

Selective Alkylation of Phenol to 2,6-Xylenol over Vanadia–Chromia Mixed Oxide Catalysts^a

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ABSTRACT

Vapour-phase alkylation of phenol with methanol was carried out over a series of simple and mixed oxides of vanadia and chromia of different atomic ratios in a fixed-bed, continuous-flow reactor at 573–723 K and 1–20 bar pressure. Preferential *ortho* alkylation with 90% selectivity took place with the formation of *o*-cresol and 2,6-xylenol. The acidity of the catalysts was measured by *n*-butylamine titration and by cyclohexanol dehydration at 523 K, which was also used as an acidity index. Variation of the activity with the atomic ratios of V and Cr in the mixture was correlated with acidity, total phenol conversion and selectivity for *o*-cresol and 2,6-xylenol. An increase in acidity increases the selectivity for 2,6-xylenol. Pure vanadia is a better alkylation catalyst than pure chromia. However, addition of a small amount of chromia to vanadia improves the acidity and also the total activity and selectivity for 2,6-xylenol.

INTRODUCTION

Alkylation of phenol is an industrially important reaction but the information available in the literature is scanty. Several of the organic intermediates are produced through alkylation of phenols, which are used in paints and herbicides; e.g., *o*-cresol is used in the synthesis of herbicides. 2,6-Xylenol is used in the manufacture of polyphenylene oxide (PPO) and in special-grade paints. Eventhough Friedel–Crafts catalysts have been used for the alkylation of phenol, selective methylation of phenol on the aromatic carbon atoms has not been very successful [1]. Solid acid catalysts are very good alternatives to proton acids or Friedel–Crafts-type catalysts. There have been only a few studies on the use of such catalysts. The acidic and basic nature of solids provide a fascinating opportunity to study these reactions by varying their catalytic characteristics. A few investigations on the alkylation of phenol with methanol using oxides and zeolites indicate that the reaction is sensitive to acidic and basic properties of catalysts [1–6].

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Oxides can be used as catalysts alone or in combination. It is believed that a mixture of oxides brings out a combined effect or a sort of synergistic behaviour enhancing the catalytic activity [7,8]. Further, the acidic and basic character of simple and mixed oxide catalysts would also affect the product selectivity. Tanabe and Nishizaki [3] showed that catalysts with higher acidic strength are more active but less selective to *ortho* alkylation. However, TiO₂-MgO mixed oxides were found to be more active and selective than pure MgO for 2,6-xylenol, which has been attributed to a combined effect of weak acidity and strong basicity of the catalyst. With zeolites, alkylation of phenol with methanol proceeds both at carbon and oxygen but with predominant formation of anisole [4]. However, over HZSM-5 this reaction gives products other than anisole [9]. The competitive nature for the preferential formation of O- or C-alkylated products is a subject of interest [4,5,10].

In this investigation we studied the alkylation of phenol with methanol over a series of simple and mixed oxide catalysts of vanadia and chromia to produce selectively valuable *o*-cresol and 2,6-xylenol. The acidic properties of the oxides are correlated with the alkylation behaviour.

EXPERIMENTAL

Catalyst preparation and characterization

Mixed oxides of vanadia and chromia with different atomic ratios were prepared. Chromium hydroxide, precipitated from an aqueous solution of chromium nitrate with dilute ammonia solution, was slurried with a solution of ammonium metavanadate in oxalic acid. The slurry was dried overnight at 393 K and was further calcined at 773 K for 8 h. This sample was used for physical characterization. The surface area as measured by nitrogen adsorption at 77

TABLE 1

Catalyst characteristics

Catalyst	V:Cr atomic ratio	Surface area (m ² g ⁻¹)	Acidity (mmol <i>n</i> -butylamine per gram catalyst)	Cyclohexanol dehydration (%)
VCR 1	0:100	31	0.05	0.0
VCR 2	5: 95	31	0.07	0.5
VCR 3	20: 80	41	0.30	1.5
VCR 4	40: 60	44	0.47	3.4
VCR 5	60: 40	40	1.02	5.1
VCR 6	80: 20	36	1.60	6.7
VCR 7	95: 5	36	1.65	8.9
VCR 8	100: 0	31	1.55	6.1

