

Catalysis of C-alkylation of phenol using V_2O_5 - La_2O_3 system

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Vapour phase methylation of phenol is carried out over La_2O_3 supported vanadia systems of various composition. The structural features and physico chemical characterisation of the catalysts are investigated. Orthovanadates are formed in addition to surface vanadyl species on the metal oxide support. No V_2O_5 crystallites are detected. The acid base properties of the oxides are studied by Hammett indicator method and decomposition of cyclohexanol. The data are correlated with the catalytic activity and selectivity of the products. Ring alkylation is found to be predominant over these catalysts.

Supported vanadia are active components of practical catalysts for ammoxidation reactions¹, oxidation of hydrocarbons^{2,3}, selective catalytic reduction⁴ etc. due to their attractive catalytic features. Dispersion of vanadia on the catalyst surface depends strongly on acid base properties of the support and its vanadium content. At low % of vanadia, a finely dispersed layer is observed which includes mono oxo species and two dimensional vanadium oxide clusters. If the composition exceeds a particular value, crystalline vanadia formation is reported along with poly vanadates⁵. Preferential formation of orthovanadates on highly basic catalysts has been reported by Corma *et al.*⁶. With more acidic supports V_2O_5 crystallites are formed.

Phenol alkylation is an important reaction from the industrial point of view. Both O- and C-alkylated products are formed during alkylation which include anisole, *o*-cresol and 2,6-xyleneol. Formation of trimethyl phenol is also reported⁷. Anisole is an additive in gasoline, *o*-cresol is an intermediate for the preparation of herbicides and insecticides and 2,6-xyleneol is used in the manufacture of paints. Selectivity of the products in this reaction is found to depend on the acid base property of the catalyst. Enhancement of C-alkylated products by strong acidic sites have been reported by Balsama *et al.*⁸. On the other hand, Benzouhanava *et al.* have claimed that strongly acidic catalysts favour O-alkylation⁹. Tanabe has reported

that *ortho* alkylated product selectivity increases with basicity of the catalyst employed¹⁰. Nature of the products formed is governed by the orientation of phenoxide anion while adsorbed on the catalyst surface. If it is a highly basic catalyst, interaction of the electron cloud of the benzene ring with the surface will be negligible and the ring will be almost perpendicular resulting in O-alkylated products. In this paper, we report the surface properties of La_2O_3 - V_2O_5 system. The characterisation of La_2O_3 - V_2O_5 catalysts are performed by means of FTIR, XRD, EDX and measurement of surface area and pore volume. The acid base property of the system is studied by Hammett indicator method and cyclohexanol decomposition. The data have been correlated with the catalytic activity of these oxides towards phenol alkylation as a test reaction.

Experimental

Catalyst preparation

Wet impregnation method was adopted for preparing supported catalysts. A solution of NH_4VO_3 in oxalic acid was stirred with the support material, which in turn was prepared via hydroxide method by precipitation from its nitrate solution. The resulting mass was evaporated in a water bath, kept at 110°C overnight and calcined at 450°C for 6 h. All the catalysts were sieved to a mesh size < 100 microns and activated at 500 °C before each experiment. Catalysts are denoted by their wt % of vanadia; L3, L7, L11 and L15 for 3,7,11 and 15 wt% of V_2O_5 .

Characterisation

The chemical composition was determined by Energy Dispersive X-ray analysis (Stereoscan 440 Cambridge, UK). XRD of the samples were measured by a Ni filtered $Cu K_{\alpha}$ radiation using a DNAX-C Rigaku X-ray diffractometer. Shimadzu FTIR-8101 instrument was used to record IR spectra of the supported samples by KBr disk method. The specific surface area of the catalysts were determined by BET method by nitrogen adsorption using a Micromeritics Flow-prep-060 instrument. Mercury porosimeter (Quantachrome, Auto scan-92 porosimetry, USA) was used for measuring pore volume.

Titrimetric method using Hammett indicators was used to measure the acid base property of the cata-

Table 1—Surface properties of vanadia supported on lanthana

Catalyst	V ₂ O ₅ , %	Basicity (mmol g ⁻¹)			BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
		pKa ≥ 3.3	pKa ≥ 4.8	pKa ≥ 7.2		
L	0	0.530	0.170	0.097	45.23	1.00
L3	2.82	0.384	0.110	0.063	31.53	1.11
L7	6.34	0.220	0.101	0.048	32.12	1.01
L11	9.32	0.448	0.138	0.067	40.52	1.40
L15	13.10	0.570	0.181	0.099	48.15	0.86

lysts. Indicators tried are the following; pKa values are given in the parenthesis: Crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). For basicity determination, two drops of 0.1 % solution of indicators in benzene was added to a suspension of trichloroacetic acid until a permanent colour change was obtained. Cyclohexanol decomposition reaction was also conducted to investigate the acid base property.

The reaction was carried out in a down flow reactor consisting of 2.2 cm I.D and 30 cm length, kept in a cylindrical furnace mounted vertically. Catalysts in pellet form was loaded in the middle of the reactor and packed with glass beads. The catalysts were activated in a current of dry air prior to each experiment at 773 K for 6 hours and then brought to the reaction temperature in the presence of nitrogen flow. The reactant feed was introduced at the top of the reactor by means of an infusion pump (SAGE, USA). The products were analysed in a gas chromatograph (GC15-A) fitted with a SE30 column and FID.

