

**A Correlation of Vanadia–Chromia Catalyst
Composition with Acidity and Selective C-Alkylation
Activity of Phenol***

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Alkylation of phenol is an important industrial reaction, studies on which are rather limited and available information is mainly through the patent literature. For example, *o*-cresol is an important organic intermediate for herbicides and insecticides, and 2,6-xylenol is used in the manufacture of polyphenylene oxide (PPO) and in special grade paints. Studies on the alkylation of phenol with methanol on oxides and zeolites reveal that the reaction is sensitive to the acidity and basicity of the catalysts [1 - 4]. Therefore a direct correlation between the acidic nature and the alkylation product selectivity deserves a detailed investigation. Alkylation of phenol with methanol over zeolites proceeds at both carbon and oxygen, with anisole usually being formed in abundance [5, 6]. It is interesting to find anisole absent [7] in the reaction product of phenol with methanol over HZSM-5. The competition for the preferential formation of O- or C-alkylated products is not quite understood. This investigation attempts to find a new combination of vanadia–chromia mixed oxides as catalysts to selectively produce 2,6-xylenol by vapor phase alkylation of phenol and to correlate the catalytic activity and selectivity with acidity of the oxides.

Mixed oxides of vanadia and chromia of different atomic ratios were prepared from ammonium metavanadate and chromium nitrate by the precipitation method, washed, dried overnight at 393 K and calcined at 773 K for 8 h. BET surface area and acidity measurements by non-aqueous titration methods using *n*-butylamine as titre and bromothymol blue as indicator were carried out on these samples. Dehydration of cyclohexanol, taken as an acidity index of the catalysts, was carried out over these oxides at 523 K. This reaction is very simple and serves as a test reaction for acidity measurements, and will be especially useful where acidity measurements of coloured catalysts by non-aqueous titration involving indicators is difficult to carry out. The added advantage is that no deactivation due to coking

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occurs, and hence a direct correlation between dehydration activity and acidity is possible.

Approximately 1 g of the mixed oxide, pelletized with a binder, crushed to 1600 - 1800 μm and diluted with ceramic beads of the same size, was loaded in a fixed bed tubular metal reactor. The catalyst was activated at 723 K for 8 h in nitrogen at 10 bar before the start of the experiment. A mixture of phenol and methanol (PhOH:MeOH = 1:5 W/W) was fed from the top using a mechanical pump at a specified flow rate. Nitrogen was used as the carrier gas, and the pressure in the system could be controlled between 1 and 25 bars. Increasing the pressure above 10 bars had no significant effect on the activity and selectivity. Alkylation reactions were carried out in the temperature region 573 - 773 K, and revealed that beyond 673 K there is very little change in the conversion. The results reported here are for alkylation reactions carried out at 673 K and 10 bar. For a given experiment lasting 6 - 8 h, the activity remained constant throughout. The products were collected in a trap with circulating ice water, and were analyzed by a HP 5880 gas chromatograph with a 10% SE-30 column. The main products were 2,6-xylenol, *o*-cresol and unreacted phenol, along with other alkylated products as minor constituents (< 2% of the total). The percentage composition reported is based on methanol-free phenol feed.

The atomic ratios of vanadia-chromia catalysts and their BET surface areas are given in Table 1. All catalysts have nearly identical surface area. Figure 1 depicts the variation of acidity, as measured by *n*-butylamine titration and cyclohexanol dehydration, with atomic ratios of vanadia and chromia. In Fig. 2, the correlation between phenol conversion to selective C-alkylation and vanadia-chromia composition is shown. The superposition of these two figures gives us a clear picture of the direct correlation between composition, acidity and alkylation selectivity.

The acidity of pure chromia (VCR 1) is very low, and is increased by addition of vanadia, VCR 7 exhibiting the maximum (Fig. 1). Conversion of phenol and selective formation of 2,6-xylenol follow the same trend as the acidity variation with vanadia-chromia composition. On the other hand, *o*-cresol formation follows exactly the reverse trend. VCR 1 alkylates only 10 - 14% of phenol to give *o*-cresol, whereas other catalysts with higher

TABLE 1
BET surface area of vanadia-chromia catalysts

Catalyst	V:Cr	BET ($\text{m}^2 \text{g}^{-1}$)
VCR 1	0:100	31
VCR 3	20:80	30
VCR 6	80:20	36
VCR 7	95:5	36
VCR 8	100:0	31

