



Vapour phase alkylation of phenol with methanol over vanadium oxide supported on zirconia[☆]

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Abstract

A series of vanadium oxide supported on zirconia catalysts with varying vanadium oxide content (2.5–12.5 wt.%) were prepared by wet impregnation method. The catalysts were characterised by X-ray diffraction (XRD), temperature-programmed reduction (TPR) of hydrogen, temperature-programmed desorption (TPD) of NH₃ and specific surface area measurements. X-ray diffraction patterns indicate the presence of crystalline V₂O₅ phase from 7.5 wt.% of V₂O₅ on zirconia. TPR patterns reveal the presence of V³⁺ species on zirconia. Ammonia TPD results suggest that acidity of the catalysts increased with increase in V₂O₅ loading up to 7.5 wt.% and decreased with further increase in V₂O₅ loading. The catalytic properties were evaluated for the vapour-phase alkylation of phenol with methanol. During alkylation of phenol with methanol exclusively C-alkylated (alkylation proceeds through ring) products were formed. The selectivity towards 2,6-xyleneol was high when compared to *o*-cresol. The activity of the catalysts was found to increase with V₂O₅ loading up to 7.5 wt.% of V₂O₅ and decreased with increase in further vanadia content.

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1. Introduction

In the recent past, alkylation of phenol has gained much attention because practical uses have been found for the products of alkylation by the oxygen atom (O-alkylation) or in the ring (C-alkylation). Several organic intermediates are produced through alkylation of phenol, which are used in agrochemical and pharmaceutical industries; e.g. *o*-cresol is used in the synthesis of herbicides. Dialkyl phenols such as 2,6-xyleneol

are used in the manufacture of polyphenyleneoxide (PPO) and in special grade paints. Trimethyl phenols are precursors for the synthesis of Vitamin E. Anisole and methyl aryl ethers (MAE) are considered as octane number booster for gasoline. It was found that a mixture of MAE can effectively substitute for the non-metallic additives such as methyl tertiary butyl ether (MTBE) [1].

Friedel–Crafts catalysts such as AlCl₃, BF₃, TiCl₄ and liquid HF have been used for the alkylation of phenol. Selective alkylation of phenol on the aromatic carbon atoms has not been very successful [2]. Furthermore, several problems associated with these catalysts such as low selectivity, separation of the catalyst from reactants and products, and disposal of effluents

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restrict the use of these catalysts for industrial application. Solid acid catalysts are found to be very good alternatives to the problems associated with proton acids or Friedel–Crafts type catalysts. A wide variety of catalysts like zeolites [3–5], pure oxides, mixed oxides [6–14] and hydrotalcites [15–17] have been used.

Transition metal oxides can be used as catalysts alone or in combination during vapour phase catalytic reactions. It is believed that a mixture of oxides brings out a combined effect or a sort of synergistic behaviour enhancing the catalytic activity [9,18,19]. The acidic and basic nature of solid acids provide a fascinating opportunity to study these reactions by varying their catalytic properties. 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 [3–5]. Furthermore, the acidic and basic character of simple and mixed oxide catalysts would also affect the product selectivity. Tanabe and Nishizaki [20] showed that catalysts with higher acidic strength were more active but less selective to *ortho*-alkylation. However, TiO₂–MgO is more active and selective than pure MgO for 2,6-xyleneol [8], which has been attributed to a combined effect of weak acidity and strong basicity of the catalyst. The competitive nature for the preferential formation of O- or C-alkylated products is a subject of interest [3,4].

Some of the products mentioned are extensively employed in industry particularly anisole, *o*-cresol, *p*-cresol and 2,6-xyleneol [21–23]. Recently, Grabowska et al. [24] reported the catalytic alkylation of phenol with methanol over zinc aluminate spinel. Samolada et al. [25] reported the selective O-alkylation of phenol with methanol over sulphates supported on γ -Al₂O₃. Phenol methylation on a Fe–V–O/SiO₂ catalyst is one of the catalytic processes, which has been developed in Japan [26]. Santacesaria et al. [27] compared the behaviour of different solid acids: γ -alumina, containing strong acid sites; Nafion-H containing strong Brønsted acid sites; silica–alumina with both Brønsted and Lewis acid sites, and phosphoric acid on kieselghur with moderate and weak Brønsted acid sites. The alkylation of phenol with methanol over zeolites proceeds at both carbon and oxygen, with anisole usually being formed in abundance [3]. It is interesting to find out the absence of anisole in the reaction product of phenol with methanol over HZSM-5 [28].

