



# Friedel-Crafts Alkylation of *o*-xylene over V<sub>2</sub>O<sub>5</sub>/ ZrO<sub>2</sub> Catalysts

Sreejarani K Pillai,\* O Gheevarghese† and I V Tleane‡

## Abstract

The present study has undertaken the Friedel-Crafts benzylation of aromatics over the V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> catalysts systems. Catalysts with different V<sub>2</sub>O<sub>5</sub> content (0-15wt %) was prepared by wet impregnation method and characterized by XRD, BET surface area, FTIR and <sup>51</sup>V NMR techniques. The surface acidic properties were determined by temperature programmed desorption of NH<sub>3</sub>, cumene cracking and perylene adsorption. Under the optimized reaction conditions, these catalysts are found to be very effective and considerably more selective than the conventional homogeneous Lewis acid catalysts. The investigation of vanadia systems-catalyzed benzylation of *o*-xylene with benzyl chloride revealed that the catalytic activity and product selectivity are sensitive to the precise reaction parameters and can be related to the Lewis acidity of the systems. The reaction is found to be very clean and produces the desired monoalkylated product with high yield.

**Keywords:** V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> catalysts, Friedel-Crafts alkylation, Lewis acidity

---

\* DST/CSIR Nanotechnology Innovation Centre, National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, Pretoria 0001, South Africa, SKPillai@csir.co.za

† Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa, gheevargheseo@tut.ac.za

‡ Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa, tleaneiv@yahoo.com

## 1. Introduction

The Friedel-Crafts alkylation reactions are of great interest due to their importance and common use in synthetic and industrial chemistry [1]. The alkylation is traditionally performed with alkyl halides using Lewis acid catalysts such as HF and  $\text{AlCl}_3$  or with alcohols using Brønsted acids, typically  $\text{H}_2\text{SO}_4$  [2]. However, these homogeneous catalysts encounter major disadvantages like corrosion, unfriendliness to environment due to the waste by-products induced by isomerization in the reaction and heavy expense due to the requirement of large quantity of reagents. As a result, there was a long felt demand to substitute these reagents by less corrosive and more environment friendly materials [3]. Intensive research in this direction revealed the possible suitability of the materials in the form of solid acids developed from heteropolyacid [4], clays [5], zeolites [6], sulfated zirconia [7], transition metal cations [8], etc. The single metal oxide catalysts have shown drawbacks such as lower product selectivity, formation of higher amount of polyalkylated products and drastic reaction conditions. It is believed that introduction of a second component oxide to the support metal oxide could bring out a combined effect or a sort of synergistic behaviour enhancing the catalytic activity and product selectivity [9-11].

Zirconium oxide is a widely studied material in catalysis field due to its potential to be used as a catalyst support or promoter for a variety of catalyst systems [12-15]. The use of vanadia based catalysts in the synthesis of fine chemicals is an increasing area of application and growing importance in recent years [16-18]. Furthermore, from a reaction point of view, it has been well documented that the selectivity and activity of these supported vanadia catalysts depends on the acid-base properties of the support, calcination temperature and percentage of vanadia loading apart from its surface acidity [19]. By contrast, the utility of vanadia catalysts in the Friedel-Crafts alkylation of aromatic compounds has not been explored in sufficient detail.

The objective of this study is to investigate the possibility of enhancing the conversion of aromatics and selectivity to the monoalkylated products, consequently to minimize the formation

of polyalkylated products. We report the results obtained in the alkylation of *o*-xylene by benzyl chloride over vanadia supported on ZrO<sub>2</sub>. The results obtained are compared with the efficiency of the Lewis acid catalyst AlCl<sub>3</sub>.

## 2. Experimental

### 2.1 Catalyst preparation

#### 2.1.1 Pure ZrO<sub>2</sub>

Hydrous zirconium oxide was prepared by the hydrolysis of zirconyl nitrate with 1: 1 ammonia. Zirconyl nitrate was dissolved in minimum amount of doubly distilled water. To a boiling solution of zirconyl nitrate in water, aqueous ammonia was added drop wise with constant stirring till complete precipitation was achieved. The pH of the final solution was in the range 10-11. The solution was solidified and was made into a colloidal state which was boiled for about 15 minutes and then it was allowed to stand overnight. The precipitate was filtered and washed repeatedly with distilled water until it was free of nitrate ions. Then it was oven dried at 383 K for 12 h, powdered and calcined for 5 h at 823 K.

