



REGULAR ARTICLE

Mixed cerium nanooxides as efficient and selective C-alkylation catalysts for gas phase methylation of phenol

CHRISTY KUNJACHAN and MANJU KURIAN*

Department of Chemistry, Mar Athanasius College, Kothamangalam, Kerala 686 666, India
E-mail: mk@macollege.in

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Abstract. Phenol methylation is an acid-base catalysed reaction that produces valuable chemicals that are used in fine chemical synthesis. Methylation of phenol was studied over iron, vanadium and zirconium doped cerium nano oxides under optimized reaction conditions such as catalyst weight 0.5 g, phenol/methanol molar ratio 1/3 and WHSV 1.4 h^{-1} at $300 \text{ }^\circ\text{C}$ and 2 h. 80-90% conversion and 90% *ortho* selectivity are achieved with all prepared mixed oxides. *o*-cresol and 2,6-xylenol are the major products of the reaction. Catalytic activity depends on the number and strength of moderate and strong acidic sites on the surface which in turn depends on the nature and composition of the catalyst. Structural stability of the catalyst substantiates the heterogeneous nature of the catalyst.

Keywords. Ce-Fe; Ce-V/Ce-Zr oxides; vapour phase reaction; phenol methylation.

1. Introduction

Phenols and alkylated phenols are industrially important raw materials for pharmaceuticals, agrochemicals, plastics, dyes, resins, various additives, polymerization inhibitors, antioxidants and other chemicals.¹⁻³ Methylation of phenol produces O and C alkylated products that have bacteriostatic, bacteriocidal and fungicidal properties. Methyl-substituted derivatives of phenol are used as preservatives in the food industry, antimicrobial agents in the pharmaceutical industry, decontamination and disinfection agents and also in the production of pesticides.^{4,5} The major products during methylation of phenol are cresols, xylenols, anisole and methylanisole.^{6,7} 2,6-xylenol is used as the monomer for the production of poly-(2,6-dimethyl) phenylene oxide resin which possesses excellent mechanical, dielectric and chemical properties.^{8,9} 2-methyl phenol (*o*-cresol), the monomer for the synthesis of epoxyresol paints and special grade paints is also used as an intermediate in the synthesis of herbicides.^{10,11} Epoxy cresol novolac (ECN) derived from *o*-cresol is used in electronic and automobile industries.¹² *Ortho* methylated phenol (anisole) is an intermediate in perfumes, flavoring agents, and organic synthesis. Anisole and other methyl aryl ethers

have applications as octane boosters for gasoline.¹³ 2,3,6-trimethylphenol and 2,4,6-trimethylphenol (mesitol) are starting materials for vitamin E (tocopherols, tocotrienols) synthesis. 2,4,6-trimethylphenol is a comonomer for the modification of polyphenyleneoxide (PPO) resins and is used as an antioxidant in food and cosmetics.¹⁴

Active research have been reported on vapor phase methylation of phenol over catalysts like metal oxides such as Mn_3O_4 , CeO_2 , Fe_2O_3 , and MgO (with or without promoters), mixed metal oxides, hydrotalcites, zeolites, Nafion-H and phosphoric acid, sulfated zirconia, $\text{SO}_3\text{-HMS}$, alkali metal loaded silica, rare earth promoted metal phosphates, sulfates supported on γ -alumina.^{15,16} Alkali loaded zeolites gave selective O-alkylated product whereas metal oxide catalysts such as MgO , $\text{Mg-Al-hydrotalcite}$, TiO_2 , silica-manganese mixed oxide, $\text{V}_2\text{O}_5\text{-ZrO}_2$, and spinel catalysts like CoFe_2O_4 , $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$, Mg/Fe/O generated specifically C-alkylated products, *o*-cresol or 2,6-xylenol.^{17,18} Bronsted acid catalysts like Nafion-H resin, HY-zeolite, H-beta zeolites and heteropoly acid (HPA) on silica generated mixtures of anisole, *o*-cresol, xylenols and methyl anisole at lower temperatures.¹⁹ Preparation of O and C alkylated phenols depends on reaction conditions, nature of the catalyst, and surface acid-base properties.^{20,21} Barman *et al.*, reported that stronger acid sites are required for

*For correspondence

C-alkylation compared to O-alkylation.²² Sad *et al.*, reported the pathway of the gas-phase alkylation of phenol with methanol to obtain cresols 473K on SiO₂-Al₂O₃, Al-MCM-41, tungstophosphoric acid (TPA) supported on silica, zeolites like HBEA, HZSM5 and HY. *Ortho*- and *para*-cresols were formed *via* direct C-alkylation of phenol, and also by conversion of anisole intermediate obtained by O-alkylation of phenol. The activity was attributed to the presence of strong Lewis and Bronsted acid sites.^{15,23} Though several attempts have been made to shape up catalysts by modifying acidity/basicity to achieve desired product selectivity, none of the reported catalysts gives cost-effective methods.^{24,25} In the present study, we attempt the use of simple and mixed oxides of Ce, V, Fe and Zr for methylation of phenol. Our objective was to design and develop a better catalyst for phenol methylation which could be used at milder conditions. The present study involves a thorough optimization of the best catalyst composition and process parameters such as weight hourly space velocity (WHSV), molar ratio, temperature and stability of the catalyst in terms of time on stream study (TOS) which are outlined in subsequent sections. The effect of surface acidity in the catalytic efficiency of the prepared catalysts is also correlated. The major reaction products are *o*-cresol, 2,6-xyleneol and anisole whereas 2,4,6-xyleneol, *m*-cresol and *p*-cresol obtained in small quantities are collectively termed as others.

