), therefore increase in benzene to isopropyl alcohol ratio increases the possibility of interaction of benzene with the catalyst surface resulting higher selectivity of alkylated products. As expected, the selectivity of IPB increased with the increase in B/IPA molar ratio, and accompanied with the decrease in the selectivity of DIPBs and TIPB. It is clear that the decrease in the selectivity for DIPBs and TIPB is due to the fact that transalkylation of these products was more favored with the increase of B/IPA ratio. Therefore, under the best reaction conditions, B:IPA molar ratio of 8 was selected to get high selectivity towards cumene.

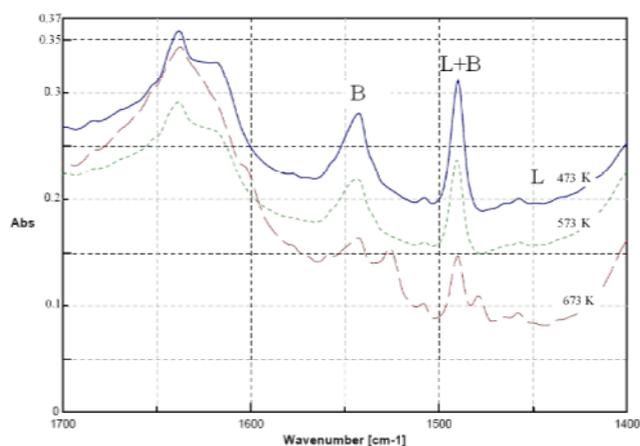


Fig. 2: FTIR spectra of pyridine adsorption at different temperatures over 11.0 % P-ZSM-5(60) catalyst, after evacuation.

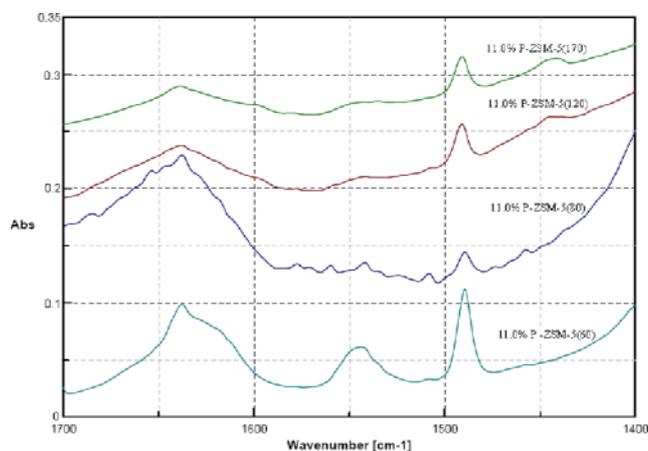


Fig. 3: IR spectra of adsorbed pyridine over 11.0% P-ZSM-5 having various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Pyridine was adsorbed at 473 K. The samples were preheated at 673 K for 2 h in a flow of dry nitrogen (50 ml/min) before IR measurements.

Effect of time-on-stream

Figure 5 illustrates the effect of time on stream on catalytic activity and product distribution studied at 523 K over 11.0 wt.% P-ZSM-5-60 for more than 15 h. The conversion of benzene remained approximately steady for three hours, and then decreased with time slowly. The slow decrease in the activity of the catalyst with time on stream might be due to the temperature of reaction, and probably mildness of the acid used. Let us compare results from Tables 3 and 4 obtained for the catalyst 11.0 wt.% P-ZSM-5-60 under similar conditions but for different TOS. For TOS = 3 (Table 3), only cumene was observed in the product, whereas for TOS = 6 (Table 4) diisopropylbenzenes (DIPBs) isomers were detected beside cumene. This suggests the influence of selective sorption and retention of DIPBs and especially 1,3-DIPB inside the pores of the catalyst, because of its sieving effect, at least for a period of time that the concentration of cumene on the surface of the catalyst increases and alkylation of it is in competition with alkylation of benzene. Therefore, we observe an unusual decrease in the benzene conversion for a period of time (TOS = 6-10 hrs) (Fig. 5). Probably by increasing the concentration of the DIPBs and TIPB on the surface of the catalyst, these products could participate in the transalkylation reactions with benzene (reactions 4 and 6). Therefore, the cumene production should stay approximately steady for a long period of time.

