

VAPOUR PHASE AMMONOLYSIS OF PHENOL ON ZSM-5-TYPE CATALYSTS

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ABSTRACT

Catalytic activity of copper, sodium and decationated form of ZSM-5 catalyst for vapour phase ammonolysis of phenol is investigated. The activity of all three forms of catalyst is comparable. Acidities are measured by temperature programmed desorption of ammonia. Calculated values of activation energies are low indicating that the reaction is diffusion controlled.

INTRODUCTION

CATALYTIC activity of zeolites for aromatic nucleophilic substitutions has been recently demonstrated by Warawdekar and Rajadhyaksha¹. They reported vapour phase ammonolysis of phenol and anisole on zeolite Cu-Y. Warawdekar *et al*² further studied ammonolysis of anisole on copper and the decationated form of zeolites X and Y and ZSM-5-H. Ammonolysis of anisole was significantly faster than that of phenol which indicated that the dissociation of the leaving group is likely to be the rate controlling step. Zeolite X and Y displayed similar activity for ammonolysis of anisole giving mainly aniline as the product and small quantities of cresols as side products. Zeolite ZSM-5 showed very different catalytic behaviour in the reaction of anisole and ammonia leading to formation of phenol and methylamine. This observation indicated that ZSM-5 is probably not active in ring substitution reactions. To investigate this aspect further, the catalytic activity of ZSM-5 for ammonolysis of phenol is reported on copper, sodium and decationated form of zeolite ZSM-5.

EXPERIMENTAL

Zeolite ZSM-5 was obtained from an industrial source. To prepare sodium and copper exchanged form, 10 g of catalyst was contacted with 100 ml of 1 molar solution of respective nitrates and the slurry was stirred for eight hours at room temperature. The catalyst was filtered and the above exchange procedure was repeated

three times. The catalyst was then washed by distilled water until free of cation. The decationated form was prepared by exchanging the zeolite with 1 molar ammonium nitrate solution in the above manner and the ammonium cations were decomposed in a stream of air at 500°C for six hours.

The reaction was carried out in a stainless steel integral reactor, employing 7.5 g of catalyst in the form 1 × 10 mm extrudates. The reaction was studied in the temperature range of 415 to 475°C. The product samples were collected periodically and analysed by gas chromatography. The analysis was carried out on a Perkin Elmer Sigma 3B gas chromatograph using 2.7 m column containing 15% Carbowax 20 M on Chromosorb W as the stationary phase. The absence of external mass transfer limitations was ensured by measuring the conversion at constant W/F (W is the weight of catalyst in g and F is the feed rate of phenol in g. mol/hr) but at different mass velocities.

The acidity of the catalysts was measured by temperature programmed desorption (TPD) of ammonia. The catalysts in the powder form were saturated with ammonia at room temperature and reversibly adsorbed ammonia was desorbed in the stream of nitrogen. TPD was then studied by increasing the temperature of the catalyst at the rate of 10°C/min.

RESULTS

Figure 1 shows the variation of conversion of phenol with time on stream on ZSM-5-Cu for