2. Experimental

Cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) by Aldrich Chemical Co. Inc. (St. Louis, MO, USA), vanadium(IV) oxide sulphate pentahydrate (VOSO₄·5H₂O) and zirconium(IV) oxynitrate hydrate (ZrO(NO₃)₂·xH₂O) by Loba Chemie and iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) and ammonia by Merck Chemicals (Mumbai, India) were used for the preparation of oxide catalysts. For catalytic activity studies, phenol and methanol (Merck Chemicals) were used. A detailed description of the preparation of Ce-Fe, Ce-V and Ce-Zr oxides nanoparticles by coprecipitation method and characterization by various physicochemical methods is given in our previous publications.²⁶⁻³⁰ Prepared oxides with composition Ce_xM_{1-x}O₂ (x = 0, 0.25, 0.5, 0.75, 1 and M = Fe, V or Zr) are labeled as M1, 1C3M, 2C2M, 3C1M and C1 (M = F for iron, V for vanadium, Z for zirconium and C for cerium).

The vapor phase alkylation of phenol with methanol was carried out in a fixed bed continuous down-flow reactor at atmospheric pressure. The temperature of the reaction was controlled by a PID temperature controller. Technical specifications are: Split type electrical heating with 240V AC power supply; Flange type reactor with maximum

pressure 50 bar and temperature 600 °C; dimensions: 19.1 mm OD x 13.1 mm ID x 360 mm length; Shell and tube type condenser with capacity 120 cm³. A pre-mixed solution with phenol/methanol was fed at the top of the reactor pumped with controlling flow rates by pump (FP-201) to reactor section. The upper portion of the reactor served as a vaporizer pre-heater, and the mixture was heated to vapor phase. The products were cooled in a condenser, collected in a receiver and analyzed by Perkin Elmer Clarus 580 Gas Chromatograph equipped with an Elite-5 capillary column. X-ray diffractograms of the reused catalyst were obtained using a Rigaku MiniFlex 600 X-ray diffractometer using CuK α radiation. Phase identification was carried out by comparison with JCPDS database cards. The average crystallite size was determined by Scherrer equation: $D = K\lambda/(\beta\cos\theta)$ where D is the average crystallite size, K the shape factor (0.89), the wavelength of the incident X-rays (1.5418), the diffraction angle, and h,k,l the full width at half maximum in radian of the Bragg peak corrected using the corresponding peak in micron-sized powder. Specific surface area measurements were done by nitrogen physisorption at 77K using a Micromeritics Gemini VII instrument. The specific areas of the samples were determined according to the standard Brunauer-Emmett-Teller (BET) procedure using nitrogen adsorption taken in the relative equilibrium pressure interval.

3. Results and Discussions

The catalytic activity of different compositions of Ce-Fe, Ce-V and Ce-Zr oxides was studied systematically for vapour phase phenol methylation reaction. Before estimating the catalytic activity of the prepared catalysts, it is pre-eminent to optimize reaction variables such as reaction temperature, the molar ratio of substrates, flow rate, time-on-stream and catalyst loadings by keeping other variables under controlled conditions. The effect of reaction conditions for alkylation of phenol was initially experimented in non-optimized conditions by taking 1C3F, 1C3V and 1C3Z as the reference catalysts from each series.

3.1 Effect of temperature

Figure 1 depicts the effect of temperature on methylation of phenol over four different temperatures viz., 200, 250, 300 and 350 °C keeping catalyst weight 0.5 g, phenol/methanol mole ratio 1:3 and weight hourly space velocity (WHSV) 1.4 h⁻¹. From the results, it can be observed that reaction temperature has a pronounced effect on the catalytic activity as well as selectivity towards different products. For 1C3F catalyst, conversion (%) increases from 66.6 to 87.7, as the temperature is raised from 200 to 350 °C.

The selectivity of *o*-cresol increases from 200 to 300 °C but decreases on further increase in temperature to 350 °C due to the formation of higher alkylated products. 2,6-xylenol selectivity also increases with an increase in temperature due to the higher activation energy needed for its formation whereas, anisole selectivity remains almost the same. In the case of 1C3V catalyst, conversion (%) increases from 63 to 86, as the temperature is increased from 200 to 350 °C. The selectivity of *o*-cresol decreases and that of 2,6-xylenol increases with temperature since further alkylation of *o*-cresol take place over 1C3V catalyst rather than consecutive methylation of phenol. Phenol conversion (%) increases from 63.5 to 86.4 over 1C3Z catalyst, as the temperature is raised from 200 to 350 °C. The selectivity of *o*-cresol increases from 42.6 to 47.1% with an increase in temperature from 200 to 350 °C. 2,6-xylenol selectivity also increases with a rise in temperature. The conversion rate is low at

lower temperatures due to the association of molecule that reduces adsorption and dissociation on the active sites.

3.2 Effect of catalyst amount

The dependence of catalyst weight on the reaction rate was investigated by taking different catalyst loadings of 0.25, 0.5, 0.75 and 1 g, while keeping the other variables constant. Figure 2 portrays the dependence of catalyst weight on phenol methylation reaction. Increase in 1C3F catalyst amount from 0.25 to 1 g increases the conversion % from 78.3 to 88.2. For 1C3V, as the catalyst dosage is increased from 0.25 to 0.5 g, conversion percentage increases from 76.5 to 85.1. A similar trend is shown by 1C3Z catalyst also. Conversion rate increases with an increase in catalyst weight due to the availability of more active surface