Our previous study on this type of catalyst [10] has shown that strong Brønsted acid sites have been removed by phosphoric acid treatment. Therefore, we believe that the alkylation of benzene with isopropyl

alcohol or propene, as an acid catalyzed reaction, readily takes place on the moderate acid sites. The catalyst was found to retain its activity for the desired reaction for more than 15 h. Physical inspection of the catalyst displayed its color change to black suggesting

coke formation. This proves that the catalyst deactivation was mainly due to coke formation on the surface active sites during alkylation, and they could be removed completely by oxidizing the used catalyst at 823 K for 5 h under the flow of air.

Table 3. Effect of the H₃PO₄ loading and Si/Al ratio on conversion and selectivity for isopropylation of benzene with isopropyl alcohol over ZSM-5.^a

Catalyst	Conversion (mol%)		Selectivity to alkylbenzenes (mol%)			Undesired aliphatics (mol%)
	B	IPA	Cumene	DIPBs	TIPB	
4.7% P-ZSM-5 (60)	10.4	100	94.5	trace ^b	5.5	<1
7.9% P-ZSM-5(60)	8.4	100	100	-	-	11
11.0% P-ZSM-5(60)	12 ^c	100	100	-	-	1.3
14.2% P-ZSM-5(60)	7.6	100	90.3	trace	9.7	3.3
18.9% P-ZSM-5(60)	8.2	100	91.8	trace	8.2	4
4.7% P-ZSM-5(80)	10.2	100	87.1	trace	12.9	>1
7.9% P-ZSM-5(80)	12.1	100	94.2	trace	5.8	1
11.0% P-ZSM-5(80)	8.6	100	99.9	-	trace	4
14.2% P-ZSM-5(80)	8.0	100	99.9	-	trace	12
18.9% P-ZSM-5(80)	7.6	100	100	-	-	13
4.7% P-ZSM-5(120)	0	100	-	-	-	100
7.9% P-ZSM-5(120)	0	100	-	-	-	100
11.0% P-ZSM-5(120)	0	100	-	-	-	100
14.2% P-ZSM-5(120)	0	100	-	-	-	100
18.9% P-ZSM-5(120)	0	100	-	-	-	100
4.7% P-ZSM-5(170)	0	100	-	-	-	100
7.9% P-ZSM-5(170)	0	100	-	-	-	100
11.0% P-ZSM-5(170)	0	100	-	-	-	100
14.2% P-ZSM-5(170)	0	100	-	-	-	100
18.9% P-ZSM-5(170)	0	100	-	-	-	100

^a Reaction conditions: catalyst weight = 0.5 g, reaction temperature = 523 K, Flow rate = 0.02 (ml min⁻¹), TOS = 3 h, WHSV = 2.5 h⁻¹, and B:IPA molar ratio = 8. Legends: B, benzene, IPA, isopropyl alcohol, DIPB, diisopropylbenzene, TIPB, triisopropylbenzene.

^b Less than 0.1%.

^c theoretical maximum conversion of benzene based on B/IP = 8 is 12.5%.

Table 4. Effect of reaction temperature on the selectivity for isopropylation of benzene on 11% P-ZSM-5-60.^a

Reaction temperature (K)	Conversion (mol%)		Selectivity (mol%)			
	B	IP	Cumene	1,3-DIPB	1,4-DIPB	1,3,5-TIPB
423	6.6	98	57.4	11.3	27.1	4.2
473	11.1	98	75.2	24.8	-	-
498	9.6	100	86.4	1.7	2.6	9.3
523	11.5	100	97.3	1.6	1.1	-
548	6.1	100	95	5	-	-
573	5.2	100	96.4	3.6	-	-
623	5.8	100	96.3	3.7	-	-
673	8.2	100	92	8	-	-

^a Reaction conditions: catalyst weight = 0.5 g, Flow rate = 0.02 (ml min⁻¹), TOS = 6 h, WHSV = 2.5 h⁻¹, and B: IP molar ratio = 8.