The use of zirconium oxide as a catalyst support has several advantages over other conventional oxide supports such as alumina, silica and titania. The advantages of using zirconia as a catalyst support include: (i) interacts strongly with the active phase; (ii) possesses high thermal stability and more chemically inert than the conventional supported oxides; (iii) it is the only metal oxide which may possess four chemical properties, namely acidity, basicity as well as the reducing and oxidising ability; (iv) exhibits super-acidic properties when modified with small quantities of sulphate ions.

In the present investigation, we report the alkylation of phenol with methanol over a series of pure zirconia and vanadium oxide catalyst supported on zirconia to produce selectively valuable *o*-cresol and 2,6-xyleneol (C-alkylated products). The aim of this investigation is also to study the effect of vanadium oxide on zirconia during vapour phase alkylation of phenol with methanol. The catalysts were characterised by various techniques like XRD, BET surface area, temperature-programmed reduction (TPR) of H₂, and temperature-programmed desorption (TPD) of NH₃. These findings have been related to the catalytic properties.

2. Experimental

2.1. Catalyst preparation

A series of V₂O₅/ZrO₂ catalysts with V₂O₅ loading in the range of 2.5–12.5 wt.% was prepared by wet impregnation method with requisite amounts of ammonium metavanadate dissolved in oxalic acid solution. The ZrO₂ support (BET surface area of 44 m² g⁻¹) prepared from zirconium hydroxide obtained from MEL chemicals (681/01) and was calcined at 773 K for 5 h.

2.2. X-ray diffraction

X-ray diffraction (XRD) studies were carried out on a Philips PW 1051 diffractometer using Ni-filtered Cu K α radiation. Surface areas were measured by static method using an all pyrex glass system capable of attaining 10⁻⁶ Torr pressure. The specific surface areas of the catalysts were determined by the BET method

using nitrogen physisorption at 77 K taking 0.162 nm^2 as its cross-sectional area.

2.3. Temperature-programmed reduction of hydrogen

Temperature-programmed reduction (TPR) of hydrogen studies were carried out on an AutoChem 2910 (Micromeritics USA) instrument. The unit had a programmable furnace with a maximum operating temperature of 1373 K. The instrument was interfaced to a computer which performs tasks such as programmed heating and cooling cycles, continuous data recording, gas valve switching, data storage and analysis.

In a typical TPR experiment, ca. 250 mg of oven-dried $\text{V}_2\text{O}_5/\text{ZrO}_2$ sample (dried at 383 K for 16 h) was taken in a U-shaped quartz sample tube. The catalyst was packed on a quartz wool plug in one arm of the sample tube. The temperature was monitored with the aid of thermocouples located near the sample from outside and on the top of the sample. The gas flows were monitored by highly sensitive mass-flow controllers. Prior to TPR studies, the catalyst sample was pre-treated at 673 K for 2 h in flowing hydrocarbon free dry air in order to eliminate the moisture and to ensure complete oxidation. After pre-treatment, the sample was cooled to ambient temperature and the carrier gas consists of 5% hydrogen in argon (50 ml min^{-1}), purified by passing through oxy-trap and molecular sieves was allowed to pass over the sample. The temperature was increased from ambient to 1273 K at a heating rate of 10 K min^{-1} and the data was recorded simultaneously. The hydrogen concentration in the effluent stream was monitored with the thermal conductivity detector and the areas under the peaks were integrated using the GRAMS/32 software to determine hydrogen consumption. Calibration of the TCD was performed by stoichiometric reduction of a known amount of high purity Ag_2O to metallic silver, a method that was found to be more reliable and reproducible than sending the known volumes of hydrogen pulses through the reactor.

2.4. Temperature-programmed desorption of NH_3

Temperature-programmed desorption (TPD) studies were carried out on the same instrument used for temperature-programmed reduction analysis. In a

typical experiment, ca. 200 mg of oven dried $\text{V}_2\text{O}_5/\text{ZrO}_2$ sample (dried at 383 K for 16 h) was taken in a U-shaped quartz cell. The catalyst sample was packed in one arm of the sample tube on a quartz wool bed. Prior to TPD studies, the catalyst sample was pre-treated by passing high purity helium (50 ml min^{-1}) at 473 K for 2 h. After pre-treatment of the sample, it was saturated by passing (75 ml min^{-1}) high purity anhydrous ammonia at 353 K and subsequently flushed at 373 K for 2 h to remove the physisorbed ammonia. TPD analysis was carried out from ambient temperature to 1273 K at a heating rate of 10 K min^{-1} . The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector, and the areas under the peaks were integrated using the software GRAMS/32 to determine the amount of desorbed ammonia during TPD.