K was between 30 and 44 m² g⁻¹ catalyst. X-ray diffraction (XRD) patterns of the samples were taken with a Philips PW 1051 X-ray diffractometer. Chromia is slightly crystalline and as the vanadia content increased the crystallinity of the mixed catalysts increased, pure vanadia being the most crystalline of all. Total acidity was determined by non-aqueous titration using *n*-butylamine as a titrant and bromothymol blue ($pK_a=7.0$) as an indicator. Dehydration of cyclohexanol carried out over these samples at 523 K and 1 bar was also used as an index of acidity. The experimental set-up for this reaction was described previously [11]. The characteristics of the catalysts are given in Table 1.

Apparatus and procedure

Alkylation of phenol with methanol was carried out in a stainless-steel downflow tubular reactor (12 mm I.D.) at 1–20 bar and 573–723 K. About 1 g of catalyst pelletized with 1 wt.-% of stearic acid as binder, crushed to 1600–1800 μm and diluted with ceramic beads of the same dimensions loaded in the reactor. Before the start of the experiment, the catalyst was activated at 723 K in nitrogen (10 bar). The catalyst bed temperature was measured with a moving thermocouple. A premixed phenol–methanol feed (phenol-to-methanol molar ratio 1:5; Fig. 1) was pumped at 10 ml h⁻¹ (WHSV with respect to phenol = 0.035 mol h⁻¹ g⁻¹) into the reactor through a vaporizing chamber. Nitrogen was used as the carrier gas and the flow-rate was maintained at 4 l h⁻¹. Liquid products collected every hour during an 8-h experiment using an ice trap were analysed with any HP 5880 gas chromatograph with a 10% SE-30–Chromosorb W column. For a given experiment the activity remained steady throughout (Fig. 2). The products were mainly 2,6-xyleneol and *o*-cresol together with trace amounts of other C-alkylated products. The percentage composition reported is based on a methanol-free phenol feed.

RESULTS AND DISCUSSION

Selection of molar ratio of phenol to methanol

In order to choose an optimum feed mix, an alkylation reaction on a catalyst sample was carried out at 673 K and 1 bar using several molar ratios of phenol to methanol (Fig. 1). The selectivities of the products formed, namely *o*-cresol and 2,6-xyleneol, and the phenol conversion are plotted against the phenol-to-methanol molar ratio. Both the conversion and the products formed were maximal at a ratio of 1:5, so this feed ratio was maintained throughout the study.

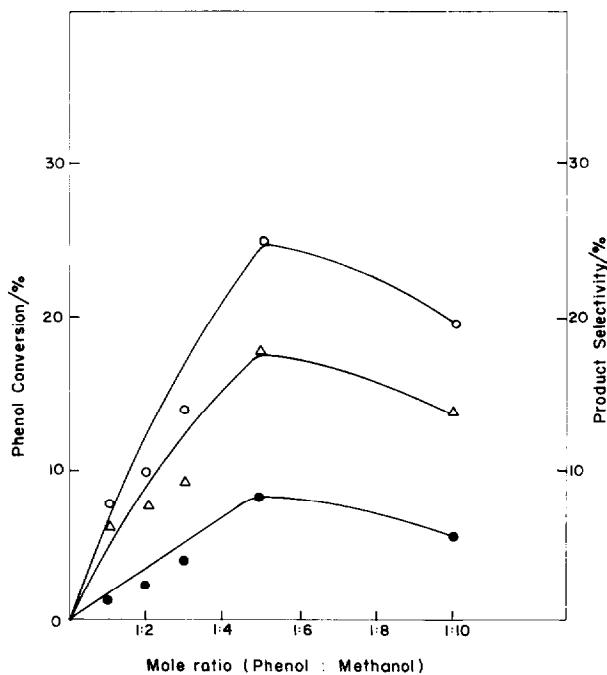


Fig. 1. Effect of molar ratio of reactants on phenol conversion and product formation. Catalyst, VCR 7; temperature 673 K; pressure, 1 bar. ○, Phenol; △, *o*-cresol; ●, 2,6-xyleneol.