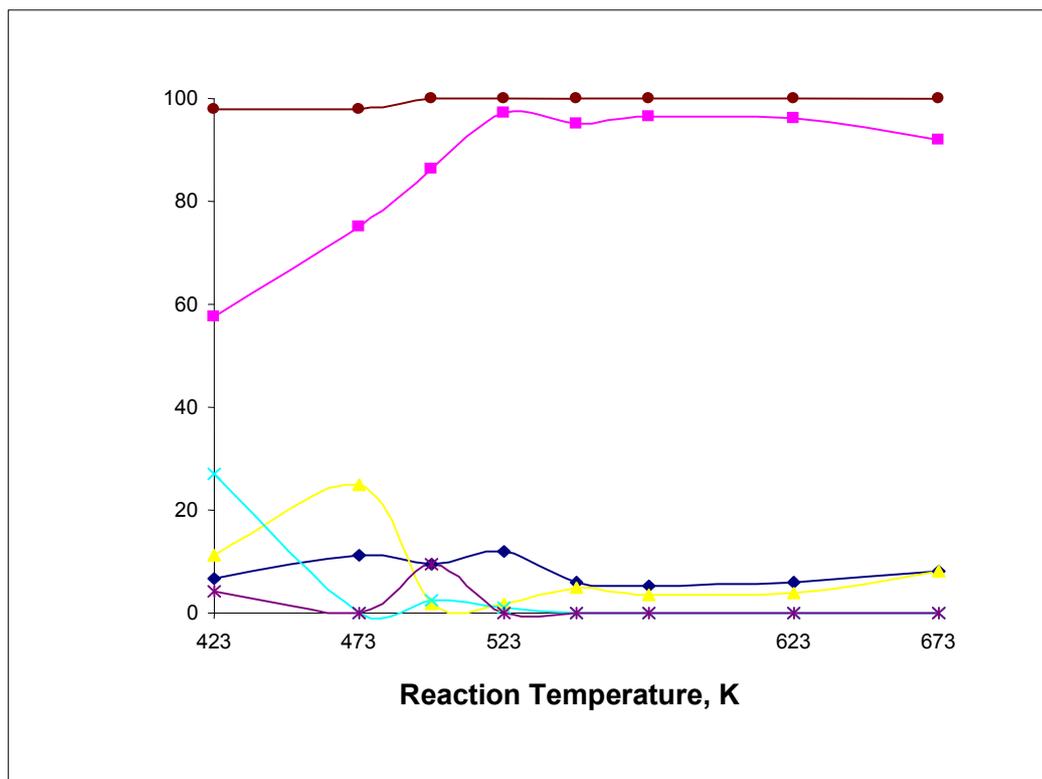


Fig. 4: Isopropylation of benzene with isopropyl alcohol over 11.0 wt.% P-ZSM-5-60. Effect of reaction temperature on the distribution of 1,3-DIPB, 1,4-DIPB and 1,3,5-TIPB selectivity. Reaction conditions: catalyst weight = 0.5 g, WHSV = 2.5 h⁻¹, TOS = 6 h, and benzene to isopropyl alcohol molar ratio = 8.

Table 5. Effect of benzene to isopropyl alcohol molar ratio on conversion and selectivity for isopropylation of benzene with isopropyl alcohol over 11% P-ZSM-5-60.

Benzene to isopropyl alcohol molar ratio	Conversion (mol %)		Selectivity (mol%)	
	B	IPA	Cumene	DIPBs + TIPB
1	2.6	40	15.8	84.2
2	4.2	64	9.6	90.4
3	6.2	78	20	80
6	6.5	100	67	33
8	5.7	100	96.4	3.6
9	5.8	100	83.4	16.6
10	6.2	100	66.5	33.5

Reaction conditions: catalyst weight = 0.5 g, reaction temperature = 598 K, flow rate = 0.02 (ml min⁻¹), TOS = 6 h, WHSV = 2.5 h⁻¹.

Discussion

By treating the ZSM-5 zeolite with phosphoric acid several authors [27-31] proposed a model in which it is assumed that the bridged OH groups between Si and Al atoms are replaced by H₂PO₄ groups. The substitution of the Brønsted acidic hydroxyl groups by the H₂PO₄ groups implies different consequences on

the strength and density of the Brønsted acid sites: (1) strong Brønsted acid sites are converted into weak ones, and it is clear that the resulting terminal hydroxyl groups have a lower acid strength than the bridged hydroxyl groups. It should also be noted that the weak Brønsted acid sites are possibly AlOH groups on extra-lattice alumina regenerated by dealumination during calcinations steps or SiOH groups of hydroxyl nests

formed by the same process. (2) The number of (weak) acid sites increased. (3) This substitution should not change the polar nature of the surface. (4) This is the question that we asked ourselves with these findings: what happens if we suspend the zeolite in an aqueous solution containing H_3PO_4 , and evaporating the mixture slowly? Presumably, in this solution we have different types of $(\text{H}_y\text{PO}_4^{y-})_m$ units with different lengths. The small units probably could penetrate into the pores and the long units have to deposit on the external surface of the zeolite. If the phosphate units are being deposited around the mouths of the pores, they might block the entrances of the pores or in the best case the phosphate units may have decorated the modification of the external surface of the ZSM-5 zeolite, and then loading the zeolite with phosphoric