2.5. Vapour phase alkylation of phenol

The catalytic performance of vanadia catalysts supported on various concentrations of V_2O_5 over zirconia has been tested for the vapour phase alkylation of phenol. The reaction was carried out in a vertical fixed bed, continuous down-flow glass micro-reactor (10 cm in length and 18 mm i.d.) at 673 K under atmospheric pressure. In a typical experiment, ca. 0.5 g of catalyst was packed between the layers of quartz wool, and the upper portion of the reactor was filled with glass beads, which served as pre-heaters for the reactants. The catalyst was kept under activation at 673 K in N_2 flow (40 ml min^{-1}) for 2 h. A mixture of phenol and methanol (1:5 molar ratio) was fed into the reactor at a calculated rate of 1 ml h^{-1} from the top of the reactor using a calibrated syringe (B. Braun, Germany) pump. Prior to the reaction, the catalyst was activated at 673 K for 4 h in nitrogen flow (40 ml min^{-1}). The reaction occurred in the flow integral mode. Since the grain size of the catalyst was large enough and the bed was sufficiently short, it was assumed that there were no limitations to mass or heat transfer. However, the present study is not devoted to the kinetic aspect. The reaction products were analysed using a HP 6890 gas chromatograph equipped with a HP-5 capillary column and a flame ionisation detector (FID). The products were mainly 2,6-xyleneol and *o*-cresol together with trace amounts of higher alkylated products. The percentage conversion was calculated based on phenol

excluding methanol from feed. Selectivity is defined as

selectivity (%)

$$= \frac{\text{desired product (mol\%)}}{\text{conversion of phenol (mol\%)}} \times 100$$

3. Results and discussion

X-ray diffraction patterns of various V_2O_5/ZrO_2 catalysts with vanadia loadings ranging from 2.5 to 12.5 wt.% are shown in Fig. 1. It can be seen from Fig. 1 that all the samples showed XRD peaks due to

