Alkylation of Phenol over Simple Oxides and Supported Vanadium Oxides[a]

V. VENKAT RAO*, K.V.R. CHARY, V. DURGAKUMARI and S. NARAYANAN

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007 (India), tel.
(+91-842) 853874

ABSTRACT

Alkylation of phenol is studied on V_2O_5, TiO_2 (anatase and rutile), SiO_2, MgO and also on supported V_2O_5 catalysts. V_2O_5 and TiO_2 are comparatively more active than MgO and SiO_2. Addition of 10 wt.-% V_2O_5 to other oxides improved the catalytic activity and 2,6-xylenol selectivity. The conversion of phenol and selectivity for 2,6-xylenol follow the order $V_2O_5/TiO_2(A) > V_2O_5 > V_2O_5/TiO_2(R) > TiO_2(A) > TiO_2(R) \gg V_2O_5/SiO_2 > V_2O_5/MgO > MgO > SiO_2$, where A is anatase and R rutile. Acidities are measured in terms of micromoles of ammonia adsorbed. V_2O_5 addition increases the acidity of simple oxides. Phenol conversion and selectivity for 2,6-xylenol increase with acidity while o-cresol selectivity shows the opposite trend.

Key words: phenol alkylation, vanadia, titania, silica, magnesia, vanadia/titania, vanadia/silica, vanadia/magnesia, selectivity (xylenol), acidity.

INTRODUCTION

Alkyl phenols are important intermediates in the pharmaceutical, agrochemical and polymer industries [1] and some methyl aryl ethers are even used as additives for fuels to boost their octane number [2]. Phenol alkylation when carried out in the liquid phase gives numerous products and their separation is difficult [3]. Vapour phase alkylation is the simplest and a promising synthetic approach to produce selectively o-cresol and 2,6-xylenols [1]. In spite of the importance of this reaction there are only a few investigations dealing with the catalytic vapour-phase alkylation of phenols [4 and references therein, 5–8]. Some of these studies carried out over oxides, mixed oxides and zeolites reveal the dependence of this reaction on acid–base properties of the catalyst [9–11]. There is always a competition between O- and C-alkylation [12–14]. The strength of acid sites plays a role in the product selectivity. However, the relation between conversion and selectivity with acidity has not been investi-

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gated in detail. It is our aim to understand the vapour-phase alkylation of phenol over oxide catalysts with the idea of selectively producing C-alkylated products, mainly 2,6-xylenol. In this endeavour we have studied the alkylation of phenol over vanadia–chromia mixed oxide catalysts [4]. A correlation of vanadia–chromia catalyst composition with selective C-alkylation activity of phenol has been reported [5]. The study also revealed that pure vanadia and vanadia with small amount of chromia are good catalysts for 2,6-xylenol. In our continued efforts to improve the selectivity of 2,6-xylenol production, alkylation of phenol over several oxides has been tried and the performance of the catalysts are evaluated and compared. The oxides are used as catalysts and as supports for vanadia to assess their behaviour individually and in combination with V_2O_5 for alkylation of phenol.

EXPERIMENTAL

Catalyst preparation

The properties of various simple and supported oxides used for alkylation of phenol are listed in Table 1. The oxides were pelletized without a binder, crushed, and particles of size 1400–1800 μm were used as catalyst and support. Supported vanadia catalysts containing about 10 wt.-% of V_2O_5 were prepared by impregnating the oxides with an aqueous solution of ammonium metavanadate of calculated concentration. The sample was dried overnight at 393 K and calcined in air at 773 K for four hours.

Adsorption measurements

The surface area of the catalyst was measured at 78 K using nitrogen as adsorbate (0.162 nm^2) following the BET method in an all-glass adsorption

TABLE 1

Characteristics of pure oxides and vanadia supported catalyst

Catalyst[a]	Surface area (m^2 g^{-1})	Ammonia adsorbed (μmol g^{-1})
SiO$_2$	672	195
TiO$_2$(A)	92	229
TiO$_2$(R)	33	40
MgO	70	23
V$_2$O$_5$	34	50
V$_2$O$_5$/SiO$_2$	450	950
V$_2$O$_5$/TiO$_2$(A)	67	417
V$_2$O$_5$/TiO$_2$(R)	18	70
V$_2$O$_5$/MgO	63	42