acid one does not block the entrances of the pores [10]. It could be interesting to study any correlation between the activity of the catalyst and the density of the weak Brønsted acid sites. As shown in Table 3, the ZSM-5 zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 120 and 170 do not show any activity in regard to the alkylation reaction, but the zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 80 and 60 show approximately the same activity in the alkylation reaction. We attribute these differences in activity to the density of the weak Brønsted acid sites and probably weak Lewis acid sites. As shown in Tables 1 and 2, the concentration of Brønsted acid sites is much higher than the Lewis acid sites and the zeolite ZSM-5(60) is superior in comparison with the other catalysts used in this work.

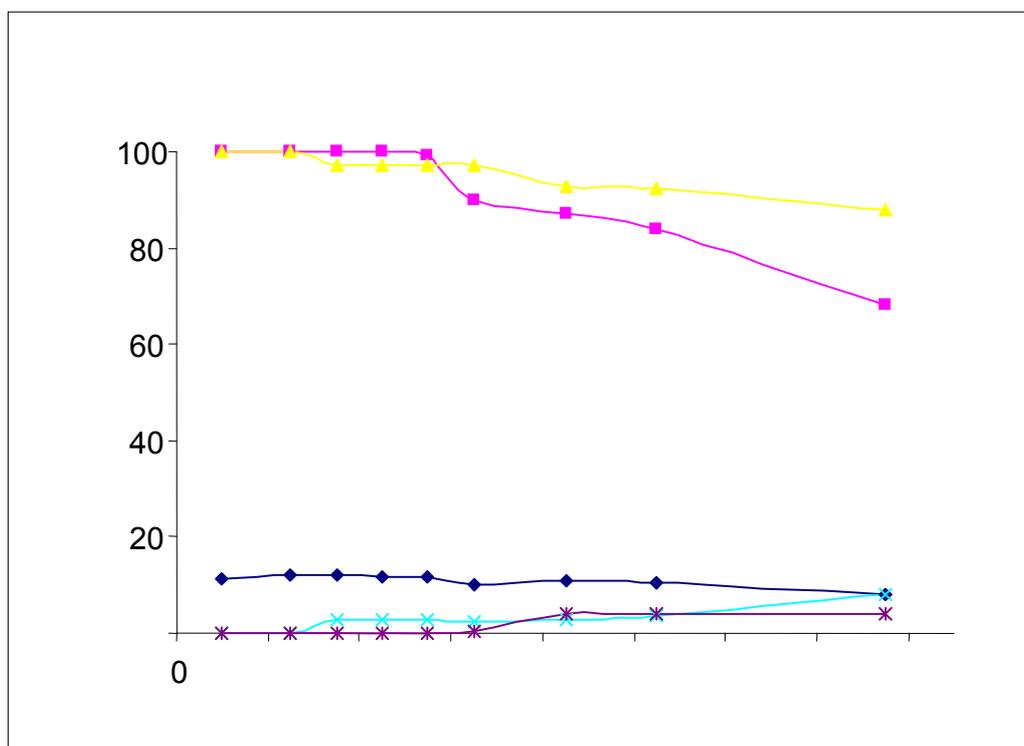


Fig. 5: Isopropylation of benzene with isopropyl alcohol over 11.0 wt.% P-ZSM-5-60. Effect of time-on-stream on the distribution of cumene, 1,3-DIPB, 1,4-DIPB and 1,3,5-TIPB selectivity. Reaction conditions: catalyst weight = 0.5 g, reaction temperature = 523 K, WHSV = 2.5 h⁻¹, and benzene to isopropyl alcohol molar ratio = 8.

By treating the ZSM-5 zeolite with H_3PO_4 , the areal activity of the catalyst and the theoretical surface area and accessible pore volume decreased which indicate that the diffusional constraints may cause additional decrease in activity. Therefore, the lower activity of the 14.2 and 18.9 wt.% P-ZSM-5-60 in comparison with the 11.0 wt.% P-ZSM-5-60 may be in part due to the diffusional constraints. Also, the samples with 14.2

and 18.9 wt.% P probably have a significant fraction of extra-framework aluminum oxide, which causes a subtle decrease in the sorption capacity of the catalyst and, as a result a decrease in activity for alkylation reaction. Although, the higher activity of the 11.0 wt.% P-ZSM-5-60 in comparison with the 4.7 and 7.9 wt.% P-ZSM-5-60 might show that other factors in addition to diffusional constraint should be involved in the

activity of the catalyst. Therefore, the catalytic activity would not be totally chemical and there would be a contribution due to the diffusion of the reactants and products in the channels of zeolite. Perego et al. have studied the possible diffusion limitations of cumene and of DIPBs by computational calculations [19]. However, in these calculations they did not consider the presence of large amount of silanols. It is clear that the different transport modes of organic molecules can affect the activity and selectivity of reaction, consequently the activation energy of the reaction.