#### 2.1.2. V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> catalysts

The catalysts with various vanadium oxide contents were prepared by wet impregnation of metal oxide in the hydroxide form with required amount of oxalic acid solution of ammonium metavanadate. The vanadia loading was varied from 3 to 15 wt%, as indicated by the number in the sample notation. The solution was evaporated to dryness with vigorous stirring. The precipitate obtained was oven dried at 383 K for 12 h, powdered and calcined at 823 K for 5 h. The general notation ZX stands for ZrO<sub>2</sub> system with X wt% vanadia loading.

### 2.2 Catalyst characterization

The crystal structure of the samples was identified by XRD (Rigaku D-max C X-ray diffractometer) measurement using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ). FTIR spectra of the powder samples were measured by the KBr disc method over the range 4000–400 cm<sup>-1</sup> using Shimadzu DR 5001 instrument. <sup>51</sup>V NMR spectra of the

prepared samples were measured with a 300 DSX Bruker spectrometer at a static magnetic field of 8.5 T. The spectra were expressed with the reference signal of  $\text{NH}_4\text{VO}_3$  at a chemical shift value of 0 ppm and the higher frequency shift from the standard was taken as positive. Simultaneous determination of BET surface area and total pore volume of the samples were achieved in a Micromeritics Gemini 2360 surface area analyzer by the low temperature  $\text{N}_2$  adsorption method.

The surface acidic properties of the prepared catalysts were measured by  $\text{NH}_3$ -TPD (373–873 K) in a conventional flow-type apparatus at a heating rate of  $10 \text{ K min}^{-1}$  and in a nitrogen atmosphere. Electron acceptor studies were carried out by stirring a weighed amount of the catalyst with different concentrations of perylene in benzene solvent. The amount of perylene adsorbed was determined by measuring the absorbance of the solution in a UV-VIS spectrophotometer (Shimadzu UV-160 A) before and after adsorption. The limiting amount of perylene adsorbed was obtained from Langmuir plots. Cumene conversion reaction was adopted for the differentiation between Brønsted and Lewis acid sites. The reaction was carried out in a continuous down-flow reactor at 623 K at a flow rate of  $6 \text{ mL h}^{-1}$  and with a time on stream of 2 h. The products were analysed by Chemito 8610 GC, SE-30 column and flame ionization detector.

### 2.3 Friedel-Crafts alkylation of *o*-xylene

The liquid phase benzylation of *o*-xylene using benzyl chloride was carried out in a 50 mL double-necked flask fitted with a spiral condenser. The temperature was maintained using an oil bath. In a typical run, *o*-xylene and benzyl chloride in the specific molar ratio was added to 0.1 g of the catalyst in the round bottom flask and the reaction mixture was magnetically stirred. The product analysis was done using a Chemito 8610 gas chromatograph equipped with a flame ionisation detector and an SE-30 column. The aromatic substrate being taken in excess, the yields were calculated based on the amount of alkylating agent. The selectivity for a product is expressed as the amount of the particular product divided by the total amount of products and then multiplied by 100.

### 3. Results and Discussion

#### 3.1 Catalyst Characterization

Table 1 presents the surface area and pore volume for pure and vanadia loaded  $ZrO_2$  samples. Vanadia-impregnated samples show higher surface area when compared to pure  $ZrO_2$ .

The surface area increases gradually upon impregnation of vanadia up to 6 wt%, and then decreases at high loadings. The trend in surface area could be explained by the fact that at smaller quantities,  $V_2O_5$  reduces sintering whereas at high loadings crystalline  $V_2O_5$  block the pores of the support [20]. The low pore volume of high vanadia-loaded system also supports surface area results.

Catalyst	BET surface area ( $m^2 g^{-1}$ )	Pore volume ( $cm^3 g^{-1}$ )	Total acid sites (amount of $NH_3$ desorbed ( $mmol g^{-1}$ ))	Selectivity to $\alpha$ -methyl styrene in cumene cracking reaction (%)	Perylene adsorbed ( $10^{-6} mol g^{-1}$ )
Z0	43	0.058	0.25	32.0	0.08
Z3	78	0.083	0.34	52.3	0.43
Z6	89	0.085	0.75	87.1	0.98
Z9	72	0.081	0.58	61.0	0.74
Z12	53	0.020	0.42	59.6	0.71
Z15	47	0.020	0.33	45.6	0.69

Table 1: Surface and acidic properties of  $V_2O_5/ZrO_2$  systems

The XRD pattern of pure zirconia (Fig. 1) shows tetragonal phase of  $ZrO_2$ , in agreement with the literature reports [21]. Introduction of vanadia seems to stabilize the tetragonal phase of zirconia by delaying the transformation to the thermodynamically favoured monoclinic phase. The absence of characteristic peaks corresponding to the vanadium oxide species in the supported systems with vanadia loading up to 6 wt% implies that the added

vanadia is highly dispersed on the  $\text{ZrO}_2$  surface in the form of  $\text{VO}_4$  tetrahedra or in the form of two dimensional oxovanadate structures [22, 23]. The additional peaks observed at  $2\theta$  values of 20 and 24 for high vanadia loaded samples may be attributed to the crystal planes of  $\text{V}_2\text{O}_5$  crystallites [24].