Results and discussion

XRD pattern gave reflections at 2θ values of 12.9 and 29.4 for supported oxides corresponding to orthovanadate species in addition to that of La₂O₃. Preferential formation of orthovanadates on basic catalysts rather than bulk vanadia is reported⁶. Peaks characteristic of crystalline V₂O₅ is not observed. Amount of orthovanadate formed increases with increase in weight % of vanadia in the supported catalysts. This is evident by the ratio of intensities of the reflections of La₂O₃ and LaVO₄. SEM patterns show that the particle size first increases followed by a decrease as the composition of vanadia is increased. This is in accordance with BET surface area (Table 1). Addition of vanadia decreases the surface area. This may be due to agglomeration of the particles. Further addition increases the surface area of the supported sys-

Table 2—Data on rate of cyclohexanol decomposition [Reaction conditions : catalyst = 2.5 g; reaction temp. = 350 °C; Feed rate = 6 ml/h; TOS = 1h.]

Catalyst	Rate(10 ⁻⁵ mol s ⁻¹ g ⁻¹)	
	Dehydration	Dehydrogenation
L3	19.35	3.24
L7	21.29	3.32
L11	15.70	3.29
L15	14.24	3.05

tem. Pore volume also show a corresponding variation.

IR spectra of the samples calcined at 500°C gave the following observations. None of these showed the significant band of crystalline vanadia which appears at 1020 cm⁻¹. Band due to amorphous vanadia was observed at 1060 cm⁻¹. Absence of a band at 1000-950 cm⁻¹ region indicated the absence of polyvanadate formation on the surface¹¹. The broad band localised at 900-700 cm⁻¹ was attributed to orthovanadate species¹².

Basicity data are also presented in Table 1. The catalyst systems responded only to dimethyl yellow, methyl red and bromothymol blue. Basicity decreases up to 6.34% of vanadia and then increases with further vanadia addition. Cyclohexanol decomposition data also support this observation (Table 2). It has already been accepted that acidity is proportional to rate of dehydration and dehydrogenation rate is proportional to both acidity and basicity¹³. Dehydration is prominent over these catalysts indicating the existence of acid sites sufficiently strong to catalyse dehydration. Cyclohexene formed by dehydration isomerises to methyl cyclopentene which suggests the presence of strong acid sites as pointed out by Pines *et al.*¹⁴. For the supported catalysts, dehydration rate (acidity) is in the order L7 > L3 > L11 > L15. The acidity generation during vanadia addition is due to surface vanadyl species. The vanadium ion present in the amorphous vanadia acts as Lewis acid site. So surface vanadyl species are supposed to be maximum

Table 3—Data on phenol methylation over $\text{La}_2\text{O}_3\text{-V}_2\text{O}_5$ system
 [Reaction conditions : catalyst = 3 g; reaction temp. = 350 °C; phenol : methanol ratio = 1 : 7 ; FR = 4ml/h; TOS = 1.5 h.]

Product distribution (wt %)	Catalyst			
	L3	L7	L11	L15
Anisole	26.71	29.18	24.77	22.65
<i>o</i> -Cresol	69.29	57.23	67.12	68.73
2,6-Xylenol	3.99	12.07	6.71	7.22
Trimethyl phenol	—	1.51	1.40	1.39
Sel. of <i>ortho</i> products	73.29	70.82	75.23	77.35
Conversion (%)	13.68	26.69	23.31	22.45

for L7 system. It has been proposed that surface Bronsted acid sites are also there in supported catalysts which are located at bridging M-O-support bond. Basicity decrease is accompanied by a concomitant increase of the acidity of $\text{V}_2\text{O}_5\text{-La}_2\text{O}_3$ system.

The % conversion and selectivity of products in the methylation of phenol are shown in Table 3. Ring alkylation takes place predominantly over these catalysts. C-alkylated product selectivity is more than 70%. This may be due to strong basic sites present on the catalysts as reported by Benzouhanava *et al.*⁹. $\text{La}_2\text{O}_3\text{-V}_2\text{O}_5$ systems are found to be effective for the synthesis of *o*-cresol, for which the system was found to have maximum selectivity. Selectivity of *ortho* products (*o*-cresol and 2,6-xylenol) is in the order L15 > L11 > L3 > L7. This is in accordance with the view of Tanabe *et al.* that *ortho* selectivity is proportional to the basicity of the catalyst¹⁰. This is explained by the mode of adsorption of phenoxide ion. On basic systems the electron cloud of the benzene ring will be repelled by the catalyst surface, giving access for the methyl groups to *ortho* positions. So *ortho* selectivity will be maximum for more basic catalyst.

Higher alkylated phenols are obtained for systems with higher percentage of vanadia. *o*-Cresol formed undergoes further methylation to give 2,6-xylenol and trimethyl phenol (TMP). But there is no considerable increase in selectivity of 2,6-xylenol and TMP as reported on $\text{Sm}_2\text{O}_3\text{-V}_2\text{O}_5$ system. Trimethyl phenol formation in the case of higher vanadia loaded catalysts is due to the generation of acidic sites on the surface. The interaction of acid sites and the benzene ring will bend the phenoxide ion towards the catalyst surface. So it will be easy for an adsorbed alkylating group for migration to other positions also generating higher alkyl phenols. Trimethyl phenol selectivity doesn't show a drastic change with acid base properties. The selectivity is maximum for L7 which is sup-

posed to be the most acidic one among the catalyst series. Selectivity of anisole formed depends upon the acidity of the system. As the acidity increases anisole selectivity also increases as evident from the higher anisole selectivity of L7.

Anisole formed can undergo 2° reactions in two different pathways. It can undergo a bimolecular reaction to give a mixture of phenol and methylanisole or a monomolecular rearrangement to give *o*-cresol. 2-Methylanisole is not observed indicating that anisole does not undergo a bimolecular reaction as observed on some other systems like MgAl-CHT catalysts in which the products are phenol and methylanisole¹⁵. Here the decrease in anisole selectivity is accompanied by an increase in *o*-cresol selectivity as acid base property changes with vanadia addition. This can be understood as a monomolecular rearrangement taking place over these samples.

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