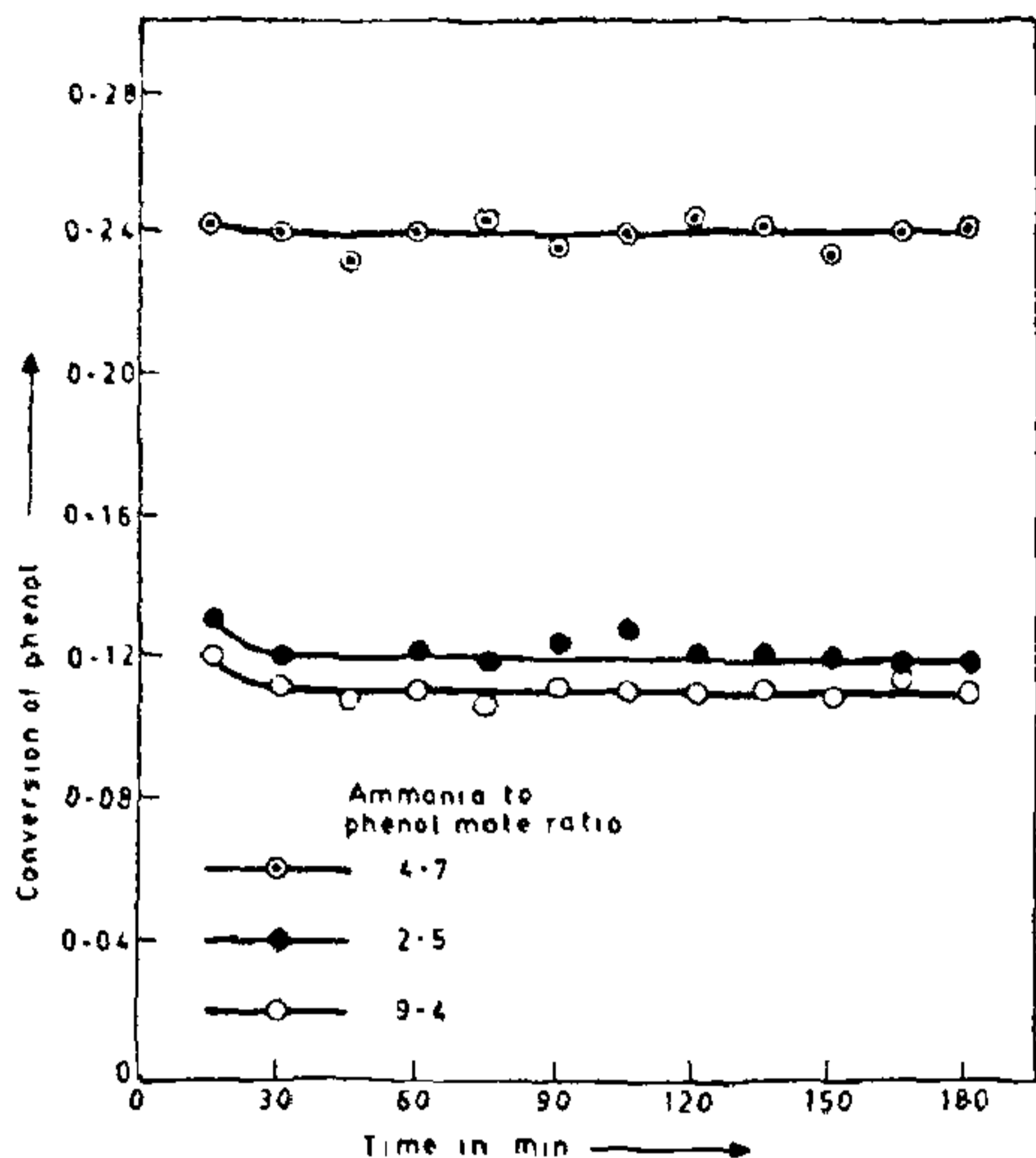


Figure 1. Effect of time and Mole ratio on activity of ZSM-5-Cu.