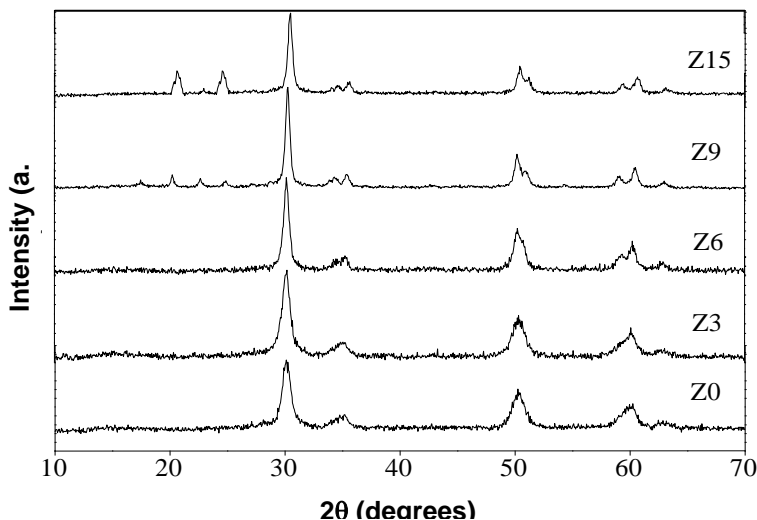


Fig. 1. XRD profiles of  $\text{V}_2\text{O}_5/\text{ZrO}_2$  systems.

FTIR spectra of different  $\text{V}_2\text{O}_5/\text{ZrO}_2$  catalysts with various vanadium oxide contents are given in Fig. 2. The two strong absorption bands around  $3429$  and  $1627$   $\text{cm}^{-1}$  in the case of pure zirconia may be attributed to the surface hydroxyl groups whereas the band at  $456$   $\text{cm}^{-1}$  is characteristic of the Zr-O bonds [25]. Z6 shows additional peaks at  $896$   $\text{cm}^{-1}$  and  $1023$   $\text{cm}^{-1}$ . A peak at  $2063$   $\text{cm}^{-1}$  appears as the vanadia content reaches 9 wt%. Obviously the intensities of these bands gradually increase as the vanadia percentage increases. The absorption band at  $1023$   $\text{cm}^{-1}$  is assigned to the V=O stretching vibration, while that at  $896$   $\text{cm}^{-1}$  is attributed to the coupled vibration between V=O and V-O-V [26]. Generally, the bands of V=O bonds of crystalline  $\text{V}_2\text{O}_5$  are observed at  $1020$ - $1025$   $\text{cm}^{-1}$  with an overtone band between  $2060$  and  $2070$   $\text{cm}^{-1}$  which is confirmed by the spectrum of pure vanadia (V) in Fig. 2. Up to 3 wt% of vanadia loading, the peaks of crystalline vanadia is not observed probably because it is well dispersed as a monolayer on the  $\text{ZrO}_2$  surface. When the vanadia loading exceeds the amount

required for the formation of monolayer, it is well crystallized and the corresponding peaks appear in the IR spectra. Marth et al. [27] reported the presence of coordinated but distorted tetrahedral  $\text{VO}_4$  species in the  $\text{V}_2\text{O}_5/\text{TiO}_2$  system which is well dispersed as a monolayer at low vanadia loadings and as multilayer having disordered  $\text{VO}_6$  octahedra which has structural similarity to bulk  $\text{V}_2\text{O}_5$  at high vanadia loading. Our observations are in line with the reported results.

The  $^{51}\text{V}$  NMR spectra of  $\text{V}_2\text{O}_5/\text{ZrO}_2$  catalysts (Fig. 3) reveal two diverse vanadium environments for the surface vanadia species. For the samples Z6 and Z12, two prominent peaks are observed at 83.8 and -95.4 ppm. A low chemical shift value (peak at -95.4 ppm) is characteristic of tetrahedral vanadium species, while a higher value (peak at 83.8 ppm) is assigned to an octahedral coordination sphere [28, 29].

