

Research Article

## Eco Friendly Nitration of Toluene using Modified Zirconia

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Received: 20th November 2012; Revised: 8th December 2012; Accepted: 7th January 2013

### Abstract

Nitration of toluene has been studied in the liquid phase over a series of modified zirconia catalysts. Zirconia, zirconia-ceria ( $Zr_{0.98}Ce_{0.02}O_2$ ), sulfated zirconia and sulfated zirconia-ceria were synthesised by co precipitation method and were characterised by X-ray diffraction, BET surface area, Infra red spectroscopy analysis (FTIR), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), and Energy Dispersive X ray analysis (EDAX). The acidity of the prepared catalysts was determined by FTIR pyridine adsorption study. X-ray diffraction studies reveal that the catalysts prepared mainly consist of tetragonal phase with the crystallite size in the nano range and the tetragonal phase of zirconia is stabilized by the addition of ceria. The modified zirconia samples have higher surface area and exhibits uniform pore size distribution aggregated by zirconia nanoparticles. The onset of sulfate decomposition was observed around 723 K for sulfated samples. The catalytic performance was determined for the liquid phase nitration of toluene to ortho-, meta- and para- nitro toluene. The effect of reaction temperature, concentration of nitric acid, catalyst reusability and reaction time was also investigated. © 2013 BCREC UNDIP. All rights reserved

**Keywords:** Nitration of toluene; zirconia; zirconia-ceria; sulfated zirconia; sulfated zirconia-ceria.

**How to Cite:** K. R. S. Devi, S. Jayashree, (2013). Eco friendly nitration of toluene using modified zirconia. *Bulletin of Chemical Reaction Engineering & Catalysis*, 7 (3): 205-214. (doi:10.9767/bcrec.7.3.4154.205-214)

**Permalink/DOI:** <http://dx.doi.org/10.9767/bcrec.7.3.4154.205-214>

### 1. Introduction

Aromatic nitro compounds are important starting materials for the manufacture of various industrial products such as pharmaceuticals, dyes, intermediates, explosives and plastics. Industrial aromatic nitration techniques require the use of corrosive liquid phase nitric acid- sulfuric acid mixture, responsible for the generation of large amounts of wastes, which are expensive to treat [1]. Nitrotoluenes are important intermediates in the chemical industry, are industrially produced by liquid phase nitration of toluene using a mixture of nitric and sulfuric acid as a nitrating agent [2].

The typical product distribution of *ortho*-, *meta*- and *para*-isomers in the conventional nitration is about 58:4:38, whereas the thermodynamic equilibrium concentration is 29:33:38, respectively [3]. A large quantity of dilute sulfuric acid is generated as waste in the conventional process and its disposal or recycle is very expensive; this makes the toluene nitration one of the most environmentally harmful processes. Over-nitration, oxidation byproducts and poor selectivity are other associated problems [4]. This necessitates the need for new, novel and simpler methods for nitration which can overcome the problems.

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Many efforts have been directed towards the development of environmentally friendly and reusable alternatives in recent years by using solid acids and heteropoly acids [5-7]. Different catalysts tested so far include  $\text{H}_3\text{PO}_4/\text{ZSM-5}$  [4], sulfated zirconia [8,9],  $\text{WO}_3/\text{ZrO}_2$  [10], sulfated titania [11],  $\text{SO}_4^{2-}/\text{TiO}_2$  doped with  $\text{CeO}_2$  [12], sulfonated ion exchange resins (polystyrenesulfonic acid) [13] perfluorinated rare earth metal salts [14, 15], lithium, molybdenum, ytterbium on silica gel [16],  $\text{H}_5\text{PMO}_{10}\text{V}_2\text{O}_{40}$  [17], and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  [18]. Among acidic zeolite catalysts such as H-mordenite, H-beta, H-ZSM-5 and H-Y, zeolite H-beta has shown higher conversion and remarkable selectivity for *para*-isomer in vapor phase nitration of toluene. Choudary et al. carried out the nitration of toluene in liquid phase employing nitric acid of 60–90% concentration over solid acid catalyst and by means of azeotropic removal of water [19]. Akolekar et al. reported on the high pressure nitration of toluene using  $\text{NO}_2$  and zeolite catalysts [20]. These catalysts effectively play the role of sulfuric acid in the reaction, assisting the formation of nitronium species. Despite this, a high concentration of nitric acid as nitrating agent is still required and the need to be carried out at high temperatures for long times [14–16], for aromatics nitration whether liquid acid or solid acid as catalysts.