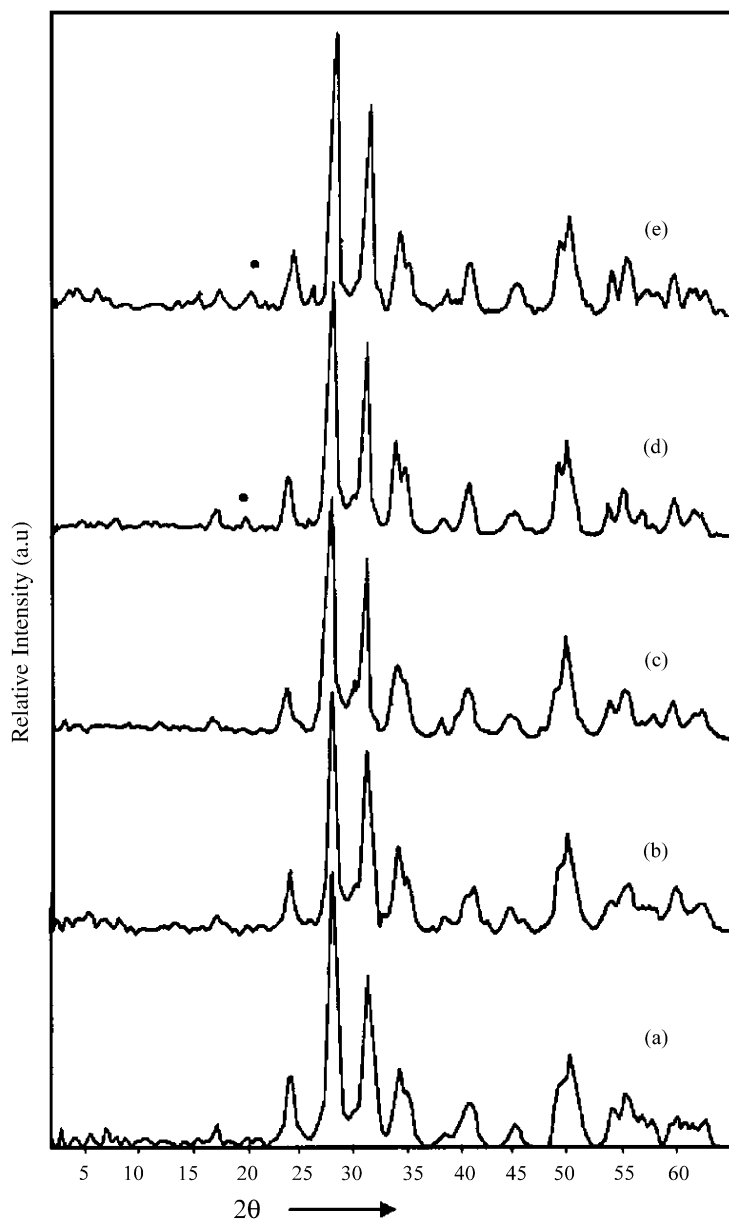


Fig. 1. X-ray diffractograms of V_2O_5/ZrO_2 catalysts: (a) 2.5% V_2O_5/ZrO_2 ; (b) 5% V_2O_5/ZrO_2 ; (c) 7.5% V_2O_5/ZrO_2 ; (d) 10.0% V_2O_5/ZrO_2 ; (e) 12.5% V_2O_5/ZrO_2 ; (●) V_2O_5 .

Table 1

Results of BET surface area and total pore area measurements of various V₂O₅/ZrO₂ catalysts

S. no.	V ₂ O ₅ loading on ZrO ₂ (w/w) (%)	BET surface area m ² g ⁻¹	Total pore area m ² g ⁻¹
1	0.0	44	63
2	2.5	52	72
3	5.0	49	–
4	7.5	44	55
5	10.0	40	–
6	12.5	36	48

monoclinic zirconia with major peaks at $d = 3.16$ and 2.834 \AA . For samples $<7.5 \text{ wt. \% V}_2\text{O}_5$, no XRD peaks corresponding to vanadium oxide crystallites were observed indicating that vanadium oxide is present in a highly dispersed amorphous state on zirconia. It is also possible that the vanadia crystallites may be present but having size $<4 \text{ nm}$, which is beyond the detection capacity of XRD technique. However, XRD peaks corresponding to V₂O₅ at $2\theta = 20.26$ can be seen only from 7.5 wt. \% sample, and its intensity is found to increase with increase of vanadia loading. The presence of crystalline V₂O₅ in the sample facilitates and accelerates the crystallisation of ZrO₂ and is reflected in the decreased surface area from $7.5 \text{ wt. \% V}_2\text{O}_5/\text{ZrO}_2$ (Table 1). The amount of vanadia needed for total coverage of support as 2D monolayer was estimated by Bond and Tahir [29] and it was 0.145 wt. \% of V₂O₅ per m² of the support surface. Therefore, ZrO₂ support having surface area $44 \text{ m}^2 \text{ g}^{-1}$ requires a quantity of $6.38 \text{ wt. \% V}_2\text{O}_5$ to yield a single monolayer. In the present study, V₂O₅ crystallites appears starting from 7.5 wt. \% of V₂O₅. This result is in good agreement with theoretical monolayer value. The present XRD results also indicate that there is no compound formation by the interaction between ZrO₂ and V₂O₅. Male et al. [30] observed the formation ZrV₂O₇ at higher loadings of vanadium oxide. The surface area of the ZrO₂ prepared was $44 \text{ m}^2 \text{ g}^{-1}$, and is decreased as a function of vanadia content as shown in Table 1. This decrease of surface area with increasing vanadia loading might be due to blockage of pores of the support by crystalline vanadium oxide. Total pore area of samples measured by mercury penetrating porosimeter has been presented in Table 1. The total pore area decreased with increase in vanadia loading in the similar lines of surface areas of the catalysts. The

Table 2

Results of temperature-programmed reduction (TPR) of hydrogen over V₂O₅/ZrO₂ catalysts

S. no.	V ₂ O ₅ on ZrO ₂ (wt.%)	T_{max} (K)	H ₂ consumption (ml g ⁻¹ ·cat)
1	2.5	713	5.6
2	5.0	700	8.3
3	7.5	710	16.9
4	10.0	717	18.3
5	12.5	738	34.7