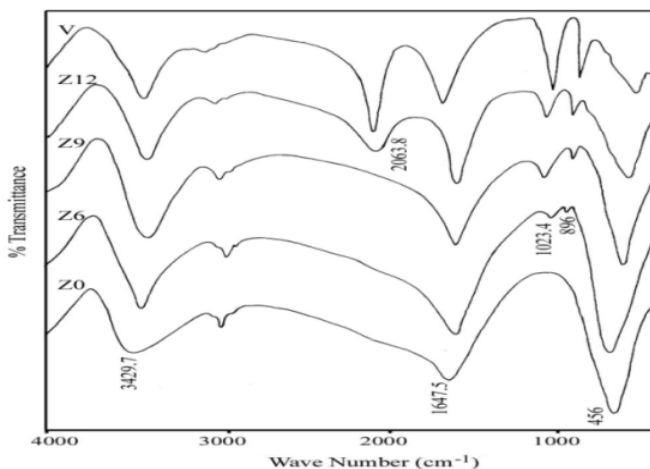


Fig. 2. FT-IR spectra of  $\text{V}_2\text{O}_5/\text{ZrO}_2$  systems

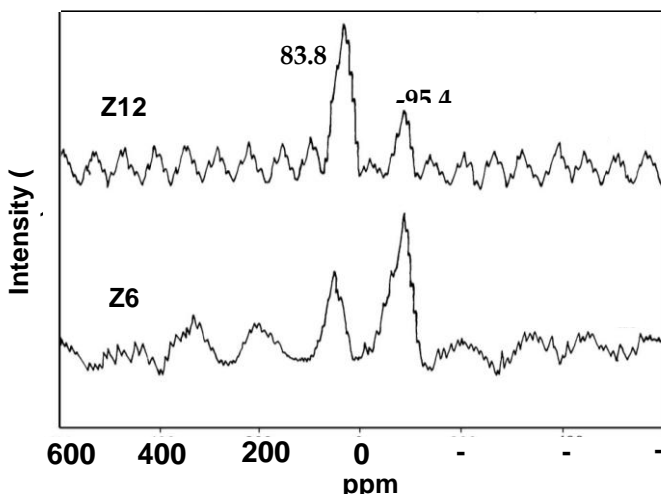


Fig. 3.  $^{51}\text{V}$  NMR spectra of  $\text{V}_2\text{O}_5/\text{ZrO}_2$  systems

From relative intensities of the peaks in the two samples it is clear that the surface V- species exist as isolated tetrahedral units in a monolayer at low  $\text{V}_2\text{O}_5$  loading and the ratio of well crystallized octahedral vanadium species increases with increasing vanadium oxide loading. The observations are in good agreement with XRD and FTIR results.

The XRD, FTIR and  $^{51}\text{V}$  NMR results strongly support Wachs model [30] for the molecular structure of surface vanadium oxide. This model proposes isolated vanadate species up to a saturation coverage above which vanadia shows small-distorted crystallites in addition to the surface vanadate species.

### 3.2 Surface acidity measurements

$\text{NH}_3$ -TPD provides general information about the number and distribution of the acid sites. Furthermore, the total amount of ammonia desorbed from the catalyst surface could be used for the quantitative measurement of total surface acidity of the catalyst [31].

From the TPD results given in Table 1, it is apparent that the incorporation of vanadia modifies the acidity of  $\text{ZrO}_2$  surface to a significant extent. The total acid sites gradually increase with vanadia content up to 6wt % and thereafter decreases. It has been



reported that the vanadia as surface monolayers imparts acidity, while the  $V_2O_5$  which crystallites, hardly exhibits acidity [32, 33]. So the increase in acidity in systems with low  $V_2O_5$  content could be due to the strong interaction of highly dispersed  $V_2O_5$  with moderately acidic  $ZrO_2$  support. This accounts for the reduction in the acidity values observed for high vanadia loaded systems. However, at high vanadia loading the degree of polymerization of surface vanadyl species will be prominent with an enhanced formation of crystalline  $V_2O_5$ .

Adsorption studies using perylene as electron donor give information regarding the Lewis acidity [34,35]. The technique is based on the ability of the catalyst surface site to accept a single electron from an electron donor like perylene to form charge transfer complexes. The perylene adsorption was done at room temperature from a solution in benzene. Perylene after electron donation gets adsorbed on the catalyst surface as radical action. The limiting amount of perylene adsorbed gives a measure of the Lewis acidity or the electron-accepting capacity, which is obtained from the Langmuir plot [36].