Phenol conversion vs. time on-stream

Activity studies on the catalysts were carried out for 6 h or more at 673 K and 10 bar (Fig. 2). The phenol conversion on all catalysts studied was steady even though their activities varied among the catalysts. This indicates that during the reaction period the catalysts did not undergo any deactivation. The activities of the catalysts for phenol conversions were compared under steady-state conditions.

Effect of pressure

The results of the alkylation of phenol at 673 K in the pressure range 5–20 bar are given in Table 2. In general, an increase in pressure seems to increase the phenol conversion on all the catalysts, except for VCR 6, where it decreased. We do not have any strong evidence to explain this peculiar behaviour of VCR 6. An interaction between vanadium and chromium, suspected from an additional XRD peak for the sample, may be a factor responsible for such behaviour. However, the effect is not very significant with VCR 1. Among the

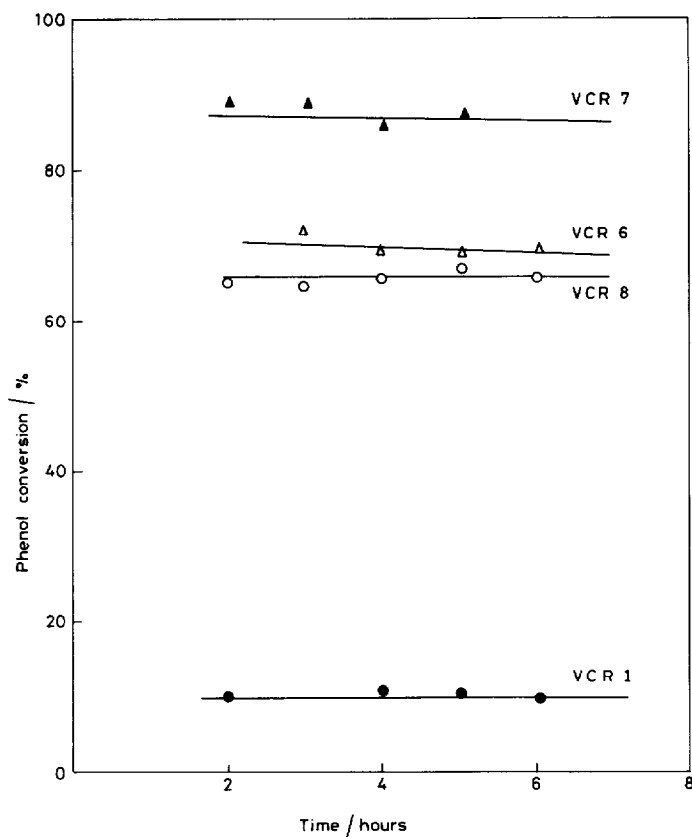


Fig. 2. Behaviour of catalysts for phenol conversion with time on-stream. Temperature 673 K; pressure, 10 bar.

TABLE 2

Effect of pressure on alkylation of phenol at 673 K^a

Catalyst	5 bar			10 bar			15 bar			20 bar		
	A	B	C	A	B	C	A	B	C	A	B	C
VCR 1	8	100	—	10	100	—	12	94	—	14	90	—
VCR 6	77	44	46	68	37	50	65	36	51	54	36	61
VCR 7	79	41	47	87	24	65	82	26	57	82	31	59
VCR 8	65	45	46	67	30	50	80	28	58	84	25	64

^aA=phenol conversion, B=*o*-cresol selectivity, C=2,6-xylene selectivity.

catalysts studied, VCR 1 has the lowest phenol conversion activity at a given pressure; VCR 7 shows the highest activity, closely followed by VCR 8.