[a]A = Anatase, R = rutile

apparatus. Acidity of the catalyst was determined by ammonia adsorption at room temperature [15]. In a typical experiment, catalyst (ca. 0.2 g) was used and the sample was degassed for 3 h at 473 K to attain a pressure of $1 \cdot 10^{-5}$ Torr (1 Torr = 133.3 Pa). The catalyst vessel was cooled to ambient temperature and the ammonia adsorption isotherm was measured by allowing ammonia from the storage bulb to come in contact with the catalyst and equilibrate. From the pressure and volume change, the amount of ammonia adsorbed per unit weight of the catalyst was calculated. After the first adsorption isotherm, the catalyst was evacuated for an hour at the same temperature and the second isotherm was measured. The parallel isotherms were extrapolated to zero pressure and the difference in amount adsorbed between them was taken as the chemisorbed ammonia.

Activity measurements

Vapour-phase alkylation of phenol with methanol (phenol-to-methanol molar ratio = 1:5) was carried out using a vertical tubular reactor at 673 K and at atmospheric pressure [4]. About 2.0 g of catalyst particles diluted with ceramic beads of same size and packed in between glass beads was activated in nitrogen flow (41 h^{-1}) at 723 K for 2 h. Phenol–methanol mixture is fed from the top with the help of a motorized syringe. Nitrogen is used as a carrier gas and WHSV of phenol is maintained at 0.73 h^{-1}. The liquid products collected in the trap kept in an ice bath were analysed by a gas chromatograph with a column of 10% SE-30 on Chromosorb W. The activity reached a steady state after two hours and the conversions reported are all based on steady-state conditions. The main products are 2,6-xylenol and o-cresol along with other ring alkylated products as minor constituents (< 2%) except in the case of TiO_2(A). p-Cresol, 2,4-xylenol and 2,4,6-xylenol and 2,4,6-trimethylphenol are also formed in considerable amounts in addition to o-cresol and 2,6-xylenol over TiO_2(A). No other products of non-selective reaction such as anisole or substituted anisoles are observed. The percentage composition is based on methanol-free phenol feed. The selectivity of the products is calculated by using the equation

$$\text{Selectivity of the product (\%)} = \frac{\text{Product (\%)}}{\text{Phenol derived products (\%)}} \times 100$$

RESULTS AND DISCUSSION

Conversion and time on-stream

Vapour-phase alkylation of phenol under the experimental conditions described in the Experimental section was carried out for a period of four hours,

collecting the products at half hour intervals and analysing them by gas chromatography. Pure oxides and supported oxides generally show a stable conversion with not much deactivation except in the case of $TiO_2(A)$. However, $V_2O_5/TiO_2(A)$ shows a steady conversion throughout the period compared with $TiO_2(A)$ alone. Activities of the catalysts for phenol alkylation are compared by taking the third hour product analysis. The activity of the simple oxides follow the order $V_2O_5 > TiO_2(A) > TiO_2(R) > MgO > SiO_2$. In the case of supported vanadia systems, the activity follows the order $V_2O_5/TiO_2(A) > V_2O_5/TiO_2(R) \gg V_2O_5/MgO > V_2O_5/SiO_2$. It is observed that phenol conversion is higher over pure vanadia and titania than on other oxides. The conversion is further improved when vanadia is supported over titania. The increase in conversion is more striking in the case of $V_2O_5/TiO_2(R)$ than in the case of $V_2O_5/TiO_2(A)$.

Comparison of activity and selectivity

Phenol conversion and selectivity for o-cresol and 2,6-xylenol on both simple and supported vanadium oxides are compared with the help of bar charts (Figs. 1, 2 and 3). It is evident that supported vanadia catalysts are better than their unsupported counterparts for phenol conversion and 2,6-xylenol selectivity. Among the catalysts, $V_2O_5/TiO_2(A)$ stands out as the most active catalyst for phenol conversion and 2,6-xylenol activity. The activity of $V_2O_5/TiO_2(A)$ is not only higher than $TiO_2(A)$ but also the selectivity for 2,6-xylenol has increased two-fold. Pure $TiO_2(A)$ has lower selectivity for 2,6-xylenol than pure
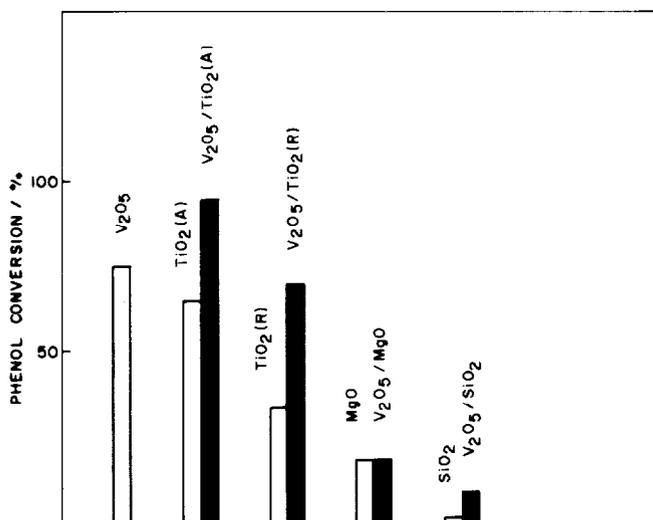