As suggested by Sugi et al. [20], the alkylation of benzene with isopropyl alcohol is a multistep reaction in which in the first step, the isopropyl alcohol dehydrates to propene and water. The water produced in this step could be harmful, because it could regenerate the strong Brønsted acid sites. However, due to a high excess of benzene only a small amount of water is formed. Perhaps one important role that phosphoric acid plays in this new catalyst (11.0 wt.% P-ZSM-5-60) is that it prevents the produced water from regenerating the strong Brønsted acid sites and decreasing the selectivity of the catalyst. The resulted propene could oligomerise in the dehydration sites (undesired reaction) or alkylate the benzene molecule in the alkylation sites and probably the role of the Brønsted acid site is to protonate the propene molecule and to produce the isopropyl carbenium ion. Then, the rate-determining step may be the addition of the isopropyl carbenium ion or desorption of the resulting product. The final step would be the cleavage of the proton from the activated complex, which is unlikely to be the rate determining step.

Probably by examining the Fig. 5 carefully, one could predict that the isopropyl alcohol dehydration and benzene alkylation takes place on different sites on the surface of the catalyst. After about 16 h TOS, the dehydration sites lose more than 20% of its activity, while the process still exhibits approximately the same activity for benzene alkylation. These sites will not deactivate in comparison with the dehydration sites, because of high monoalkylation selectivity and low diffusion constraint of cumene. However, oligomerization of propene is an important reaction over Brønsted acid sites and it plays an important role in deactivation of dehydration sites.

With respect to the increase in selectivity to cumene obtained on 11 wt.% P-ZSM-5-60 we think that the selectivity to cumene increased with decreasing the concentration of the strong Brønsted acid sites. Also the high cumene selectivity may be caused by a very slow rate of diffusion of DIPBs and TIPB. Because of

diffusional constraints of these products and high ratio of benzene to isopropyl alcohol, the process favors trans-alkylation of benzene with DIPBs and TIPB to produce cumene.

In this work, in addition to P-ZSM-5 catalysts we have conducted this reaction on H-ZSM-5 for comparison (Table 6). We think that all type of acid sites are present in H-ZSM-5, but in the phosphoric acid treated ZSM-5 there are no strong Brønsted acid sites. The results represented in Table 6, confirm that the H-ZSM-5 catalyst has lost its selectivity and by increasing the temperature it becomes worse. Therefore, one could judge on this point that this alkylation reaction does not need strong Brønsted acid sites to perform with high selectivity.

Vapor-phase isopropylation of benzene with isopropyl alcohol has been previously tested over MCM-41/ γ -Al₂O₃ [5], sulfated titania [21], H-beta and SAPO-5 catalysts [22], ITQ-7 zeolite [23], β -zeolite-based catalyst [7], sulfated ZrO₂-TiO₂ mixed-oxide catalyst [8], cesium substituted dodecatungstophosphoric acid on K-10 clay [24], AFI aluminophosphate molecular sieves [20], and large pore aluminophosphate molecular sieves [25]. We have also compared our data with the previously reported data on the other catalysts (Table 7). This new catalyst in comparison with the other reported catalysts up to now has almost the best selectivity.

Conclusion

In the alkylation of benzene with isopropyl alcohol, 11.0% P-ZSM-5-60 showed better reactivity and selectivity over the previously reported catalysts. The selectivity of IPB is over 95% for this new catalyst. The highest conversion (about 12%, based on the molar ratio of B:IP=8) was achieved for 11.0% P-ZSM-5-60. The result represented in this work suggests that a mild acidity sites are required for high selectivity. These moderate acid sites have enough acid strength for the alkylation of aromatic hydrocarbons. Finally, it deserves to be remarked that vapor phase reaction conditions stem out as the best suited for benzene alkylation with IPA while, in the case of propene, liquid phase conditions are the preferred ones, due to a quite higher catalyst deactivation usually experienced in vapor phase.

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