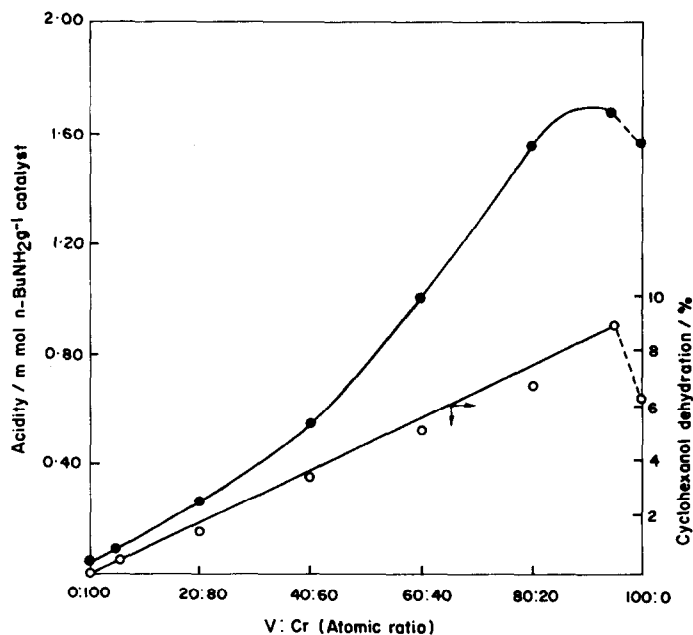


Fig. 1. Variation of acidity and cyclohexanol dehydration activity with atomic ratios of vanadia to chromia. (●) acidity, (○) cyclohexanol dehydration.

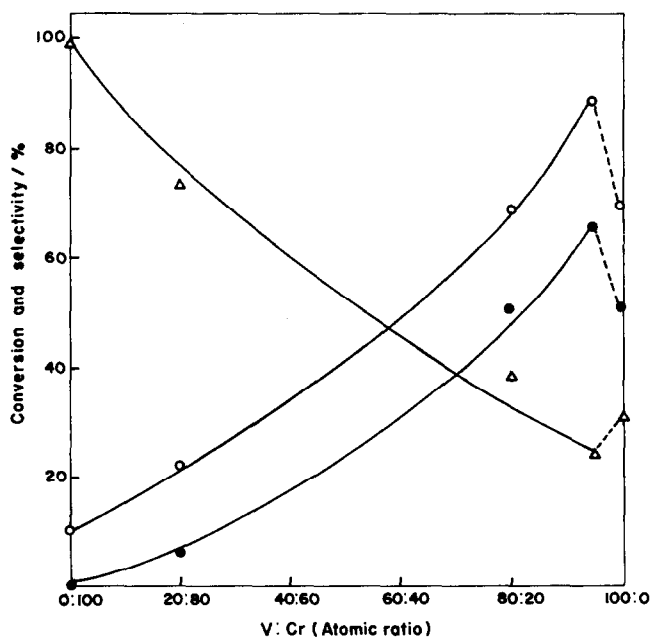


Fig. 2. Effect of variation of vanadia-chromia atomic ratios on phenol conversion and *ortho*-alkylation selectivity. (○) phenol; (△) *o*-cresol; (●) 2,6-xylene; $T = 673$ K, $P = 10$ bar.

acidity alkylate 67 - 87% of phenol preferentially to 2,6-xylenol (50 - 64%). From analysis of the two figures, it is observed that increasing the acidity increases total conversion and 2,6-xylenol selectivity at the expense of *o*-cresol selectivity. Thus, a direct correlation between phenol conversion and acidity can be drawn. It is also clear that chromia alone is a poor alkylation catalyst compared to vanadia, and addition of a small amount of chromia to vanadia (V:Cr = 95:5) is helpful in improving and stabilising the catalytic activity. There are reports in the literature supporting both the competitive and parallel mechanisms of C- and O-alkylations [1 - 7]. This is a subject for further discussion, and more evidence is necessary to support one or the other mechanism. The absence of anisole, under the present experimental conditions, suggests that only selective C-alkylation takes place to produce valuable cresols and xylenols. This study also indicates that formation of 2,6-xylenol takes place via *o*-cresol, since a selectivity increase of the former decreases the selectivity of the latter. This investigation thus reveals an optimum composition of vanadia-chromia catalyst for selective alkylation of phenol to 2,6-xylenol, which is an important reaction in the chemical industry.

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