The products formed in the pressure ranges studied are mainly *o*-cresol and

2,6-xylenol. VCR 1, a pure chromia catalyst, gives only *o*-cresol as an alkylation product. However, over vanadia (VCR 8) and vanadia–chromia (VCR 6 and 7) 2,6-xylenol is formed in addition to *o*-cresol. The selectivity for 2,6-xylenol increases with increase in pressure. On the other hand, an increase of pressure decreases the selectivity for *o*-cresol formation. Investigation of the effect of pressure on phenol alkylation indicated that the reaction can be studied conveniently at 10 bar, as a further increase in pressure did not improve the conversions to any great extent.

Effect of temperature

Alkylation of phenol was carried out in the temperature range 573–723 K at 10 bar. Studies on the effect of temperature on the conversion of phenol and the selectivity for *o*-cresol and 2,6-xylenol showed that the activity is maximum at ca. 673 K (Figs. 3–5). It is clear from the alkylation studies that there

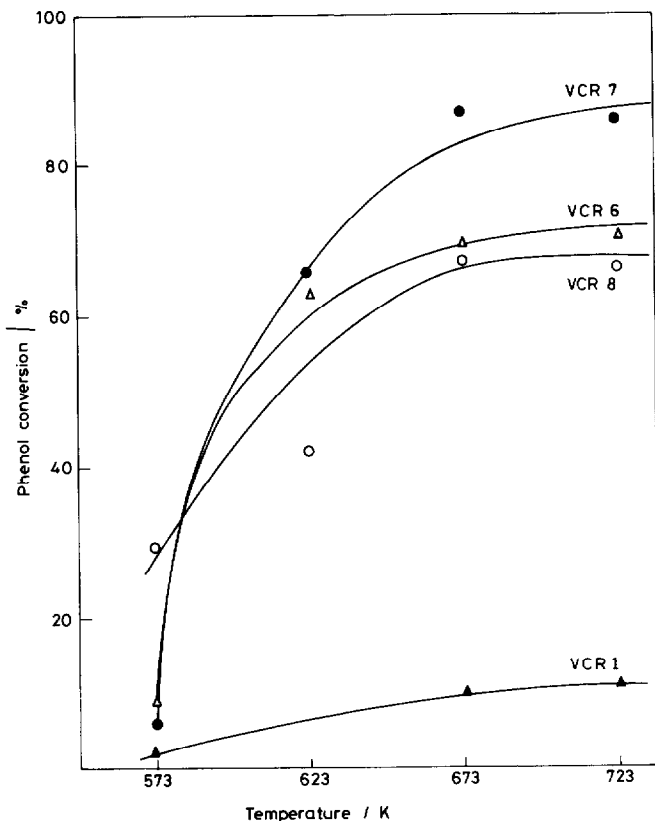


Fig. 3. Effect of temperature on phenol conversion at 10 bar.