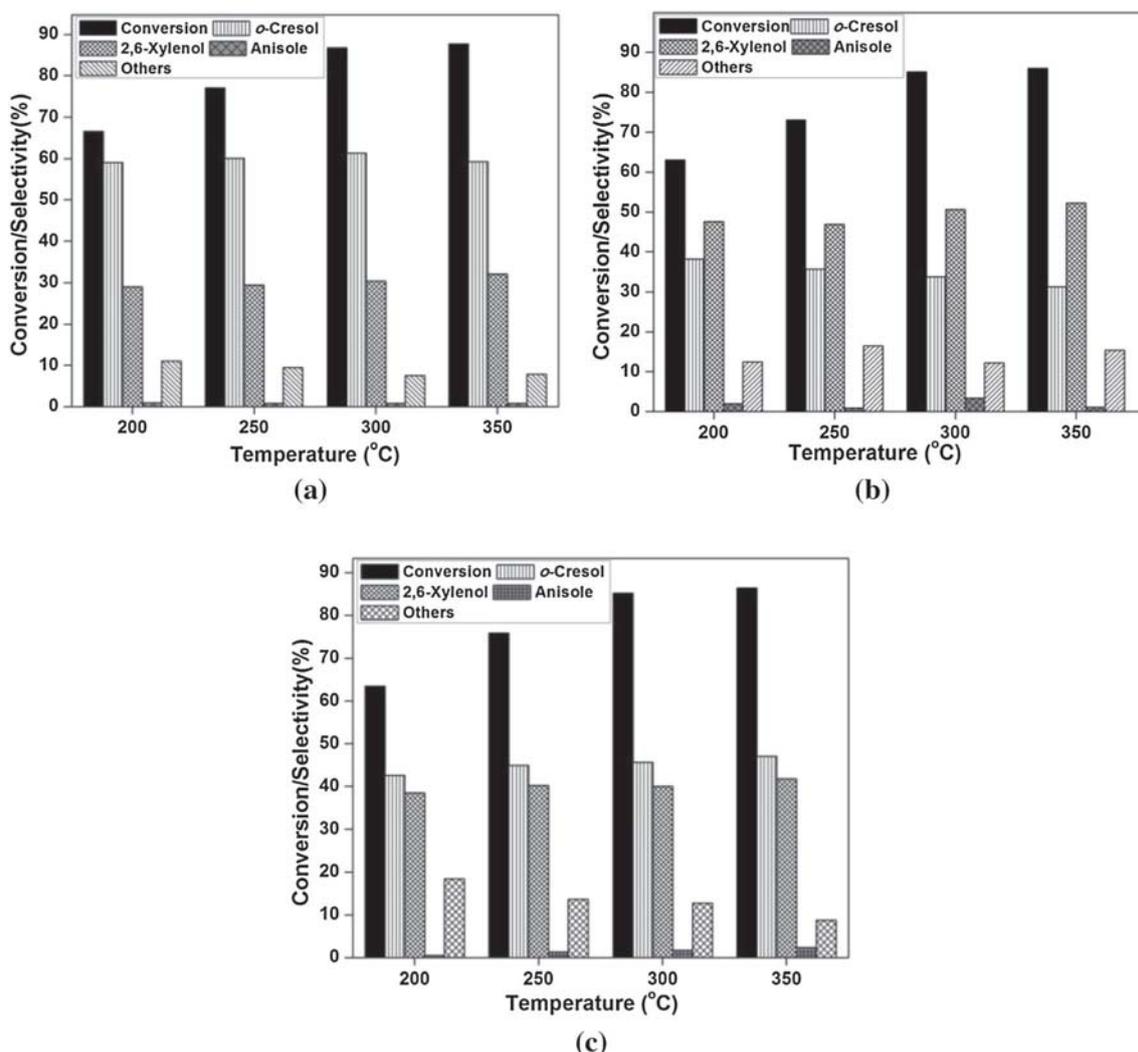


Fig. 1. Effect of temperature on phenol conversion over (a) 1C3F (b) 1C3V and (c) 1C3Z Reaction conditions: catalyst – 0.5g, phenol/methanol – 1/3 mol, WHSV – 1.4 h⁻¹.

sites and acidic sites. From the results, it could be observed that a minimum amount of catalyst is enough for appreciable conversion and hence 0.5 g catalyst is selected as an optimum catalyst weight for further studies.

3.3 Effect of flow rate

The effect of flow rate on phenol methylation reaction was carried out by changing WHSV and the results are presented in Figure 3. Over 1C3F catalyst, maximum conversion of 86.8% which corresponds to 61.3% *o*-cresol and 30.4% 2,6-xylene production is achieved at WHSV 1.4 h⁻¹. When WHSV changes from 1.4 to 3.6 h⁻¹, phenol conversion decreases as expected from 86.8 to 67.4%. The selectivity towards *o*-cresol increases from 61.3% to 71.3%, along with a decrease

in 2,6-xylene selectivity from 30.4% to 20.1%. At 1.4 h⁻¹ velocity, 1C3V catalyst shows phenol conversion of 85.1% which corresponds to 33.8% *o*-cresol, 50.6% 2,6-xylene and 3.4% anisole production. When WHSV changes from 1.4 to 3.6 h⁻¹, phenol conversion drops from 85.1 to 70.7%. The selectivity towards *o*-cresol increases from 33.8% to 59.2%, along with a decrease in 2,6-xylene selectivity from 50.6% to 35.3%. For 1C3Z also, maximum conversion of 85.2% with 45.6% *o*-cresol and 40.0% 2,6-xylene production occurs at WHSV of 1.4 h⁻¹. As WHSV changes from 1.4 to 3.6 h⁻¹, phenol conversion decreases from 85.2 to 75.3%, respectively. The selectivity towards *o*-cresol increases from 45.6% to 56.7%, with concomitant decrease in 2,6-xylene selectivity from 40.0% to 32.3%. The diffusion rate increases with a flow rate which enhances primary product formation and therefore *o*-cresol selectivity increases. With an