The incorporation of super acidity in solid acids has attracted considerable attention. The surface of zirconium oxide is known to possess catalytic activities in oxidation, reduction and acid base catalysed reactions. Zirconia when modified with anions such as sulfate ions forms a highly acidic or super acidic catalyst to catalyse many reactions like hydrocarbon isomerisation, methanol conversion to hydrocarbons, alkylation, acylation, esterification, etherification, condensation, nitration, cyclization, etc. [21]. The prominent role of ceria has been recognized in three-way catalysis, catalytic wet oxidation, water-gas-shift reaction, oxidation/combustion catalysis and solid oxide fuel cells. Incorporation of  $\text{CeO}_2$  into  $\text{ZrO}_2$  increases the acidity, which is evidenced by low  $\text{H}_0$  max values. Ceria–zirconia mixed oxides show good thermal resistance as well as enhanced redox properties [22]. Thus sulfated zirconia and modified sulfated zirconia forms an important class of catalysts. In our efforts to develop a new, efficient and eco-friendly process for electrophilic aromatic nitration, we have prepared an eco-friendly solid acid catalyst of zirconia. Here we present the results of the nitration of toluene, using zirconia (Zr), zirconia-ceria (ZrCe), sulfated zirconia (SZr) and sulfated zirconia-ceria (SZrCe). The goal of the study was to investigate the difference between the

effect of modified and unmodified zirconia on the nitration of toluene as well as the investigation of the role of sulfuric acid in improving the acidity of zirconia.

## 2. Materials and methods

### 2.1. Catalyst preparation

Hydrous zirconium oxide was prepared by the hydrolysis of zirconyl nitrate hydrate (Merck). Zirconyl nitrate hydrate was dissolved in doubly distilled water and 1:1 aqueous ammonia was added drop-wise with vigorous stirring until the pH of the solution reached 8 [5]. 2 wt% of ceria doped zirconia with nominal composition  $(\text{Zr}_{0.98}\text{Ce}_{0.02})\text{O}_2$  was prepared by co-precipitation method from zirconyl nitrate hydrate  $(\text{ZrO}(\text{NO}_3).x\text{H}_2\text{O})$  and cerium (III) nitrate hexahydrate (Merck) by adding 1:1 ammonium hydroxide until pH reaches 9 under gentle heating and continuous stirring. The solution was heated for about 15 minutes and allowed to stand overnight. The mother liquor was decanted and the precipitate was washed till it was free of nitrate ions. The precipitates were filtered and dried overnight at 383 K for 16 h. The hydroxide obtained was sieved to get particles of 75-100 microns mesh size and calcined at 823 K for 5 h to get zirconia (Zr) and zirconia ceria (ZrCe) catalysts. Hydrous zirconium oxide and hydrous zirconia ceria were immersed in 1:1  $\text{H}_2\text{SO}_4$  solution (2 mL/g) and stirred for 4 h. Excess water was evaporated and the resulting sample was oven-dried at 383 K for 16 h and calcined at 823 K for 5 h to get sulfated ceria (SZr) and sulfated zirconia - ceria (SZrCe) catalyst.

### 2.2. Catalyst characterization

Powder X-ray diffraction patterns of the solids were recorded on- PANalytical X-pert pro fitted with a secondary graphite monochromator with  $\text{Cu K}$  alpha radiation 2 deg 2 theta/min ( $\lambda = 0.154 \text{ nm}$ ) at 30 KV and 15 Ma. EDAX and SEM analysis were done by Quanta ESCM, FEI instrument. The BET surface area and pore volume of the catalyst were measured in a Micromeritics Gemini surface area analyzer using nitrogen as an adsorbate at liquid nitrogen temperature. Prior to the measurement, the samples were treated in a nitrogen atmosphere at 473 K for half an hour. Fourier Transform Infra Red (FTIR) spectra of the samples were recorded in a Bruker alpha-T instrument using KBr pellet method. TG analysis of the samples was achieved in a DSC-Thermogravimetric Analyser Standard (SDT Q600, V20.9 and Build 20) instrument in nitrogen

atmosphere at a heating rate of 10 °C/min.

### 2.3. Catalytic Activity

Catalytic activity of the prepared catalysts towards nitration of toluene was carried out in a 50 mL R.B flask fitted with a spiral condenser. The reactant (toluene and aqueous nitric acid) in desired volume ratio along with 0.1 g of the catalyst was magnetically stirred for a required period at a desired temperature. The samples were analyzed using capillary column in a Perkin Elmer Gas Chromatograph using a flame ionization detector. Prior to injection in GC, the unreacted nitric acid was neutralized using aqueous  $\text{Na}_2\text{CO}_3$  to a pH 6-7. The product analysis was achieved by comparison with authentic samples.

