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ALKYLATION OF PHENOL WITH METHANOL OVER AlPO AND SAPO MOLECULAR SIEVES

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This is the first preliminary report on alkylation of phenol with methanol over SAPO-5, SAPO-11 and SAPO-34 as well as over AlPO-5 molecular sieves at various temperatures. It has been established that on SAPO-5 only anisole, whereas on other molecular sieves cresols and anisole are simultaneously produced. On SAPO-34 and AlPO-5 formation of other cracking products were also observed. The selectivities generally determined by Broensted acidity of the molecular sieves, are also affected by other factors such as pore size and geometry. In the case of the AlPO-5 having initially high alkylation activity, a different mechanism is likely operative.

1. Introduction

Alkyl phenols being highly reactive aromatic products are used as intermediates for pharmaceuticals and agrochemicals. Alkylation of phenol over oxides, mixed oxides and zeolites produces O- and C-alkylated compounds [1–11]. Selectivity of the reaction depends on the acid-base properties of the catalysts [2,3]. In the case of vanadia-chromia system correlation was observed between the acidity and selective C-alkylation of phenol to produce 2,6-xylenol [4,5]. Several studies on the alkylation of phenol over zeolites reveal that the selectivity of the products varies with the strength of the acidic sites and the nature of the zeolite framework structure [7,8]. The product distribution also depends on the temperature of the reaction [4,10].

Aluminophosphates (AlPO) and silicoaluminophosphates (SAPO) are two new classes of molecular sieves with resemblance to synthetic zeolites [12,13]. Even though the AlPO lattice is neutral, the surface hydroxyl groups of Al-OH and P-OH may possess some residual hydrophilic and acidic character. SAPOs in general can be classified as mildly acidic with unique shape selective properties.

They are more active than AlPOs but are generally less active than their zeolite analogues. Although the structural details of AlPOs and SAPOs are well documented [14] these novel molecular sieves are not well exploited for their catalytic properties. In this preliminary communication vapour phase alkylation of phenol over AlPOs and SAPOs will be reported and the activity and selectivity patterns are discussed.

2. Experimental

SAPO-5 (NCL, Pune), SAPO-11, SAPO-34 and AlPO-5 (all from Union Carbide) are used in this study.

Alkylation of phenol with methanol was carried out in a tubular glass reactor (12 mm ID) at atmospheric pressure in the temperature region 523–573 K. About 0.22 g catalyst in powder form was loaded into the reactor and was activated at 723 K overnight in nitrogen flow. A mixture of phenol-methanol (molar ratio = 1 : 5) was pumped at 3–4 cm^3 h^{-1} with the help of a peristaltic pump into the reactor. WHSV with respect to phenol is 0.0623 mole h^{-1} g^{-1}. The liquid products collected at half an hour interval during the reaction were analyzed by gas chromatograph with 3% SE-30 column. The products were identified to be mainly anisole and a mixture of cresols. The meta and para cresols could not be separated and reported as mixture. The percentage composition reported is based on methanol free phenol.

3. Results and discussion

Alkylation of phenol on SAPOs and AlPO in terms of phenol conversion is low and decreases with time-on-stream indicating deactivation of the catalysts both at 523 and 573 K. Although it is difficult to set up an absolute sequence of activity due to the deactivation to various extent, SAPO-5 appears to be the least active sample as illustrated in fig. 1. The high initial activity of AlPO-5 is unexpected.

Change of selectivities for anisol and o-cresol with respect to time-on-stream is shown in figs. 2 and 3. It can be seen that anisole selectivity decreases and o-cresol selectivity increases with time.