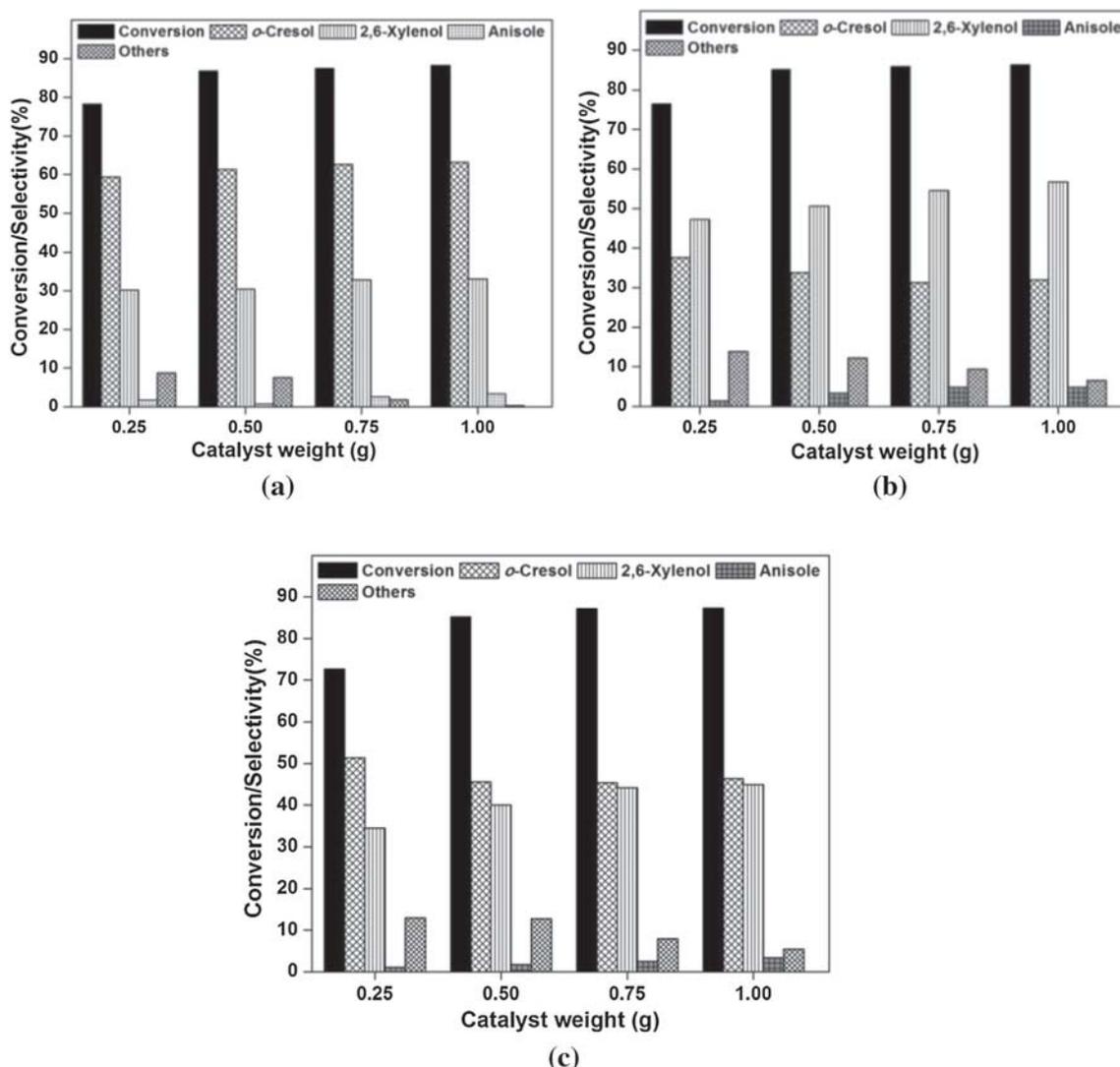


Fig. 2. Effect of catalyst weight on phenol conversion over (a) 1C3F (b) 1C3V and (c) 1C3Z. Reaction conditions: phenol/methanol – 1/3mol, WHSV- 1.4 h⁻¹, temperature – 300 °C.