## 3. Results and Discussion

### 3.1. Catalyst surface study

#### 3.1.1. X-ray Diffraction (XRD) analysis

The X-ray powder diffraction patterns of zirconia and sulfate modified zirconia samples calcined at 823 K are presented in Figure 1. Zirconia sample exhibit relatively poor crystallinity with the presence of a mixture of monoclinic and tetragonal phases from the diffraction peaks ( $24.5^\circ$ ,  $28.71^\circ$ ,  $31.76^\circ$ ,  $35^\circ$ ). The XRD results clearly reveal that the sulfate modified zirconia exhibits smaller crystallite size and has only tetragonal phase (JCPDS 17-0923). It is an established fact in the literature that  $\text{ZrO}_2$ -tetragonal phase is more active in catalysis [23]. The intensity observed for SZr is more than that of Zr. Generally, incorporation of various promoter atoms such as lanthanum, cerium and yttrium into the zirconia lattice stabilizes the tetragonal phase [24]. The present results are thus in line with earlier observations. Zirconia normally exists in the monoclinic, tetragonal and cubic structures. In pure zirconia, monoclinic phase in the absence of any impurities is stable up to 1373 K and transforms into tetragonal phase as the temperature increases to 1473 K. On cooling, the high temperature tetragonal phase transforms back to the monoclinic phase with a large hysteresis.

Recently Yu et al. studied the effect of calcination temperature on nano sulfated zirconia prepared by hydrothermal method and reported the same observation that sulfate modification stabilizes the tetragonal phase of zirconia [25]. The intensity of SZrCe is lower than ZrCe; the tetragonal phase is dominating over the monoclinic phase when ceria is incorporated into the hydrous zirconia structure. This could be due to

incorporation of promoter cations into the structure of zirconia, forming solid solutions, which substantially decrease the specific surface free energy of zirconia and favour the tetragonal phase, which has a lower surface free energy than the monoclinic form [26]. Further, no reflections corresponding to crystalline  $\text{CeO}_2$  was observed, indicating a strong interaction of the dispersed ceria with the zirconia and is well dispersed on the surface of zirconia. The average crystallite size of the samples calculated using the Scherrer's equation [27] is given in Table 2. The crystallite size was considerably reduced by the incorporation of sulfate ion in zirconia. Addition of ceria improves the dispersion of the particles thereby resulting in a higher surface area and lower crystallite size.

#### 3.1.2. Energy Dispersive X ray analysis (EDAX)

The sulfate contents of different samples as obtained from the EDX analysis is presented in Table 1. The sulfate content of the metal incorporated zirconia was higher when compared to sulfated zirconia. This point leads to the stabilization of the surface sulfate species by the incorporated metal ion. The metal content of both ceria and zirconia systems clearly indicates that the expected catalyst profile can be successfully achieved by the present preparation method. From the EDX results, it is evident that in all the samples, the amount of metal is very close to the

expected value.