The limiting amounts of perylene adsorbed for different  $V_2O_5/ZrO_2$  catalysts are given in Table 1. A steady increase in the limiting amount of perylene is observed with successive vanadium oxide addition up to 6 wt%, which thereafter reduces, with further addition of vanadia. A comparative evaluation of the results suggests that the addition of vanadia substantially improves the Lewis acidity when present in small quantities.  $Zr^{4+}$  in the surface complex becomes more positive when vanadia is introduced to the support, thereby resulting in enhanced Lewis acidity. At high vanadia loadings, a significant loss of Lewis acid sites is apparent which may be due to the blocking of the surface acidic sites by crystalline  $V_2O_5$ , which rarely contributes to the acidity of any metal oxide systems [33].

Cracking reaction of cumene was done over the prepared catalysts in order to get a better understanding of surface acidity. Cracking of cumene to benzene is attributed to the action of Brönsted sites by a carbonium ion mechanism [37] while dehydrogenation of cumene yields  $\alpha$ -methylstyrene as the major product due to Lewis acid sites [38]. The  $\alpha$ -methylstyrene selectivity (Table 1) obtained from the

cumene conversion is in good agreement with the perylene adsorption results indicating that introduction of  $V_2O_5$  up to 6 wt % increases the Lewis acid sites on the catalyst surface.

## 3.2 Friedel-Crafts alkylation of *o*-xylene

### 3.2.1 Process Optimization

Considering the sensitivity of the reaction to the reaction conditions, influence of process variables were studied in detail. The process was optimized by varying the temperature (60-120 °C), reaction time (0.5-3 h), catalyst concentration (0.05-0.35 g) and *o*-xylene to benzyl chloride molar ratio (5:1 -15:1).

Substrate and Catalyst	Amount of Catalyst (g)	<i>o</i> -xylene/BC Molar Ratio	Reaction Temperature (°C)	Time of Reaction (h)
<i>o</i> -xylene Z6	0.1	5: 1	100	1.5

Table 2: Optimized reaction conditions for Friedel crafts alkylation of *o*-xylene

The optimized conditions for a reasonably good conversion of benzyl chloride (BC-C) and selectivity to mono-alkylated products (MAP) for *o*-xylene over Z6 catalyst are given in Table 2.

### 3.2.2 Performance of different catalyst systems

Table 3 summarizes the experimental results of benzylation of *o*-xylene over  $V_2O_5/ZrO_2$  catalysts.  $ZrO_2$  as a single oxide catalyst is found to be much less active than the supported catalysts in alkylation reaction. Among  $V_2O_5/ZrO_2$  catalysts, the benzyl chloride conversion increases with  $V_2O_5$  loading only up to 6 wt %.

Catalyst	BC-C <sup>a</sup> (Wt %)	Selectivity		
		MAP		PAP
		<i>Para</i>	<i>Ortho</i>	
Z0	12.6	100		-
Z3	36.4	100		-
Z6	89.3	95.4	0.8	3.8
Z9	54.7	100		-
Z12	48.1	100		-
Z15	39.2	100		-

Table 3: Catalytic performance of V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> systems for Friedel crafts alkylation of *o*-xylene

<sup>a</sup> Amount of catalyst: 0.1 g, temperature: 100°C, *o*-xylene/benzyl chloride molar ratio: 5:1, Time: 1.5 h w.r.t Table 3.

The benzylation in general give 100 % yield of monoalkylated products, except in the case of Z6. A small amount of polyalkylated product is observed in the case of Z6. However, the selectivity of 95.4% to mono-alkylated products is still quite good where we get benzyl chloride conversion of 89.3% when compared to the value of 67.1% obtained for the traditional catalyst AlCl<sub>3</sub>.

Benzylation of *o*-xylene yields 3,4-dimethyldiphenylmethane. Good correlation is also obtained between catalytic activity and amount of total acid sites (ammonia desorbed in the temperature region of 401-600°C) (Table 2). Though the catalyst surface provides both Lewis and Brönsted acid sites, the above observations clearly indicate the dominating impact of Lewis/strong acid sites for the benzylation of *o*-xylene with benzyl chloride. Friedel-Crafts alkylation is an aromatic electrophilic substitution reaction in which the carbocation is formed by the complexation of alkyl halide with the catalyst used. The carbocation attacks the aromatic species for alkylation and hence formation of carbocation is an important step in the reaction mechanism. Lewis acidic centers on the catalyst surface facilitate the carbocation formation [39, 40].