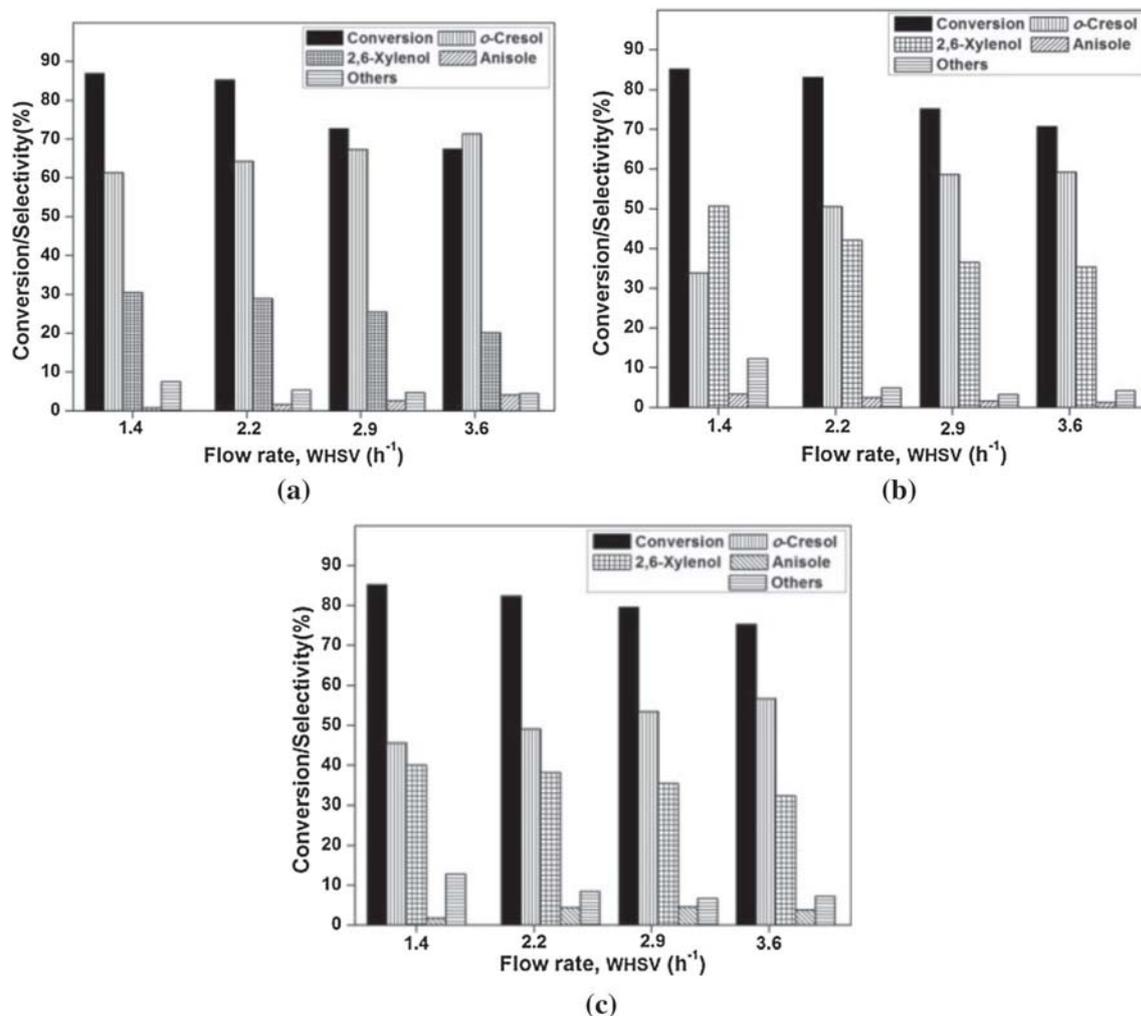


Fig. 3. Effect of flow rate on phenol conversion over (a) 1C3F (b) 1C3V and (c) 1C3Z. Reaction conditions: catalyst – 0.5 g, phenol/methanol – 1/3 mol, temperature – 300 °C.

increase in the flow rate, consecutive methylation of phenol is higher than secondary alkylation of produced *o*-cresol. Raising the feed velocity results in an increase in WHSV (catalyst weight is constant) followed by a gradual reduction in the phenol conversion as expected. From the results, it could be observed that the WHSV at 1.4 h⁻¹ is the optimum velocity for the phenol conversion.

3.4 Effect of methanol: phenol molar ratio

Methanol to phenol stoichiometry on phenol methylation was studied by changing the molar ratio of reactants, keeping the amount of catalyst as 0.5 g, WHSV as 1.4 h⁻¹ and reaction temperature as 300 °C. The results are shown in Figure 4. For 1C3F catalyst, the increase in molar ratio of methanol to phenol from 1 to 3 results in an increase in phenol conversion from 74.2% to 86.8% while further increase in the molar ratio produces only a

marginal increase in conversion. *Ortho*-cresol selectivity decreases from 67.1% to 47.2% and 2,6-xylenol increases from 24.5% to 37.2%. With 1C3V catalyst, the maximum conversion of 86.8% is obtained at 3:1 methanol/phenol molar ratio. The selectivity towards 2,6-xylenol increases from 48.1% to 54.3%, accompanied by a decrease in *o*-cresol selectivity from 38.2% to 30.1%. In the case of 1C3Z catalyst, the conversion rate increases from 75.1% to 88.9%. However *o*-cresol selectivity decreases from 51.9% to 30.4% whereas 2,6-xylenol increases from 38% to 52.1%. It can be seen that phenol conversion increases distinctly with the increasing mole fraction of methanol due to the availability of an additional methyl group for further alkylation of *o*-cresol.

3.5 Effect of time

To study the activity and stability of the catalyst, time on stream (TOS) studies were conducted at optimized