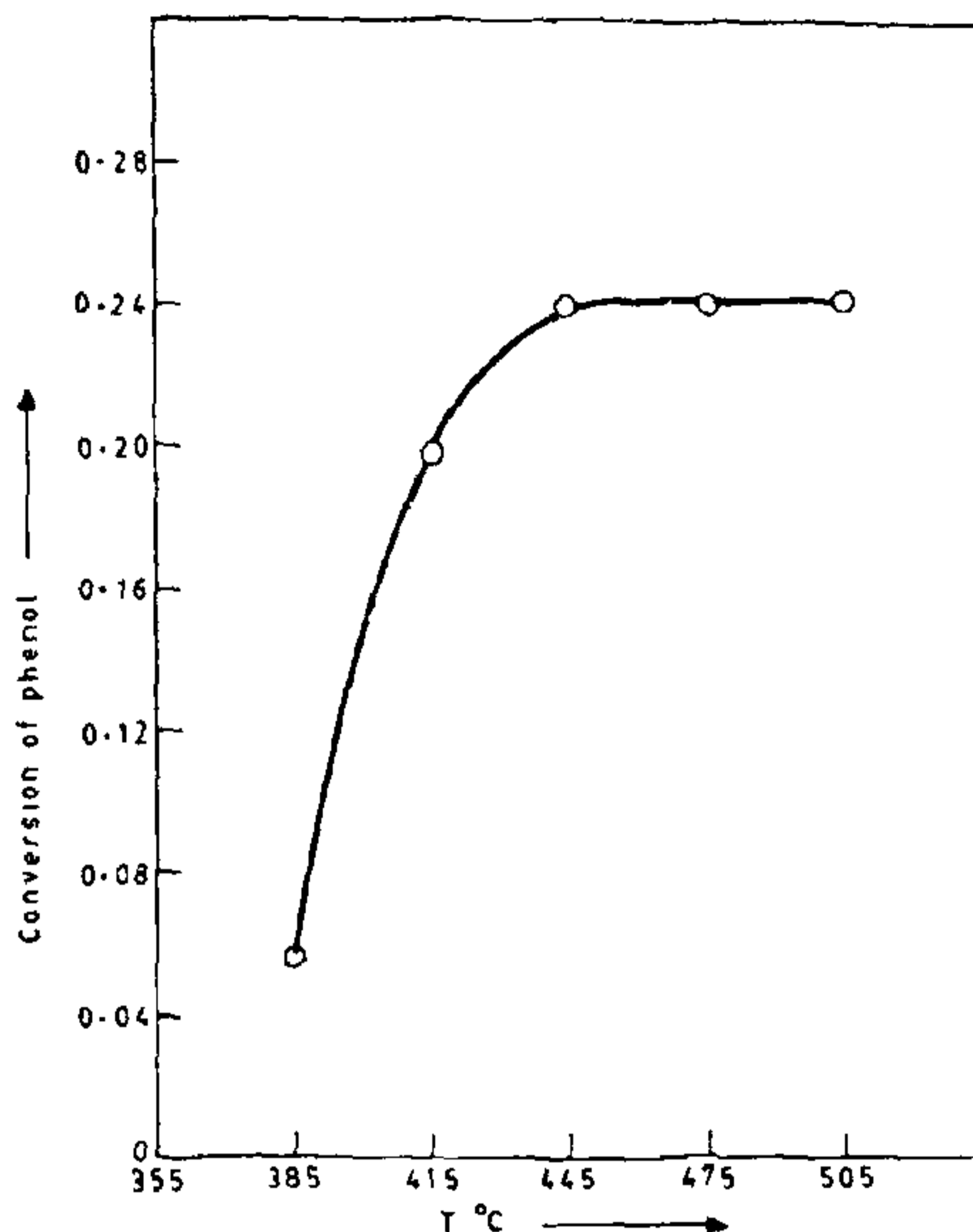


Figure 2. Effect of temperature on activity of ZSM-5-Cu

three different compositions and the temperature of 475°C. The figure indicates a constant activity with time. Further it shows a maximum activity at the intermediate feed composition of ammonia to phenol mole ratio of 4.7. In view of this observation all the rest of the experiments were carried out at this feed composition. Figure 2 compares the activity of copper, sodium and H form of ZSM-5. All the three catalysts exhibit stable catalytic activity. The activity of the three cationic forms is very comparable. The conversions were measured at different W/F and specific rate constants (k_{avg}) and activation energies (E) were evaluated on the three catalysts at three different temperatures in the range of 415 to 475°C. Table 1 gives the values of rate constants and the activation energies. The activation energies are indeed low.

The temperature dependence of the reaction rate was studied over a more extended range of temperature on ZSM-5-Cu. Figure 3 shows the variation of conversion obtained at a constant W/F of 48.7 with temperature. The plot clearly indicates that the reaction exhibits variable acti-

Table 1 Specific rate constants and activation energies on ZSM-5 catalysts

Catalyst	Temperature °C	K_{avg}		E kcal/ g.mol
		g. cat. hr.	atm ²	
ZSM-5-Cu	415	0.046		
ZSM-5-Cu	445	0.065		4.91
ZSM-5-Cu	475	0.065		
ZSM-5-H	415	0.054		
ZSM-5-H	445	0.058		3.78
ZSM-5-H	475	0.067		
ZSM-5-No	415	0.049		
ZSM-5-Na	445	0.059		3.73
ZSM-5-Na	475	0.061		

vation energy which approaches zero value at higher temperatures.