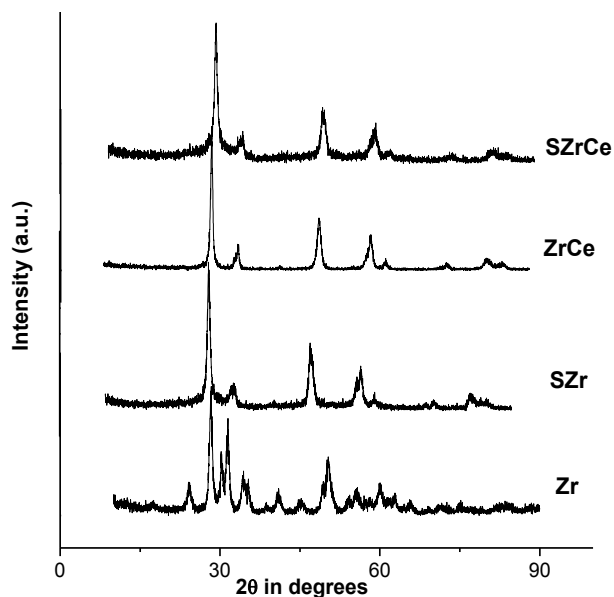


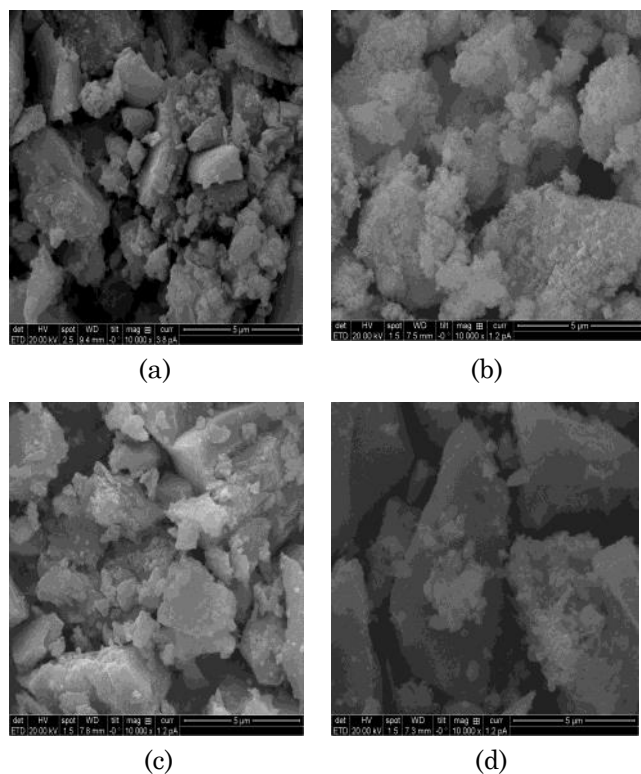
Figure 1. XRD patterns of Zr, SZr, ZrCe and SZrCe

**Table 1.** Elemental Composition from EDX

Catalyst	O %wt	S % wt	Ce %wt	Zr %wt
Zr	9	-	-	90
ZrCe	9	-	2	87
SZr	25	2	-	71
SZrCe	24	2	5	67

**3.1.3. Scanning Electron Microscopy (SEM) analysis**

To understand the surface topography and to assess the surface dispersion of sulfate ions over the zirconia support, SEM investigations on the prepared catalysts were done as shown in Figure 2. The ZrO<sub>2</sub> composite particles are of irregular shape and size with good dispersion of the component oxides. The pictures reveal some crystallinity with less porosity for Zr. There are certain cracks on the surface, which may be attributed to the loss of water molecules during calcination. As can be noted from the micrograph of the SZr sample, the sulfate ions strongly interacted with the zirconia and equally spread on the surface of the support generating porosity.



**Figure 2.** SEM pictures of (a) Zr (b) ZrCe (c) SZr (d) SZrCe

**3.1.4. BET surface area and pore volume measurements**

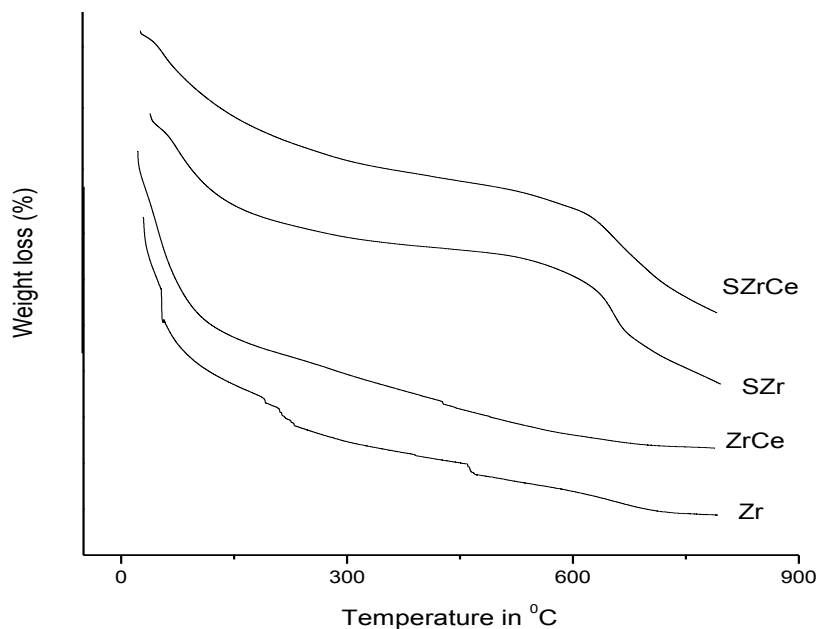
The results of surface area and pore volume measurements are given in Table 2. The retention of surface area by the sulfated zirconia samples can be explained on the basis of the higher resistance to sintering acquired by doping with sulfate ions [28]. Suppression of particle growth is evident from the enhanced surface area of modified zirconia in comparison with unmodified zirconia. Addition of ceria species causes a further setback to the crystallization and sintering process, which is evident from the higher surface area of the samples in comparison with the pure zirconia. In SZrCe the metal oxide species along with the sulfate ions prevent the agglomeration of zirconia particles resulting in a higher surface area.