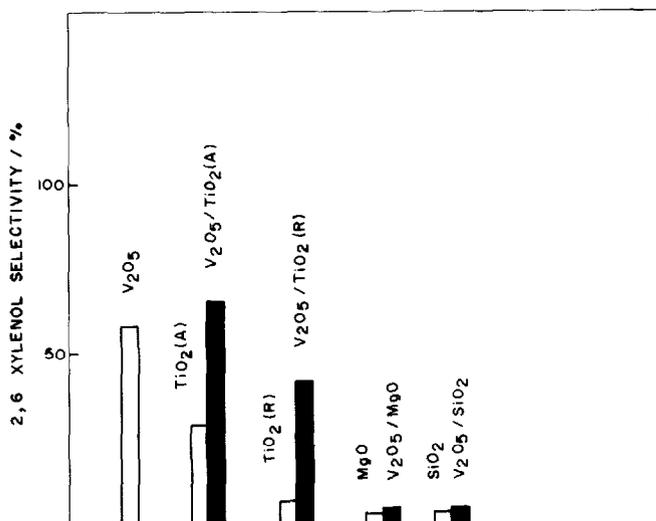Fig. 1. Comparison of phenol conversion over oxides and supported vanadium oxides.

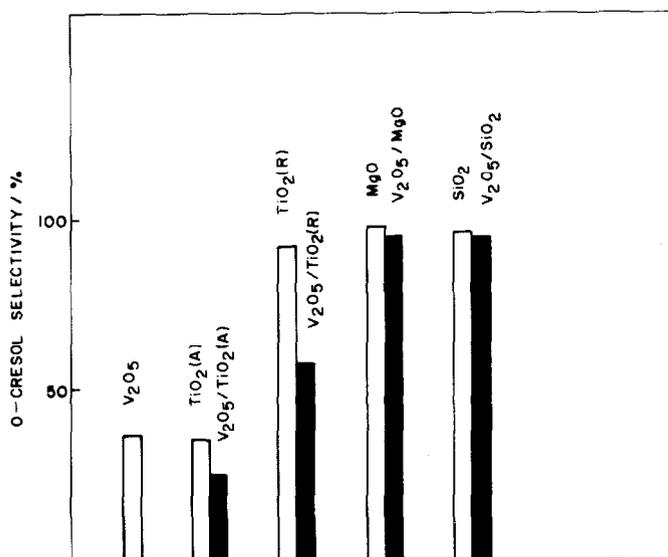Fig. 2. Comparison of 2,6-xylenol selectivity over oxides and supported vanadium oxides.

Fig. 3. Comparison of o-cresol selectivity over oxides and supported vanadium oxides.

V_2O_5, though the conversion does not vary much. This is mainly due to the formation of products other than o-cresol and 2,6-xylenol. Addition of vanadia to titania (A) helped to increase 2,6-xylenol selectivity, and reduced the formation of undesired products. The addition of vanadia to other oxides also increased the selectivity of 2,6-xylenol. MgO and SiO_2 with and without van-