Closer insight into the selectivity of phenol alkylation indicates that on SAPO-5 and SAPO-11 only anisol and anisol plus o-cresol, respectively, are formed while on SAPO-34 and AlPO-5 m- and p-cresols and other aromatics are also observed. This is presented in table 1 at 523 and 573 K. Anisole seems to be the major product over weak acid sites and cresols are formed predominantly on medium to strong acid sites [7]. Since Broensted acidity increases in the order of SAPO-5 < SAPO-11 < SAPO-34 [14] cresol is already formed on SAPO-11 possessing higher acidity and narrower channel (12 vs 10 member channel on

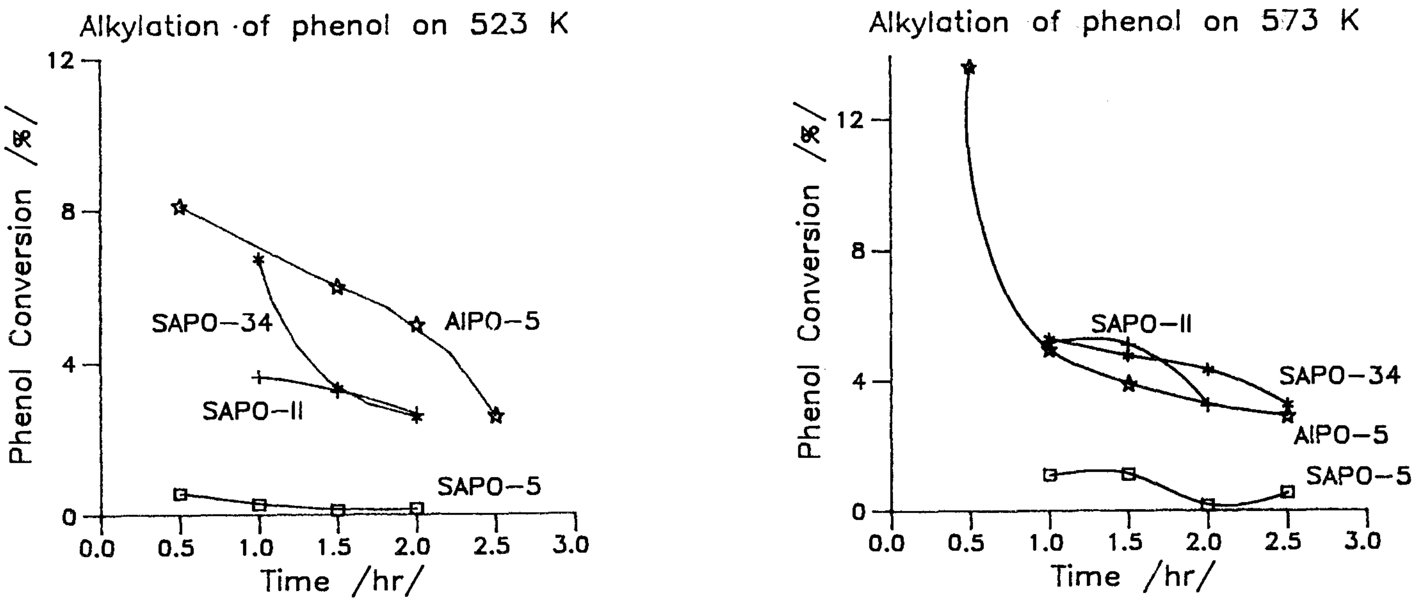

Fig. 1. Phenol conversion in percent vs time on stream (h) on various molecular sieves. (a) at 523 K, (b) at 573 K.