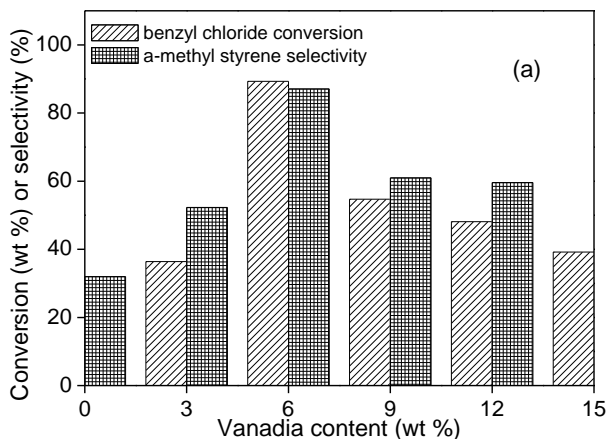


Fig.4. Catalytic performance of  $V_2O_5/ZrO_2$  systems for Friedel crafts alkylation of *o*-xylene

Hence an attempt was made to correlate the catalytic activity with the acidic characteristics of different catalyst systems. Figure 5

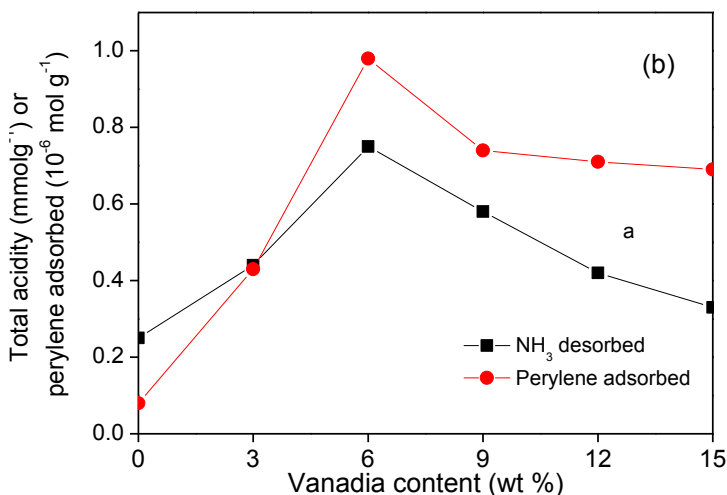


Fig.5. Correlation of Catalytic performance of  $V_2O_5/ZrO_2$  systems with acidity

compares the activity of systems with limiting amount of perylene adsorbed on the catalyst surface and  $\alpha$ -methyl styrene selectivity from cumene conversion reaction. The results show a linear relationship which indicates that the Lewis sites are active in benzylation reaction with benzyl chloride.

- (a) benzyl chloride conversion and  $\alpha$ -methyl styrene selectivity
- (b) Total surface acidity measured by different techniques
- (a) benzylchloride conversion and  $\alpha$ -methyl styrene selectivity
- (b) Total acidity and amount of perylene adsorbed

### 3. Conclusion

The catalyst samples prepared by supporting vanadia on ZrO<sub>2</sub> show potential as Friedel-Crafts alkylation catalysts giving good activity and selectivity. Reaction parameters such as temperature, reaction time, substrate to alkylating agent molar ratio and catalyst concentration are critical factors influencing the activities of the systems. The reaction is found to be clean without the formation of significant amount of polyalkylated products. The Lewis acidity /strong acid sites of the prepared catalysts seem to play an important role in explaining the activity and selectivity pattern of Friedel-Crafts alkylation of *o*-xylene. The results indicate that benzylation reaction under the optimized conditions occurs on the surface Lewis acid sites.

### References

- [1] G. A. Olah, *Friedel-Crafts Chemistry*, New York: Wiley, 1973.
- [2] J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock, "Environmentally friendly chemistry using supported reagent catalysts: structure-property relationships for clayzic," *J. Chem. Soc. Perkin Trans.*, vol. 2, pp. 1117, 1994.
- [3] B. M. Chodhary M.L. Kantam, M.Sateesh,. K.K. Rao, P.L. Santhi, "Iron pillared clays efficient catalysts for Friedel-Crafts reactions," *Applied Catalysis A: General*, Vol.149, pp. 257-264, 1997.
- [4] Y. Izumi, N. Natsume, H. Takamine, J. Tamoki and K. Urabe,"Photoelectrochemical Properties of Thin Films of Zinc Porphyrin Derivatives with Pyridyl Group," *Bull. Chem. Soc. Jpn.*, vol. 62, issue 2, pp. 386-391, 1989.
- [5] A. Cornelis, C. Dony, P. Lazlo and K. M. Nsunda, On the transition state for "clayzic"-catalyzed Friedel-Crafts reactions upon anisole," vol. 34, issue 24, pp. 3849-3852, 11 June 1993.