adia are poor alkylating catalysts. o-Cresol selectivity on the other hand decreased with V_2O_5 addition especially in the case of TiO_2 (A and R). The effect of V_2O_5 addition to MgO and SiO_2 is insignificant with respect to phenol conversion and selectivity patterns. From the foregoing it is clear that V_2O_5, V_2O_5/TiO_2(A) and V_2O_5/TiO_2(R) are good alkylating catalysts and phenol conversion follows the order V_2O_5/TiO_2(A) $> V_2O_5 > V_2O_5/TiO_2$(R) and selectivity for 2,6-xylenol also follows the same trend. It may be worth while comparing here the performance of V_2O_5/TiO_2(A) with other solid acid catalysts in the alkylation of phenol. The reaction of phenol with methanol over X-, Y- and ZSM-type zeolites gives a mixture of cresols, xylenols, anisoles and substituted anisoles. Selectivity to 2,6-xylenol is only 5–6% at 40–50% phenol conversion [12]. The alkylation of phenol with methanol over $La_2(HPO_4)_3$, $BaSO_4$, $SrSO_4$ and Al_2O_3 by vapour- and liquid-phase reaction also yields mainly anisoles [7]. Methylation of phenol over acidic oxides such as WO_3, MoO_3, Al_2O_3 and SiO_2–Al_2O_3 by liquid phase reaction yields cresols and anisoles [16]. However, these catalyst systems showed low selectivity to 2,6-xylenol and large amount of other derivatives of phenol in addition to o-substituted phenols are formed. It may also be mentioned here that the alkylation activity and stability of vanadia was improved by the addition of 5–10% chromia which by itself is a poor alkylation catalyst [4,5]. In the same way, the activity and stability of vanadia and titania (pure oxides) may be improved by the proper combination of one with the other as in the case of V_2O_5/TiO_2(A).

Influence of acidity on activity and selectivity

It is believed that the acidity of the oxide determines the alkylation activity. The nature and strength of acid sites may influence the activity and selectivity character of oxides. A simple method of determination of total acidity can give a clue to the acidic strength of the catalyst and hence to their activity differences. Ammonia adsorption is helpful in measuring and distinguishing acidities of the catalysts. In Fig. 4 a variation in the conversion of phenol with ammonia adsorption is shown. Ammonia adsorption of supported oxides is comparatively higher than the corresponding pure oxides. In other words, addition of 10 wt.-% of vanadia increases the acidity of pure oxides (Table 1). The acidity variation is reflected in phenol conversion and selectivity also (Figs. 1–3). Surface areas of pure oxides vary widely. Addition of vanadia (10 wt.-%) decreases the surface area. Because of the wide differences in surface areas, it is rather difficult to compare the acidity of the catalysts. Hence acidity per unit area is used for comparison. It can be seen that the phenol conversion varies almost linearly with ammonia adsorption per unit area of the oxides and supported oxides. Phenol conversion is dependent on the acidity irrespective of the oxide type or the total surface area.

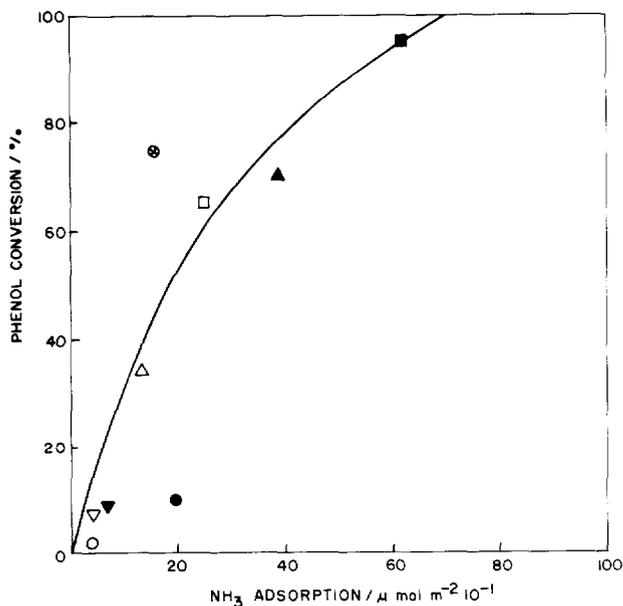As was discussed earlier, addition of vanadia to the other oxides, especially