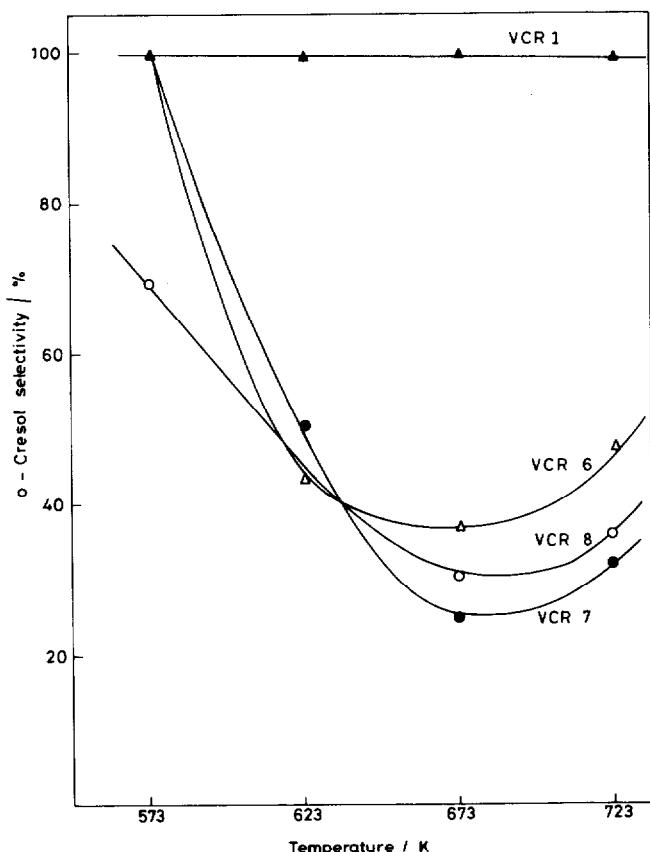


Fig. 4. Effect of temperature on the selectivity of *o*-cresol at 10 bar.

is hardly any O-alkylation product under the experimental conditions used. It is also evident from Figs. 3-5, that only C-alkylation takes place with a maximum of about 90% *ortho* selectivity. With pure chromia (VCR 1) only *o*-cresol is formed with 100% selectivity. As the vanadia content increases the selectivity for 2,6-xylenol increases and that for *o*-cresol decreases. VCR 7, with a small content of chromia, showed maximum conversion of phenol with a maximum selectivity for 2,6-xylenol and a minimum selectivity for *o*-cresol. Of course, pure vanadia (VCR 8) follows VCR 7 in its activity and selectivity patterns. An increase in temperature increases the 2,6-xylenol selectivity with VCR 6 and 7, with a maximum at 673 K. On the other hand, an increase in temperature does not influence VCR 1 and the *o*-cresol selectivity is maintained at 100% between 573 and 723 K. VCR 8 starts with a higher conversion of phenol with higher selectivity for both *o*-cresol and 2,6-xylenol compared with VCR 6 and 7 at 573 K. With increase in temperature the activity and selectivity for

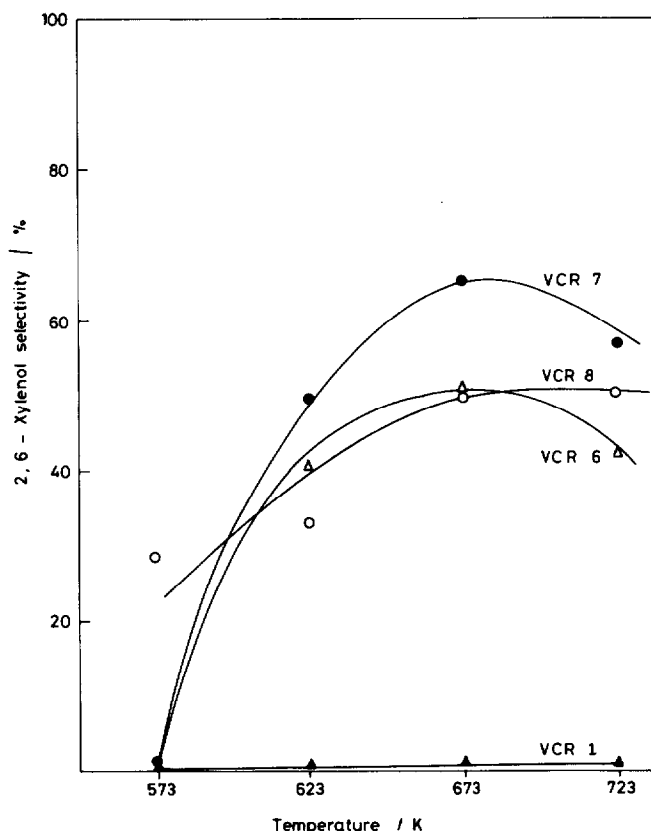


Fig. 5. Effect of temperature on the selectivity of 2,6-xyleneol at 10 bar.

2,6-xyleneol increased, as with VCR 6 and 7. The activity follows the order VCR 7 > VCR 6 > VCR 8 at 673 K. The selectivity order is VCR 7 > VCR 8 \approx VCR 6 for 2,6-xyleneol and VCR 7 < VCR 8 < VCR 6 for *o*-cresol.