[6] J. Strerte, "Synthesis and properties of titanium oxide - cross-linked montmorillonite", *Clays and Clay Minerals*, vol. 34, no. 6, pp. 658-664, 1986.

[7] G. D. Yadav, T. S. Thorat and P. S. Kumbhar, "Inversion of the relative reactivities and selectivities of benzyl chloride and benzyl alcohol in friedel-crafts alkylation with toluene using different solid acid catalysts: An adsorption related phenomenon," *Tetrahedron Lett.*, vol. 34, issue 3, pp. 529-532, January 1993.

[8] P. Lazlo and A. Mathy, "Catalysis of Friedel-Crafts Alkylation by a Montmorillonite Doped with Transition-Metal Cations," *Helvetica Chimica Acta*, vol. 70, issue 3, pp. 577-586, 6 May 1987.

[9] V. V. Rao, V. Durgakumari, S. Narayanan, "Vapour phase methylation of phenol over nanocrystalline ferrosipinel system," *Appl. Catal.* 49, pp. 165, 1989.

[10] K. Tanabe, J.R. Anderson, M. Boudart (Eds.), "Iron-based catalysts for slurry-phase fischer-tropsch synthesis," *Catalysis - Science and Technology*, Springer, Berlin, vol.2, 1981.

[11] H. Noller, J.A. Lercher, H. Vinek, "Decomposition of isopropanol on magnesium oxide/silica in relation to texture, acidity and chemical composition," *Mater. Chem. Phys.*, vol. 18, pp. 577, 1988.

[12] P. Mongkolbovornkij, V. Champreda, W. Sutthisripok, N. Laosiripojana, "Production of steam cracking of feed stocks by mild cracking of plastic wastes," *Fuel Processing Technology*, vol. 91, pp. 1510-1516, 2010.

[13] Idriss Atribak, Noelia Guillén-Hurtado, Agustín Bueno-López, Avelina García-García, "Influence of the physico-chemical properties of CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides on the catalytic oxidation of NO to NO<sub>2</sub>," *Applied Surface Science*, Vol. 256, pp. 7706-7712, Oct. 2010.

[14] Jeong Gil Seo, Min Hye Youn, Sunyoung Park, Jin Suk Chung, In Kyu Song, "Hydrogen production from glycerin by steam reforming over nickel catalysts", *International Journal of Hydrogen Energy*, Vol. 34, pp. 3755-3763, May 2009.

[15] Yue-Qin Song, De-Hua He, Bo-Qing Xu, "Study of the surface and redox properties of ceria-zirconia oxides", *Applied Catalysis A: General*, Vol. 337, pp. 19-28, March 2008.

[16] Hongying Zhao, Simona Bennici, Jingxuan Cai, Jianyi Shen, Aline Auroux, "Carbon deposition on Co catalysts during Fischer-Tropsch

synthesis: A computational and experimental study, *Journal of Catalysis*, Vol. 274, pp.259-272,September 2010.

[17] H. Feng, J.W. Elam, J.A. Libera, M.J. Pellin, P.C. Stair, "Investigations on the properties of ceria-zirconia-supported Ni and Rh catalysts and their performance in acetic acid steam reforming", *Journal of Catalysis*, Vol. 269, pp.421-431,February 2010.

[18] Yuebing Xu, Jiangyin Lu, Mei Zhong, Jide Wang, " Natural gas pyrolysis in double-walled reactor tubes using thermal plasma or concentrated solar radiation as external heating source, *Journal of Natural Gas Chemistry*, Vol. 18, pp. 88-93, March 2009.

[19] Sreejarani K. Pillai, Omanakkutty Gheevarghese, Sankaran Sugunan, " Catalytic properties of  $V_2O_5/SnO_2$  towards vapour-phase Beckmann rearrangement of cyclohexanone oxime", *Applied Catalysis A: General*, vol. 353, pp. 130-136, 2009.

[20] K. V.R. Chary, K. Ramesh, G. Vidyasagar, V. V. Rao, " Vapour phase alkylation of phenol with methanol over vanadium oxide supported on zirconia", *J. Mol. Catal. A: Chem.*, vol. 198, pp. 195-204,2003.