Figure 4 shows the TPD behaviour of the different catalysts. The TPD curves are essentially similar to those observed by previous workers^{3,4}. The peaks having maxima in the temperature range 80–90°C and 180–210°C are designated as

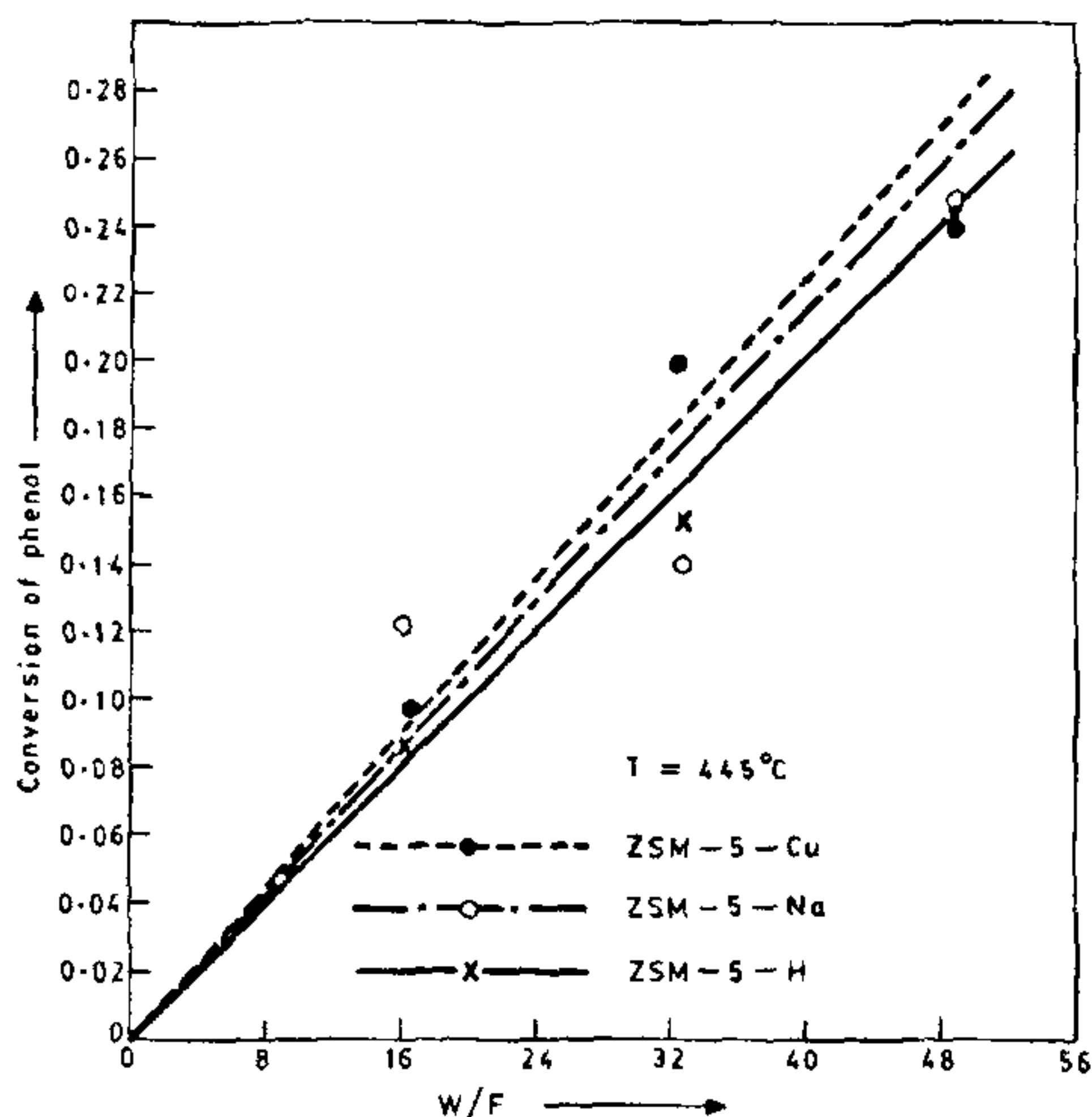


Figure 3. Comparison of catalytic activity for ZSM-5-type catalysts.