TPR profile of unsupported V₂O₅ has been shown in Fig. 2 and the TPR profiles of supported V₂O₅/ZrO₂ samples are shown in Fig. 3. Sato et al. [31] discussed the effect of redox properties of CeO₂ with $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ and basic sites on the propylation of phenol and 1-propanol transformation into 3-pentanone. The results of TPR by various V₂O₅/ZrO₂ catalysts show a schematic change in the reduction of vanadia with increase of vanadia loading. The TPR profiles for all samples have shown only one prominent peak maximum (T_{max}). The dependence of T_{max} on V₂O₅ content and the amount of hydrogen consumed during TPR are given in Table 2. Baiker et al. [32] reported that titania supported vanadium oxide catalysts exhibited only one reduction peak during TPR, if less than four layers of vanadium oxide was deposited. Our previous studies [33] also confirm this result. From Fig. 3 and Table 2, it has been observed that the T_{max} values increases from 700 to 738 K with increase of vanadia loading suggesting the presence of the same kind of vanadia species, probably due to the crystalline vanadia phase as evidenced from the XRD results of the samples. The increase in intensity of TPR profiles with vanadia content indicates that the quantity of hydrogen consumed is proportional to the vanadia loading (Table 2). The amount of hydrogen consumed during TPR indicates that the reducibility of vanadia increases with the vanadia loading on ZrO₂. TPR results also suggest that at low vanadia loadings the interaction of vanadia with zirconium oxide is stronger compared to higher vanadia contents. TPR of unsupported V₂O₅ (Fig. 2) reveals that it reduces at higher temperature when compared to V₂O₅/ZrO₂ catalysts which is in consistent with the work of Koranne et al. [34] and Bosch et al. [35]. They have shown that supported vanadium oxide catalysts reduce at much lower temperature than bulk vanadia

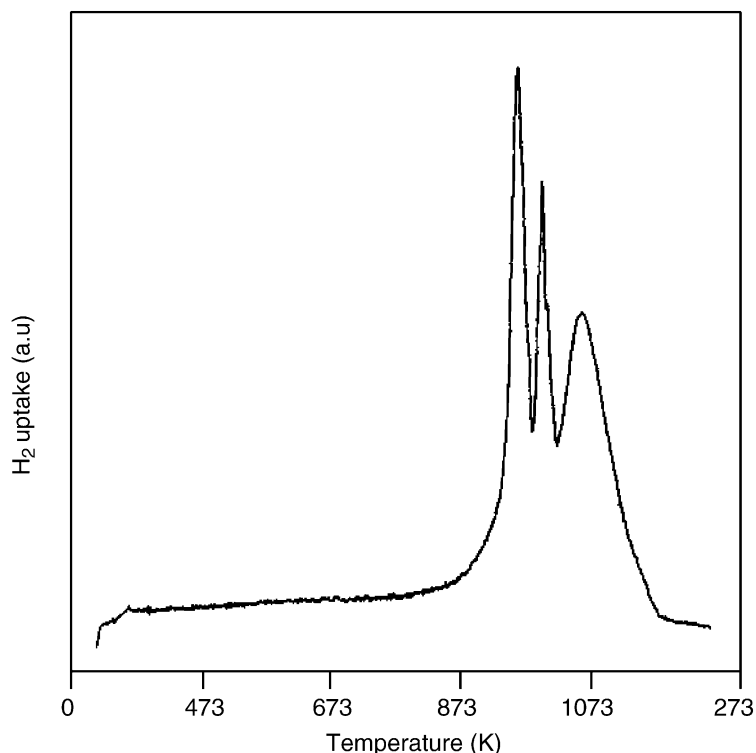


Fig. 2. Temperature-programmed reduction (TPR) profile of unsupported V_2O_5 .

and the reducibility of vanadia is strongly influenced by the kind of support used. They have attributed this phenomenon to the following reduction sequence.



The sharp peak at 965 K corresponds to the reduction of V_2O_5 to V_6O_{13} (first peak), the peak at 1003 K is associated with the reduction of V_6O_{13} to V_2O_4 (second peak), and the third peak at 1067 K corresponds to V_2O_3 formed by the reduction of V_2O_4 . The reduction conditions applied were similar to those of the supported V_2O_5/ZrO_2 catalysts. Bond et al. [36] reported that the VO_x monolayer species are reduced in a single step from V^{5+} to V^{3+} .