Correlation between acidity and activity

As is evident from Fig. 6, the variation in acidity is smooth and increases from pure chromia to pure vanadia and as the vanadia content increases in the mixture. This observation was confirmed by dehydration of cyclohexanol carried out on these catalysts as a measure of the acidity index (Table 1). An interesting observation on the variation in acidity with the vanadia-to-chromia atomic ratio is that vanadia with a small amount of chromia (VCR 7, V:Cr = 95:5) is more acidic than pure vanadia itself. On the other hand, the formation of *o*-cresol decreases from pure chromia to pure vanadia with increasing vanadia content and is the lowest at VCR 7, increasing slightly for

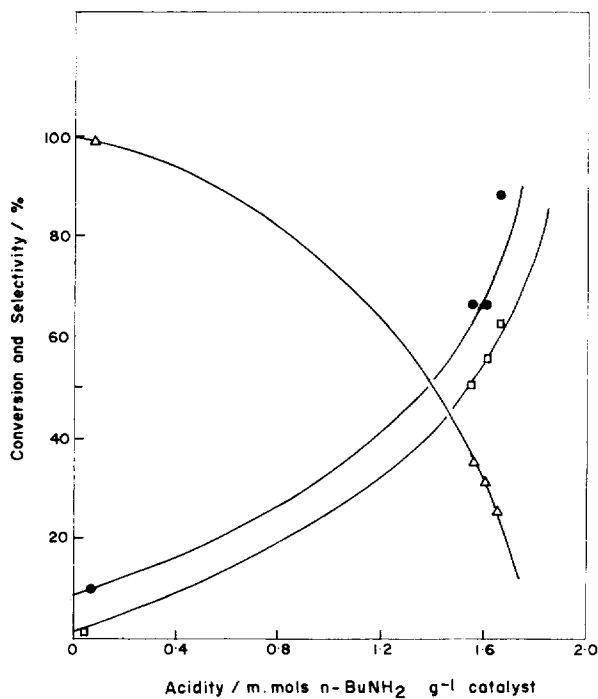


Fig. 6. Variation of phenol conversion, selectivities of *o*-cresol and 2,6-xyleneol with acidity over vanadia-chromia catalysts. Temperature, 673 K; pressure 10 bar. ●, Phenol; □, 2,6-xyleneol; △, *o*-cresol.

VCR 8. Fig. 6 clearly shows the correlation between variation in the acidity of the catalysts and phenol conversion activity and selectivity. This observation supports the dependence of alkylation selectivity on acidity. A change in the acidity causes a change in the alkylation selectivity. Acidic catalysts lead to preferential C-alkylation, forming 2,6-xyleneol. This investigation is interesting not only because of the direct correlation between acidity and phenol conversion but also because only *ortho* alkylation takes place on this catalyst system.

Alkylation of phenol to produce *o*-cresol and 2,6-xyleneol over acidic and basic catalysts has been reported earlier [2]. It was found that basic catalysts gave predominantly C-alkylation whereas an increase in acidity decreased C-alkylation, selectively increasing O-alkylation. A detailed investigation by Namba et al. [5] on the reaction of phenol and methanol over zeolite Y revealed that alkylation at C- and O-positions is competitive. Balsama et al. [4] reported the formation of anisole and cresols in alkylation of phenol with methanol. They also correlated the selectivity of *o*- and *p*-cresol with surface acidity of the material, indicating that strongly acidic catalysts promoted ring

alkylation. Hence there is no clear picture of the influence of the acidic and basic properties of solids on the alkylation of phenol with methanol.

This study on pure and mixed oxide catalysts is important to the understanding of phenol alkylation and in helping to optimize selectivity by varying the proportions of oxides, thus varying their acidity. The study also gives a good example of the exclusive production of *o*-cresol and 2,6-xyleneol. It has been reported [3] that the *ortho* selectivity is due to the perpendicular adsorption of phenol on the active sites of catalysts. As *ortho* alkylation is taking place exclusively on vanadia-chromia, the same mechanism may operate in this instance also.

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