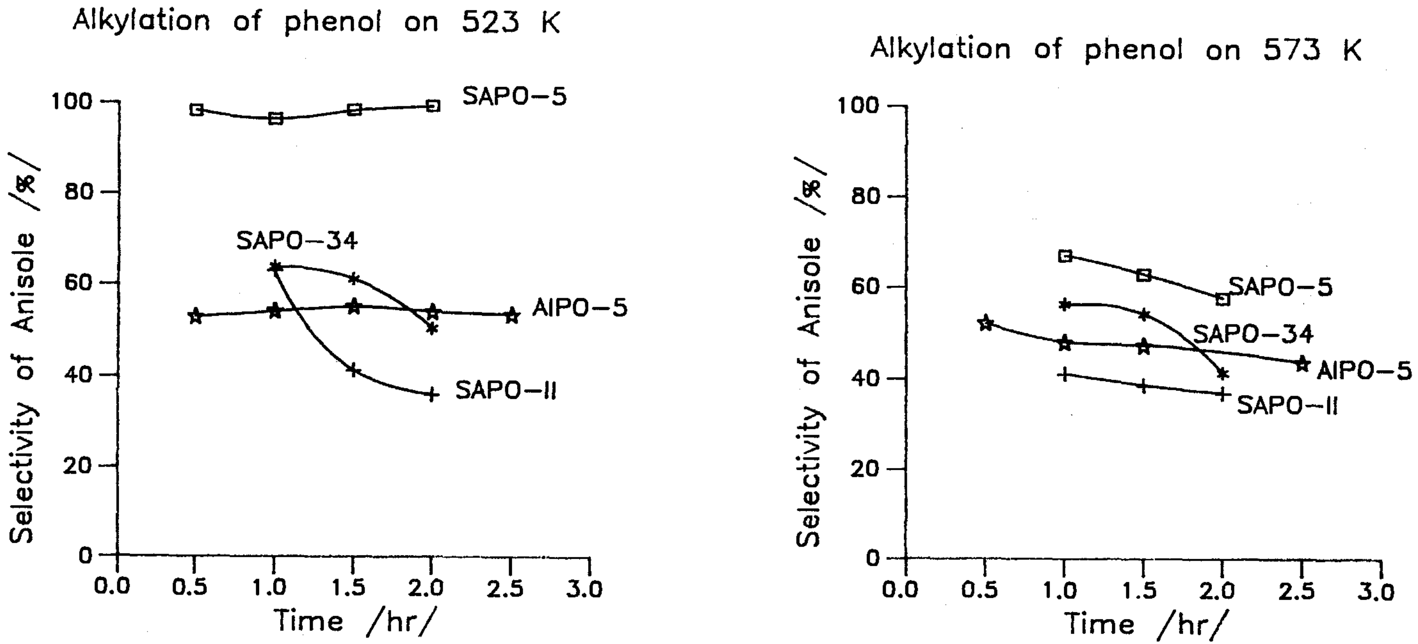

Fig. 2. Selectivity of anisole vs time in alkylation of phenol over various molecular sieves. (a) at 523 K, (b) at 573 K.