Temperature-programmed desorption (TPD) of probe molecules like ammonia and pyridine is a popular method for the determination of acidity of solid catalysts as well as acid strength. Ammonia

is used frequently as a probe molecule because of its small molecular size, stability and strong basic strength ($pK_a = 9.2$). In the present investigation, the acidity measurements have been carried out by ammonia TPD method. The acidity values ($ml\ g^{-1}$) measured by temperature-programmed desorption of NH_3 method are given in Table 3. From the peak positions, it is clear that the acidity corresponds to desorption of NH_3 in only one temperature region associated with moderate acid strength. The acidity

Table 3
Results of temperature-programmed desorption (TPD) of NH_3 over V_2O_5/ZrO_2 catalysts

S. no.	V_2O_5 on ZrO_2 (wt.%)	Total acidity ($ml\ g^{-1}\cdot cat$)
1	Pure ZrO_2	4.6
2	2.5	7.3
3	5.0	9.8
4	7.5	11.4
5	10.0	11.2
6	12.5	9.8

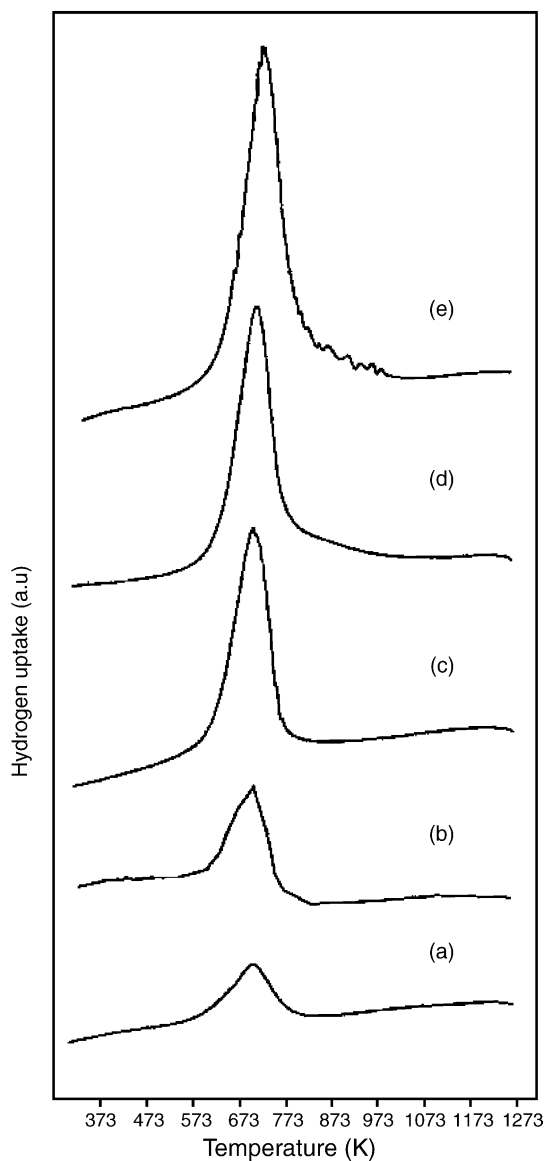


Fig. 3. Temperature-programmed reduction (TPR) profiles of V_2O_5/ZrO_2 catalysts: (a) 2.5% V_2O_5/ZrO_2 ; (b) 5% V_2O_5/ZrO_2 ; (c) 7.5% V_2O_5/ZrO_2 ; (d) 10.0% V_2O_5/ZrO_2 ; (e) 12.5% V_2O_5/ZrO_2 .

of the catalysts was found to increase with V_2O_5 loading up to 7.5 wt.% of V_2O_5 and decreased with increase in further vanadia content. The decrease in acidity above 7.5 wt.% may be due to the vanadium crystallites and subsequent decrease in surface area of the catalyst. This result is further supported by XRD

and BET surface area measurements of vanadium oxide supported on zirconia catalysts. Interestingly, the conversion of phenol and the selectivity towards 2,6-xyleneol follow the same trend as shown in Fig. 4.

Activity and selectivity during the vapour phase alkylation of phenol is shown in Fig. 4. The conversion was found to increase with vanadia loading up to 7.5 wt.% and decreased with further increase in vanadia loading. During the reaction only C-alkylated products of phenol were formed. The selectivity of *o*-cresol and 2,6-xyleneol increased with vanadia content. Formation of trimethyl phenol was also found to occur during the reaction and the selectivity towards this remained constant with increase in vanadia content.