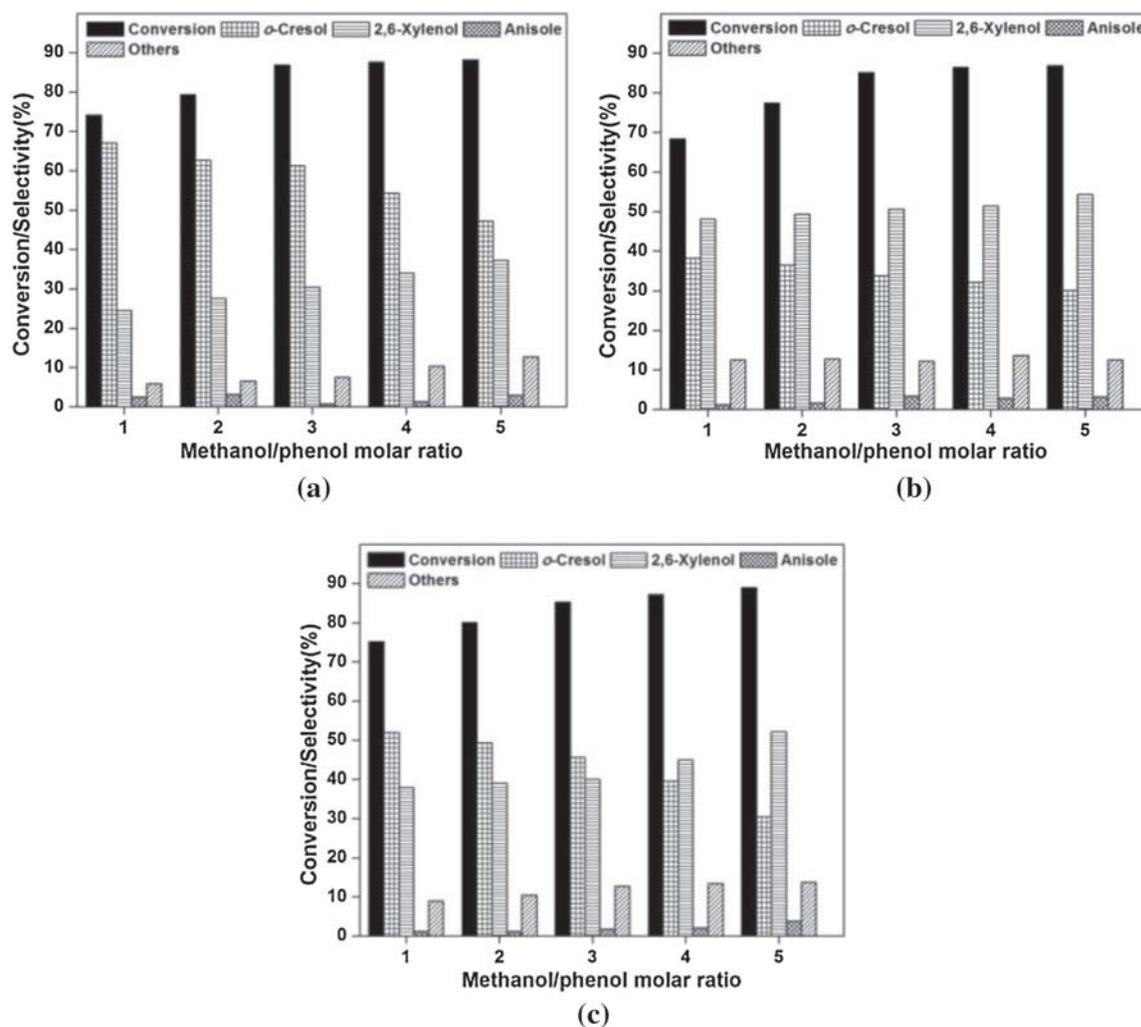


Fig. 4. Effect of phenol/methanol mole ratio on phenol conversion over (a) 1C3F (b) 1C3V and (c) 1C3Z. Reaction conditions: catalyst – 0.5 g, WHSV – 1.4 h^{-1} , temperature – $300 \text{ }^\circ\text{C}$.

conditions of 1:3 phenol: methanol mole ratio, 0.5 g catalyst weight and 1.4 h^{-1} WHSV at $300 \text{ }^\circ\text{C}$. The reaction was continued for 7 h to check the stability of the catalyst. The influence of time on stream on the conversion of phenol with methanol is presented in Figure 5. As shown, the conversion of phenol gradually increases up to 2 h and then starts to decrease marginally due to coke formation on the catalyst surface. The results show that the conversion of phenol decreases only marginally on increasing the reaction time therefore subsequently the other product formation remains the same. *Ortho*-cresol selectivity increases marginally whereas 2,6-xylenol selectivity remains almost the same after the two-hour reaction.

3.6 Catalytic activity of prepared catalysts

Results of phenol methylation reaction over prepared catalysts under optimized reaction conditions of

catalyst weight 0.5 g, phenol/methanol molar ratio 1/3 and WHSV 1.4 h^{-1} at $300 \text{ }^\circ\text{C}$ and 2 h are shown in Table 1. From the results, it can be seen that all the prepared Ce-Fe oxides show excellent catalytic activity in the range of 83–86% with pronounced selectivity to *o*-cresol. Among these catalysts, 1C3F shows the maximum conversion. In the case of Ce-V oxides, 3C1V shows maximum conversion with selectivities of 35.5% *o*-cresol and 49.5% 2,6-xylenol. Cerium-vanadium mixed oxides are more reactive compared to cerium oxide. Cerium and zirconium oxides show % conversions of 84.9 and 88, respectively. The conversion rate was higher for zirconia and oxides containing more zirconium ions. It can be interpreted on the basis of the surface acidity of the catalysts.^{31–33} 2C2Z has maximum conversion rate and acidity. All prepared catalysts except Z1 have higher *o*-cresol activity than 2,6-xylenol. Ce-Zr oxides have weak and moderate basic