[21] P. D. I. Mercera, V. I. G. Ommen, E. B. M. Doesburg, A. J. Burgraaf and J. R. H. Ross, "Zirconia as a Support for Catalysts Evolution of the Texture and Structure on Calcination in Air," *Appl. Catal.*, vol. 57, pp. 127-148, 1990.

[22] J. R. Sohn, M. Y. Park and Y. I. Pae, "Characterization by solid-state  $^{51}V$  NMR and X-ray Diffraction of Vanadium oxide supported on  $ZrO_2$ ," *Bull. Korean Chem. Soc.*, vol. 17 pp. 274-279, 1996.

[23] M. A. Vuurman and I. E. Wachs, "In situ Raman spectroscopy of alumina-supported metal oxide catalysts," *J. Phys. Chem.*, vol. 96, pp. 5008-5016, June. 1992.

[24] K. Jnumaru, M. Misono and T. Okuhara, "Structure and catalysis of vanadium oxide overlayers on oxide supports," *Appl. Cata. A: Gen.*, vol. 149, pp. 133-149, Jan. 1997.

[25] I. E. Wachs, "Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts," *Catal. Today*, vol. 27, pp. 437-455, Feb. 1996.

[26] L. Briand, L. Gambaro and H. Thomas, "Promotion Effects of Titanium on Partial Oxidation of Methanol over Vanadium Pentoxide Catalysts" *J. Catal.*, vol. 161, pp. 839-860, July. 1996.

- [27] M. S. Marth, A. Wokaun and A. Baiker, "Grafting of V<sub>2</sub>O<sub>5</sub> monolayers onto TiO<sub>2</sub> from alkoxide precursors: A diffuse reflectance FTIR study," *J. Catal.*, vol. 124, pp. 86–96, July. 1990
- [28] L. J. Lakshmi, E. C. Alyea, S. T. Srinivas and P. K. Rao, "Influence of Metal Oxide Modification of Alumina on the Dispersion and Activity of Vanadia Catalysts" *J. Phys. Chem. B*, vol. 101, pp. 3324– 3328, Apr. 1997.
- [29] L. J. Lakshmi, T. R. B. Jones, M. Gurgi and J. M. Miller, "Synthesis, characterization and activity studies of vanadia catalysts supported on sol–gel derived Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> mixed oxide," *J. Mol. Catal. A: Chem.*, vol. 152, pp. 99–110, March. 2000.
- [30] J. W. Ward, "The nature of active sites on zeolites: I. The decationated Y zeolite," *J. Catal.*, vol. 9, pp. 225–236, Nov. 1967.
- [31] F. Arena, R. Dario and A. Parmaliana, "A characterization study of the surface acidity of solid catalysts by temperature programmed methods," *Appl. Catal. A: Gen.*, vol. 170, pp. 127–137, May. 1998.
- [32] J. Le Barrs, J. C. Vedrine, A. Auroux, S. Trautman and M. Eaerns, "Microcalorimetric and infrared studies of the acid-base properties of V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts," *Appl. Catal. A: Gen.*, vol. 119, pp. 341– 354 Nov. 1994.
- [33] Khader, M.M., "Surface Acidity of V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts: IR and TPD Studies", *J. Mol. Catal.*, 104, (1995) 87
- [34] Kijenski, J., Baiker, "A. Acidic sites on catalyst surfaces and their determination", *Catal. Today* 5,(1989),1
- [35] B. D. Flockhart, J.A.N. Scott and R.C.Pink, "Electron-transfer at alumina surfaces. Part 1.—Electron acceptor properties of aluminas", *Trans. Faraday Soc.*, 62,(1966) , 730-740
- [36] H. Suja, c.s. Deepa, K. Sreeja Rani, S. Sugunan "Liquid phase benzoylation of arenes over iron promoted sulphated zirconia" *Applied Catalysis A: General* 230 (2002) 233.
- [37] A. Corma, and B.W Wojciechowski, "The Catalytic Cracking of Cumene", *Catal. Rev.-Sci. Eng.*, 24 (1982), 1– 65.
- [38] W. Przystajko, R. Fieddorow, I. G. Dalla Lana, *Appl. Catal.* 15 (1985) 115.
- [39] A. P. Singh et al., "Benzoylation of toluene with benzoyl chloride over zeolite catalysts", *J. Mol. Catal.* 102 (1995) 139-145
- [40] A. P. Singh, A.K. Pandey, "Acetylation of benzene to acetophenone over zeolite catalysts", *J. Mol. Catal.* 123 (1997) 141-147