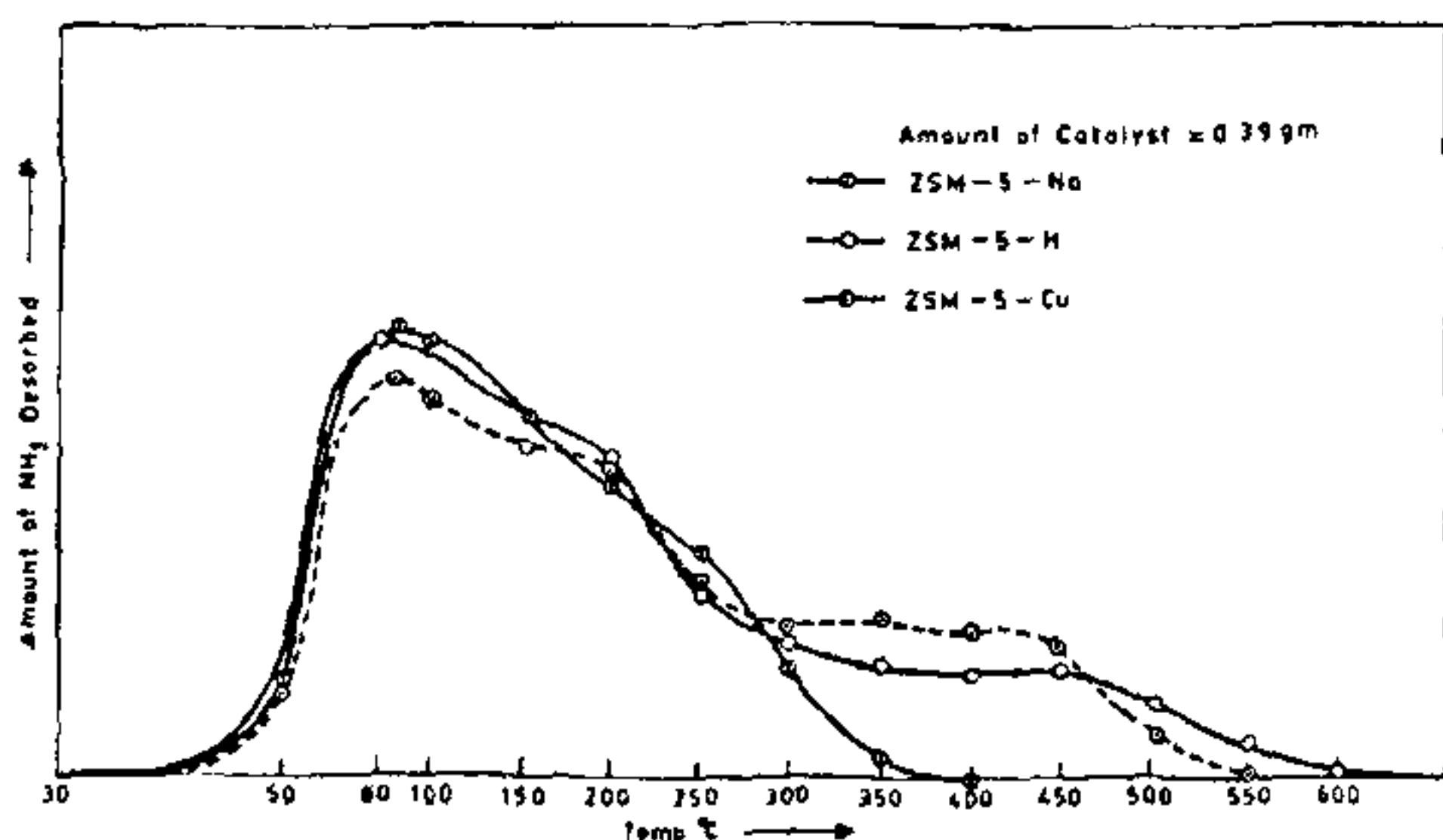


Figure 4. TPD of NH_3 on ZSM-5-type catalysts.

α and β peaks respectively and that at the high temperature as γ peak. Table 2 shows the values of acidity determined from these peak areas. The sodium form shows no strong acidity as may be expected. The total acidity varies as $\text{H} > \text{Cu} > \text{Na}$ form.