Fig. 4. Variation of phenol conversion with ammonia adsorption for ($\bigcirc$) SiO_2, ($\triangledown$) MgO, ($\triangle$) $TiO_2(R)$, ($\square$) $TiO_2(A)$, ($\otimes$) V_2O_5, ($\blacktriangledown$) V_2O_5/MgO, ($\bullet$) V_2O_5/SiO_2, ($\blacktriangle$) $V_2O_5/TiO_2(R)$ and ($\blacksquare$) $V_2O_5/TiO_2(A)$.
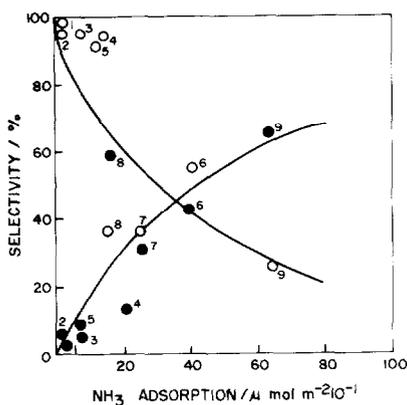
Fig. 5. Variation of selectivity to 2,6-xylenol ($\bullet$) and o-cresol ($\bigcirc$) with ammonia adsorption: ($\bigcirc^1$, $\bullet^1$) MgO, ($\bigcirc^2$, $\bullet^2$) SiO_2, ($\bigcirc^3$, $\bullet^3$) V_2O_5/MgO, ($\bigcirc^4$, $\bullet^4$) V_2O_5/SiO_2, ($\bigcirc^5$, $\bullet^5$) $TiO_2(R)$, ($\bigcirc^6$, $\bullet^6$) $V_2O_5/TiO_2(R)$, ($\bigcirc^7$, $\bullet^7$) $TiO_2(A)$, ($\bigcirc^8$, $\bullet^8$) V_2O_5 and ($\bigcirc^9$, $\bullet^9$) $V_2O_5/TiO_2(A)$.

titania, improves selectivity for 2,6-xylenol. Dependence of selectivity for 2,6-xylenol and o-cresol on acidity as measured by ammonia adsorption is clearly shown in Fig. 5. The selectivity for o-cresol decreases with acidity. It is inferred

that the increase in selectivity for 2,6-xylenol is at the expense of o-cresol. Such a dependence of conversion and selectivity on acidity has also been reported in a vanadia–chromia system [4,5].

Conversion and selectivity

The variation of selectivity to 2,6-xylenol and o-cresol with phenol conversion over $V_2O_5/TiO_2(A)$ is shown in Fig. 6. The WHSV of phenol is varied from 0.73 to 7.3 h^{-1}. The selectivity to 2,6-xylenol increases with increase in phenol conversion and on the other hand the selectivity to o-cresol decreases with the conversion of phenol. The same observation is made in the case of pure oxides and other vanadia supported catalysts. This indicates that the reaction proceeds through the consecutive steps: Phenol→o-cresol→2,6-xylenol. It is inferred that selectivity to 2,6-xylenol and o-cresol depends on acidity and variation in phenol conversion.

It may be concluded that V_2O_5 is a good alkylating catalyst and so also is titania, especially $TiO_2(A)$. However, the selectivity for 2,6-xylenol is higher over vanadia than on the titania (Fig. 2). Addition of 10 wt.-% of vanadia to titania improves the activity and the selectivity for 2,6-xylenol. Other oxides such as MgO and SiO_2 are not good alkylation catalysts, and addition of vanadia does not improve the activity either.

Ammonia adsorption is a simple method of measuring the acidity of oxides. Variations in catalytic behaviour are explained on the basis of acidity. Vanadia improves the acidity of pure oxides. In general, increasing the acidity increases
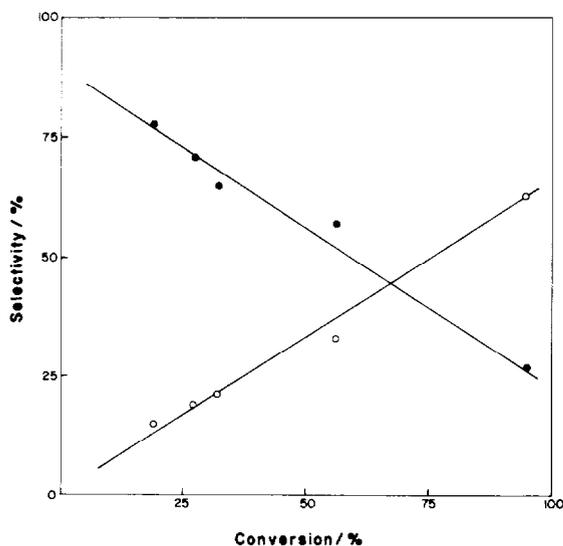

Fig. 6. Variation of selectivity with phenol conversion $V_2O_5/TiO_2(A)$ at 673 K: (○) 2,6-xylenol; (●) o-cresol.

phenol conversion activity and selectivity for 2,6-xylenol. Vanadia in combination with titania offers an interesting mixed oxide system worth studying in greater detail. The structural variations in vanadia and titania and the formation of vanadia–titania species which may influence the alkylation activity has to be looked into.

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