Alkylated products of phenol are governed by the type of phenol adsorption on the catalysts surface, depending on its acidic strength. On highly acidic or strong Brønsted acid sites, the phenol ring takes a position parallel to the surface as shown in Scheme 1. In this case, all the activated positions of phenol are available for the reaction resulting substitution in the *ortho*, *meta*, as well as *para* in addition to the formation of ethers occur. Here, the selectivity mainly depends on the distance between acid sites and acidic strength. In the case of catalyst with moderate acidity or Lewis acid sites coupled with basic sites, phenol ring adsorbs vertically and dissociatively to the surface giving preference to an attack in the *ortho* position or on oxygen of phenol as shown in Scheme 2. In the present investigation, we observed mainly *ortho*-products. This could be due to the reaction proceeding through an attack of methyl carbocation of methanol at *ortho* position of the ring rather than oxygen of phenol. Such reaction pathway for the methylation of phenol over hydrotalcites was also described in the literature [16]. Since the formation of 2,6-xyleneol takes place via *o*-cresol, the increase in selectivity of former decreases the selectivity of latter. Acidity of the catalysts plays an important role in the activity of the catalysts. Table 4 suggests that pure zirconia is also active for the reaction and the selectivity towards *o*-cresol is higher compared to vanadium oxide supported catalysts. Alkylation of phenol with methanol over 10 wt.% vanadium oxide catalysts supported on magnesia, silica, titania has been reported earlier. The authors correlated the acidity of the catalysts measured per unit area of 10 wt.% V_2O_5 on

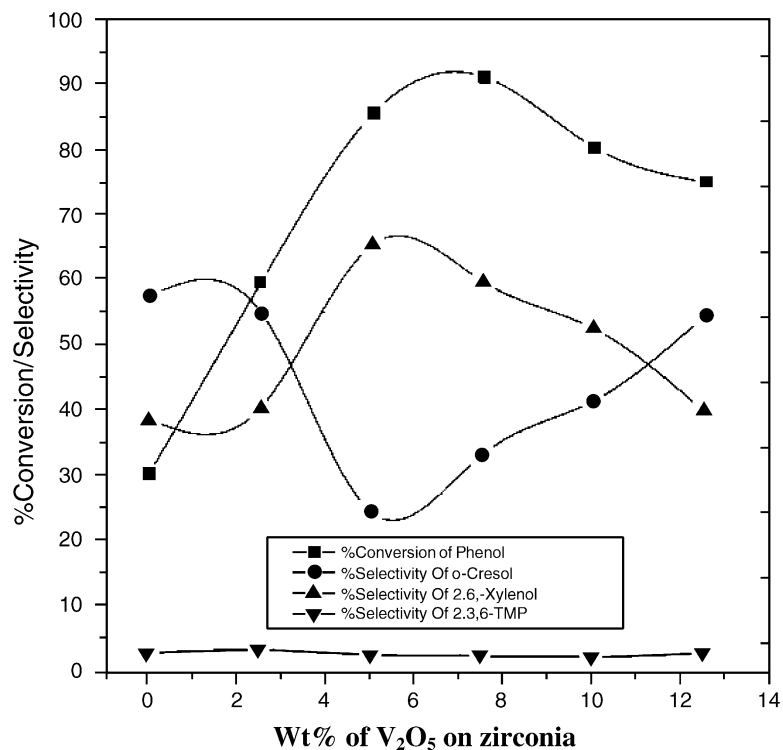


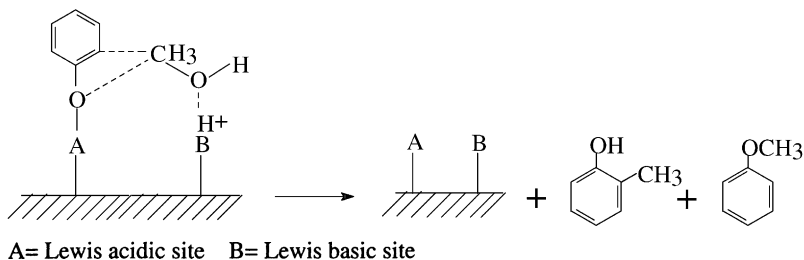
Fig. 4. Alkylation of phenol with methanol over V₂O₅/ZrO₂ catalysts (reaction temperature, 673 K).



Scheme 1.

different supports with its activity and found that the phenol activity varies almost linearly with ammonia adsorption on unit area [10]. The alkylation of phenol with methanol over La₂(HPO₄)₃, BaSO₄ and Al₂O₃

by vapour- and liquid-phase reactions also yields mainly anisoles [7]. Methylation of phenol over acidic oxides such as WO₃, MoO₃, Al₂O₃, SiO₂-Al₂O₃ by liquid phase reaction yields cresols and anisoles [2].