DISCUSSION

All the three cationic forms of ZSM-5 exhibit considerable activity for ammonolysis of phenol. The maximum in rate observed at an intermediate feed composition indicates dependence

Table 2 Acidities of ZSM-5 catalysts

Catalyst	nmol $\text{NH}_3/\text{g cat.}$		Total
	$\alpha + \beta$	γ	
ZSM-5-Na	0.498	0	0.498
ZSM-5-Cu	0.485	0.216	0.701
ZSM-5-H	0.534	0.196	0.729

of the reaction rate on partial pressure of phenol as well as ammonia and suggests that both the species are probably involved in the rate determining step. The specific activities are comparable to that of copper and decationated Y zeolite observed by Warawdekar and Rajadhyaksha^{2,5}. A noteworthy feature is that the ZSM-5 shows a very stable activity unlike the zeolite X and Y catalyst. This is in agreement with the known noncoking properties of zeolite ZSM-5⁶.

In spite of considerable difference in the acidity and nature of cations, the three catalysts showed very comparable activity. This is probably because the reaction rate is controlled by intracrystalline diffusion. Very low and variable activation energies lend credence to this hypothesis. The fact that the activity of ZSM-5 is comparable to that of zeolite Y in spite of the strong intracrystalline diffusion limitations suggests that the intrinsic activity of ZSM-5 is probably higher than that of zeolite Y. It has been pointed out by Palekar and Rajadhyaksha⁷ that unlike in the case of large pore catalysts (where the apparent activation energy becomes half the true activation energy due to strong influence of pore diffusion) the activation energy can be falsified to a very low value and can even become negative due to influence of intracrystalline diffusion in the case of zeolite catalysts. The behaviour observed in the present work supports this view.

30 January 1985

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ANNOUNCEMENTS

SYMPOSIUM ON 'CYTOGENETIC RESEARCH: ACHIEVEMENTS AND RELEVANCE'

The Indian Society of Genetics and Plant Breeding will hold a three day symposium on 'Cytogenetic Research: Achievements and Relevance' from August 5-7 at Hyderabad. Osmania University, Hyderabad is hosting the symposium. The venue of the symposium will be Regional Research Laboratory, Hyderabad.

The tentative scientific programme includes invited presentations on cytogenetics of lower plants; cytogenetics and taxonomy; cytogenetics of crop plants; structure and function of chromatin; linear differentiation of chromosomes; chromosome aberrations—basic and applied aspects; cytogenetics of abnormal human development; sex chromosomes and sex determination; control of cell division; cytogenetics of

cell hybrids and chromosome mapping; transposable elements; fate mapping of cells; molecular probes in identification of genes; synthetic chromosomes and localization of oncogenes on human chromosomes. Contributed papers will be accepted for poster presentation only.

Further details can be had from:

Prof. V. L. Chopra
Biotechnology Centre,
129-NRL Building,
Indian Agricultural Research Institute,
New Delhi 110012.

AWARD OF RESEARCH DEGREES

Berhampur University, Berhampur – Ph.D. (Chemistry) Sri Ladu Prasad Padhy (Title '*Mechanism of oxidation reactions*')

University of Bombay, Bombay – Ph.D. (Botany) Sri B. A. Giridhar, Ph.D. (Zoology) Sri Daksha Madhav Dhavale.

University of Cochin, Cochin – Ph.D. (Marine Sciences) Sri P. M. Muraleedharan (Title—'*Studies on equatorial undercurrent in the Indian Ocean*') Smt. Sosamma Cherian (Title—'*Glycogen degrading enzymes and their regulation in benthic animals and estuarine fish*')

Gulbarga University, Gulbarga – Ph.D. (Chemistry) Shri B. S. Hadimani (Title—'*Studies on some metal complexes with ligands containing N, O, & S metro-atoms*')

Kakatiya University, Warangal – Ph.D. (Chemistry) Shri A. Devender Rao (Title—'*Synthesis and evaluation of some new 4(3H)-quinozolinone derivatives as potential pharmacodynamic agents*')

Utkal University, Bhubaneswar – Ph.D. (Chemistry) Miss Suparna Ray (Title—'*Studies in vinyl polimerization and photo-polimerization*') Ph.D. (Botany) Shri Shyam Sundar Mohanty (Title—'*Parasitism of cuscuta chinensis*')