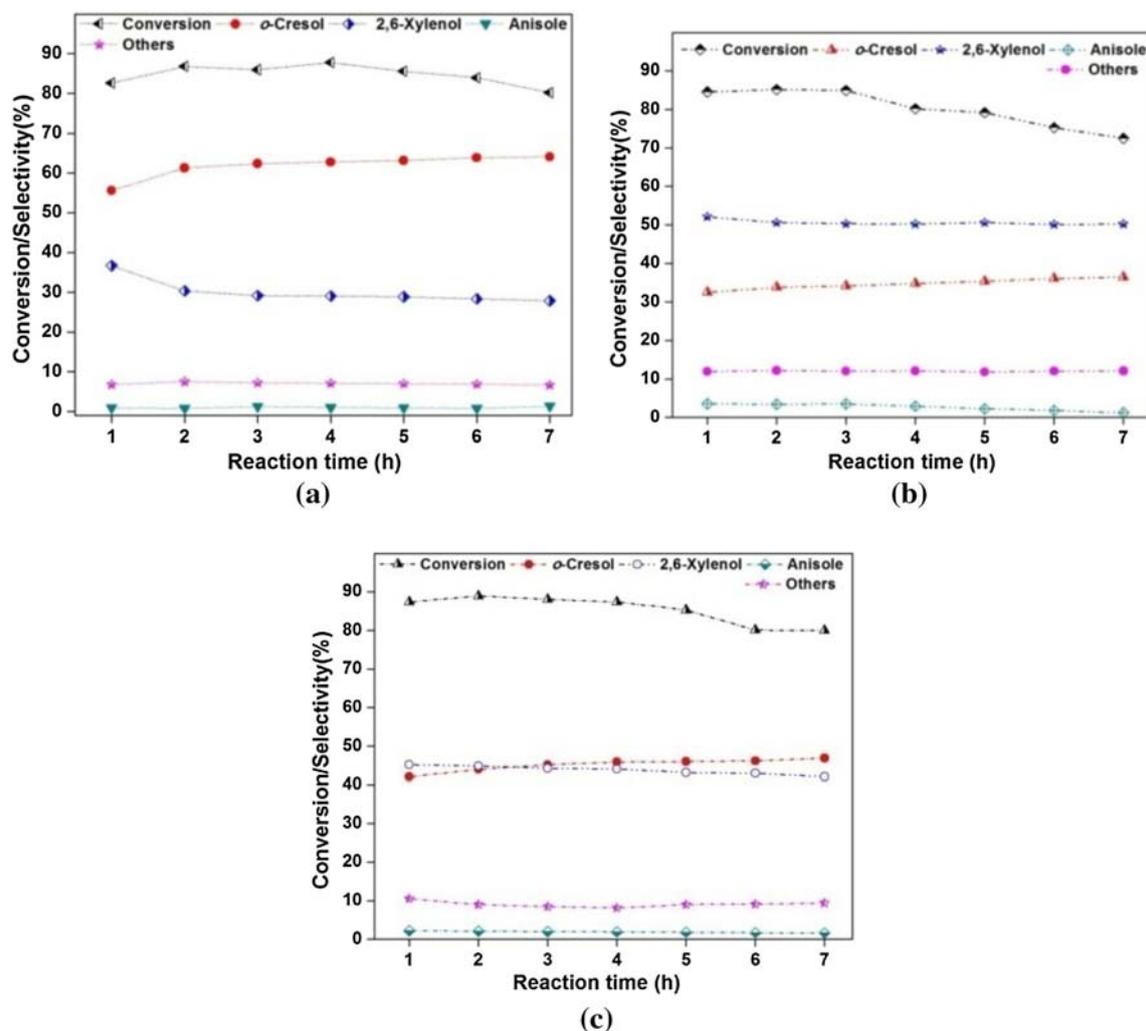


Fig. 5. Effect of time on phenol conversion (a) 1C3F (b) 1C3V and (c) 1C3Z. Reaction conditions: catalyst – 0.5 g, phenol/methanol – 1/3 mol, WHSV – 1.4 h⁻¹, temperature – 300 °C.

Table 1. Phenol methylation over prepared catalysts. Reaction conditions: catalyst – 0.5g, phenol/methanol – 1/3 mol, WHSV – 1.4 h⁻¹, temperature – 300 °C, time – 2h.

Catalyst	Conversion %	Product selectivity %			
		<i>o</i> -cresol	2,6-xylenol	Anisole	Others
C1	84.9	60.2	32.2	0.9	6.7
3C1F	84.0	55.0	33.5	1.8	9.7
2C2F	84.2	58.1	30.0	0.4	11.5
1C3F	86.8	61.3	30.4	0.8	7.5
F1	83.2	54.7	30.7	0.3	14.3
3C1V	89.7	35.5	49.5	3.2	11.8
2C2V	86.7	29.7	50.1	0.5	19.7
1C3V	86.0	31.3	52.2	1.1	15.4
V1	87.7	36.1	55.3	0.4	8.2
3C1Z	83.6	52.3	40.5	0.6	6.6
2C2Z	90.3	50.0	33.3	3.4	13.3
1C3Z	86.4	47.1	41.8	2.3	8.8
Z1	88.0	31.6	36.8	1.7	29.9