Scheme 2.

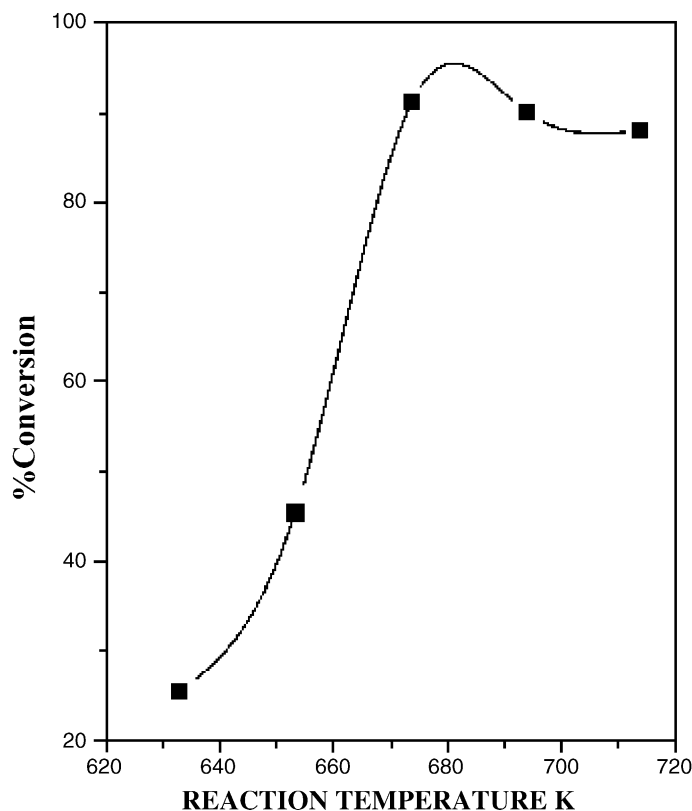


Fig. 5. Dependence of conversion on the reaction temperature (K) over catalyst 7.5 wt.% of V_2O_5/ZrO_2 .

However, these catalyst systems showed low selectivity to 2,6-xyleneol and larger amount of other derivatives of phenol in addition *o*-substituted phenols. Oxide catalysts are more selective for the synthesis of 2,6-xyleneol than zeolites because of pore constraints. In the present study, conversion of phenol increased

Table 4

Results of alkylation of phenol with methanol over V_2O_5/ZrO_2 catalysts (reaction temperature at 673 K)

V_2O_5 on ZrO_2 (wt.%)	Conversion (%)	Selectivity (%)		
		<i>o</i> -Cresol	2,6-Xyleneol	2,3,6-TMP ^a
0.0	30.2	57.5	38.6	2.8
2.5	59.7	55.0	40.5	3.5
5.0	85.8	24.6	65.7	2.7
7.5	91.5	33.5	60.0	2.7
10.0	80.7	41.8	53.0	2.6
12.5	75.6	55.0	40.5	3.4

^a 2,3,6-Trimethyl phenol.

linearly with acidity up to a certain limit and at higher acidities, the conversion was independent of acidity. In order to optimise the reaction conditions such as temperature, the reactivity of 7.5 wt.% V_2O_5/ZrO_2 was studied in the range of 633–693 K. The effect of reaction temperature on the catalytic behaviour during vapour phase alkylation of phenol is shown in Fig. 5. The conversion of phenol increases with increase in temperature and levels off at higher temperatures.

4. Conclusions

Vapour phase alkylation of phenol with methanol was investigated over V_2O_5 supported on monoclinic zirconia catalysts prepared by wet impregnation method. The V_2O_5/ZrO_2 had stable catalytic activity at 673 K under atmospheric pressure and highly active and selective towards C-alkylated products of

phenol. The highest catalytic activity for alkylation of phenol with methanol was achieved over 7.5 wt.% V₂O₅/ZrO₂ catalyst. The highest selectivity towards 2,6-xyleneol was also found on 7.5 wt.% at 673 K at atmospheric pressure. The catalytic activity during vapour phase alkylation of phenol with methanol is directly related to the total acidity and BET surface areas of the catalysts. This investigation thus reveals an optimum composition of 7.5 wt.% vanadia over monoclinic zirconia catalyst for selective alkylation of phenol to 2,6-xyleneol.

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