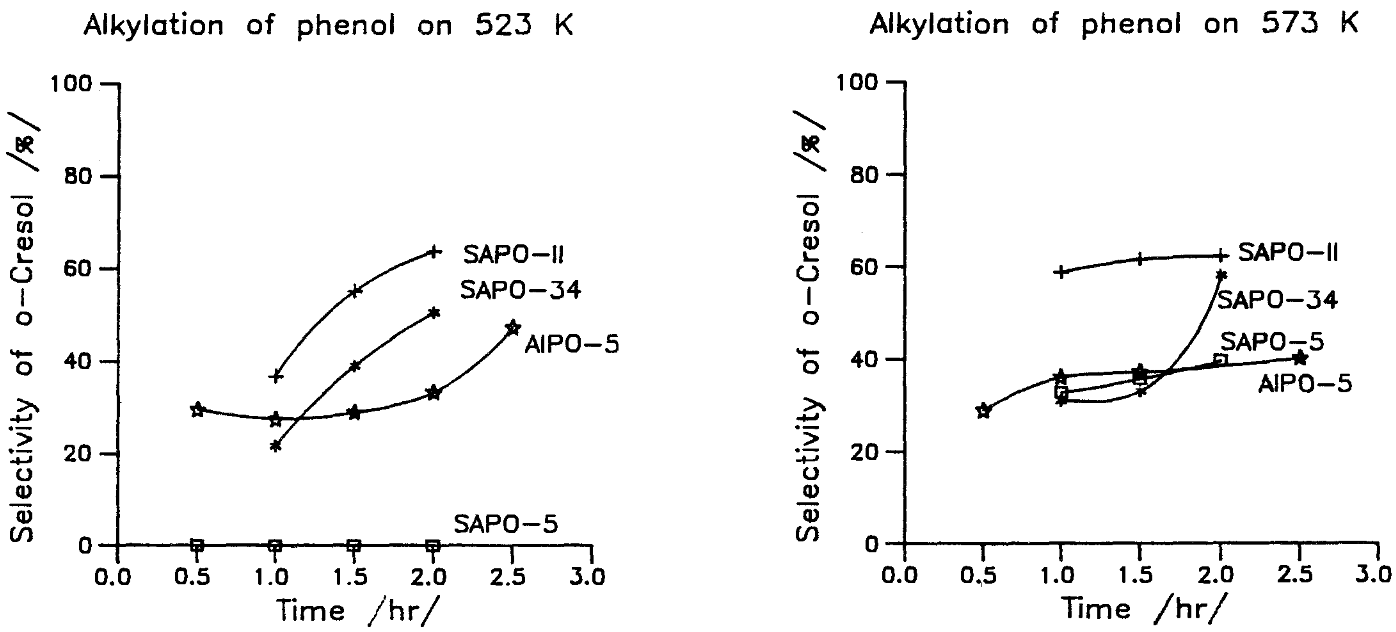

Fig. 3. Selectivity of o-cresol vs time in alkylation of phenol over various molecular sieves. (a) at 523 K, (b) at 573 K.

Table 1
Alkylation of phenol over SAPO and AlPO

Catalyst	Selectivity/%		
	anisole	o-cresol	others *
At 523 K			
SAPO-5	> 98	–	–
SAPO-11	63	37	–
SAPO-34	64	22	14
AlPO-5	54	28	18
At 573 K			
SAPO-5	67	33	–
SAPO-11	41	59	–
SAPO-34	56	31	13
AlPO-5	48	36	16

* m,p-cresols and aromatics. Conversion based on 1st hour product analysis.

SAPO-5 vs SAPO-11, respectively). From the fact that in these two molecular sieves the anisol/cresol ratio decreases with increasing temperature, we may suggest cresol formation also in secondary reactions [15]. As SAPO-34 has a chabazite structure which is not capable to accommodate a benzene ring with its long axis, we should assume that alkylation occurs also at the exterior surface of SAPO-34 as was also reported for other zeolites like H-Ferrierite and H-ZSM-22 [16].

The acidity functions measured by n-butane cracking on the AlPO and SAPO sieves indicated [17] that AlPO-5 has the weakest acidity ($k_A \approx 0.05$) while SAPO-5, SAPO-11 and SAPO-34 have stronger acidity ($k_A \approx 0.2$–16, 0.5–3.5 and 0.1–7.6, respectively). AlPO-5 has a large pore (12 member ring) with few Broensted acid sites and the majority of acid sites is associated with Lewis centres [18]. Tanabe [19,20] already discussed that the benzene ring coupled to the Lewis sites via the phenolic oxygen, strongly interact with the surface, thus, there is high chance for C-alkylation. This may be the possible explanation why AlPO-5 has a low selectivity for anisol formation. The stronger interaction is also revealed in formation of cracking products which is not the case for SAPO-5 and SAPO-11.

We may not exclude the secondary importance of pore geometry, either. Jacobs et al. [15] already emphasized the effect of pore structure in phenol alkylation. Thus, the bimolecular reactions being responsible for all primary reactions, are suppressed in penatsil as compared to Y zeolites. This phenomenon is supported by the selectivity values presented in table 1, which shows a decreasing anisole selectivity in the sequence of SAPO-5 > SAPO-11 $\geqslant$ SAPO-34. Similar effect can be observed by deactivation which is probably due to the pore narrowing effect of the carbonaceous deposits inside the channels. This is the most plausible explanation for the increase of cresol selectivity revealed in longer time-on-stream experiments.

The large difference in anisole selectivities measured on AlPO-5 and SAPO-5 both having large pores but AlPO-5 having low Broensted acidity, requires further investigations which are in progress.

The collaboration of acidity and pore structure in the phenol alkylation can be observed also in other systems. Here the recent work of Hathaway and Davis on alkylation of toluene with methanol over sodium X and Y zeolite families can be mentioned [21]. By substituting sodium with cesium not only the acidity, but also the pore size was changed and the alterations in the selectivity values were reflected in the same way as we reported in the present paper.

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