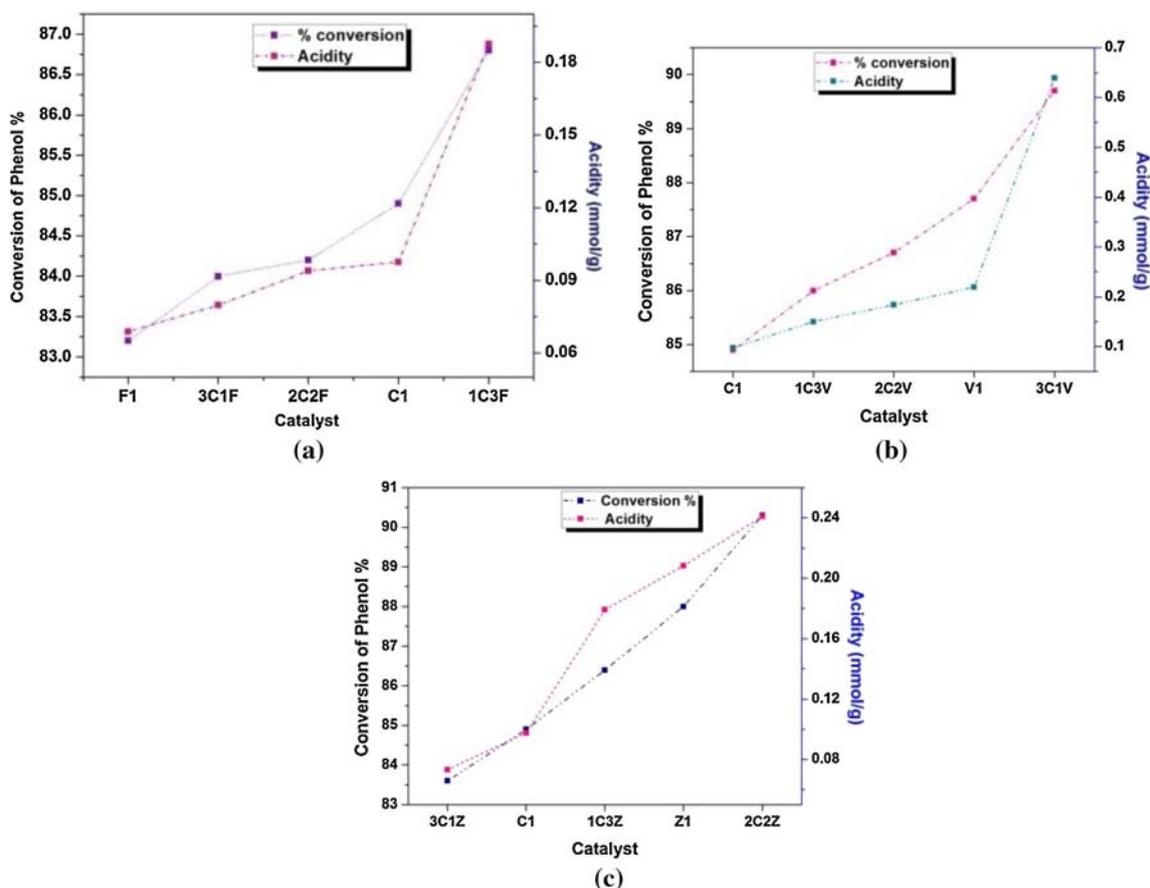


Fig. 6. Effect of acidity on phenol methylation. Reaction conditions : catalyst – 0.5 g, phenol/methanol – 1/3 mol, WHSV – 1.4 h^{-1} , temperature – $300 \text{ }^\circ\text{C}$, time – 2 h.

sites for the abstraction of the proton. Figure 6 correlates the rate of phenol conversion with surface acidity of the prepared catalysts. It clearly indicates that the rate of conversion directly relates to the total acidity of the catalysts.

3.7 Stability of the spent catalyst

Stability of the catalyst was checked after 7 h reaction using 1C3F as a model catalyst. The catalyst was separated from the reaction mixture, washed several times with acetone to remove adsorbed particles on the surface and dried at $200 \text{ }^\circ\text{C}$ in an air oven. XRD and surface area analyses were experimented to examine the catalyst stability after its reuse. PXRD pattern of the recycled catalyst compared with the freshly synthesized catalyst (Figure 7) indicate that the catalyst retains phase purity. Average crystallite size remains more or less the same. The specific surface area of the recycled catalyst is less than that of the initial catalyst which may be due to the blockage of pores (Table 2).

3.8 Mechanism of alkylation of phenol with methanol

For phenol methylation, first-order kinetics is followed with respect to phenol concentration. The calculated rate constant for 1C3F, 1C3V and 1C3Z catalysts are

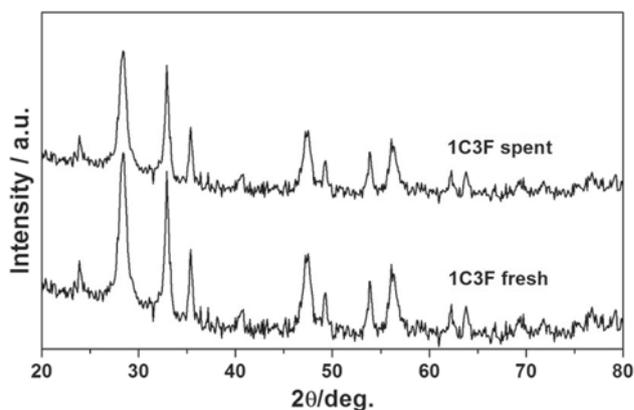


Fig. 7. PXRD pattern of fresh and spent 1C3F catalyst. Reaction conditions : catalyst – 0.5 g, phenol/methanol – 1/3 mol, WHSV – 1.4 h^{-1} , temperature – $300 \text{ }^\circ\text{C}$, time – 2 h.

Table 2. Data on the structural stability of fresh and spent 1C3F catalyst.

Sample	Surface area (m ² /g)		Total pore volume V_P (cm ³ /g)	Pore diameter (nm)	Average crystallite size (nm)
	S_{BET}	$S_{Langmuir}$			
Fresh 1C3F	30	44	0.0122	1.64	16.98
Spent 1C3F	22	39	0.0100	1.54	18.20

0.95, 1.0 and 1.09 s⁻¹, respectively. Sreekumar and Sugunan reported a plausible mechanism for methylation of phenol which involved the adsorption of phenolate ion on the Lewis acid sites and the hydrogen ion in the basic site.^{33,34} The proton site activates methanol to produce a carbonium ion, which reacts with the aromatic ring of the adjacently adsorbed phenolate species at the *ortho* position. Different products of phenol methylation are due to the nature of surface active sites. It has been reported that the phenolate ion is adsorbed on the Lewis acid sites and the hydrogen ion is bound to the adjacent basic sites. This proton site activates the molecule of methanol, resulting in the formation of the methyl carbocation, which reacts with the aromatic ring of the adjacently adsorbed phenolate species at the *ortho* position on the surface of catalysts.³⁴ Thus, high *ortho* selectivity can be explained by the vertical orientation of adsorbed phenol on the Lewis sites. Lewis acid sites and basic sites present on the surface of the catalysts, lead to the catalytic property for the *ortho*-alkylation reaction of phenol with methanol because the catalyst sites are closer to the *ortho*-positions of the phenolate ion and are readily available for the attack of the carbocation. This result in the formation of *o*-cresol and 2,6-xyleneol as major products.

4. Conclusions

The prepared cerium based oxides are efficient catalysts for alkylation of phenol with methanol. 80-90% conversion and 90% *ortho* selectivity are achieved. *o*-cresol and 2,6-xyleneol are the major products of the reaction. Optimization of reaction parameters reveals that the rate of phenol methylation is dependent on reaction variables such as reaction temperature, catalyst weight, flow rate, molar ratio of reactants and time on stream. Catalytic activity depends on the number and strength of moderate and strong acidic sites on the surface which in turn depends on the nature and composition of the catalyst. Structural stability of the catalyst substantiates the heterogeneous nature of the catalyst. The nature of surface active sites results in different products of phenol methylation and high

ortho selectivity by the vertical orientation of adsorbed phenol on the Lewis sites.

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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