**3.1.5. Thermogravimetric analysis (TGA)**

The stability of the samples was examined by thermogravimetric analysis. TG curves of different catalysts prepared are given in Figure 3. TG pattern of zirconia indicated dehydration occurring continuously over the entire temperature range. Sulfate modified samples shows two weight losses. The sulfated samples showed an initial weight loss at 293-573 K and 873-1173 K, which are assigned to the removal of surface adsorbed water of hydration and decomposition of sulfate, respectively. The onset of sulfate decomposition was observed around 723 K for simple sulfated systems. Sulfate decomposition was found to occur at around 923 K for the ceria doped sulfated samples. The weight loss in the temperature range 573 –773 K is associated with the tetragonal phase ZrO<sub>2</sub>. It is reported that, for mixed oxides of zirconia, the transformation of tetragonal phase to a monoclinic phase is observed at higher temperatures [29]. As the metal oxides are calcined at 823 K, they are stable until 1173 K.

**Table 2.** BET surface area and pore volume of the catalysts

Catalyst	Zr	SZr	ZrCe	SZrCe
Surface area (m <sup>2</sup> /g)	43	98	69	123
Pore volume (cm <sup>3</sup> /g)	0.076	0.092	0.095	0.085
*Crystallite size (nm)	8	4	6	4



**Figure 3.** TGA curves of Zr, ZrCe, SZr and SZrCe

### 3.1.6. Infra red spectroscopy analysis (FTIR)

FTIR absorption spectra of different samples calcined at 823K are shown in Figure 4. IR spectra of zirconia samples essentially show the various stretching frequencies at  $500\text{ cm}^{-1}$ ,  $572\text{ cm}^{-1}$ ,  $740\text{ cm}^{-1}$ ,  $1104\text{ cm}^{-1}$  and  $1187\text{ cm}^{-1}$  respectively as reported earlier [30]. The features particularly at  $740\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  are due to Zr-O<sub>2</sub>-Zr asymmetric and Zr-O stretching modes respectively; confirm the formation of ZrO<sub>2</sub> phases [31]. Hao et al. also reported the same observation over zirconia catalysts [32]. In sulfated samples some common peaks are seen. The peaks near  $1029$ ,  $1076$  and  $1222\text{ cm}^{-1}$  are typical of the S-O mode of vibration of a chelating bidentate sulfate ion co-ordinated to a metal cation [33]. The band around  $1342\text{ cm}^{-1}$  arises from the highly covalent character of the S=O on a highly dehydrated oxide surface [34]. According to Morterra et al. the peaks in this region correspond to isolated surface sulfates whereas generation of polynuclear sulfates at high sulfate loadings shifts the peak to around  $1400\text{ cm}^{-1}$  [35]. The absence of peaks around  $1400\text{ cm}^{-1}$  suggests the absence of polynuclear species in all the samples. The  $1390\text{ cm}^{-1}$  band representing the asymmetric stretching frequency of S=O double bond is often regarded as characteristic band of SO<sub>4</sub><sup>2-</sup> promoted super acids.

The bands around  $1626\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  corresponds to the bending and stretching modes of the -OH groups of water molecules present in the sample. The existence of these bands even after calcination at 873 K points to the presence of

Brönsted acidity in the samples even after high temperature calcination. The presence of Brönsted sites in spite of the high calcination temperature employed is consistent with earlier reports [35, 36]. For sulfated and metal promoted samples, the peak maximum was shifted to  $3429\text{ cm}^{-1}$ . This shift in the -OH peak to a lower stretching frequency suggests the enhancement in acid strength for the sulfated samples. The increase in Brönsted acidity during sulfation may be ascribed to the generation of S-OH groups [37] or to the acidity enhancement of the surface -OH groups [38].

### 3.1.7. Acidity determination - Pyridine adsorbed Infra red spectroscopy analysis

FTIR-pyridine adsorption was used to determine the acid sites on the catalysts surface [39]. From Figure 5, the bands observed for SZr and SZrCe at  $1490$  and  $1450\text{ cm}^{-1}$  were attributed to the characteristics of adsorbed pyridine bound to Lewis acid sites [40]. Pyridine adsorption band around  $1540\text{ cm}^{-1}$  assigned to Brönsted acid sites is observed in SZr and SZrCe. Thus sulfation increases the acidity of the sample.

### 3.2. Nitration of Toluene

Mixed metal oxides treated with sulphuric acid were found to be efficient for the nitration reaction [41]. The increase in the activity was attributed to the increase in the Brönsted acidity created by the high temperature treatment with sulphuric acid. The life of the catalyst depends on the support's

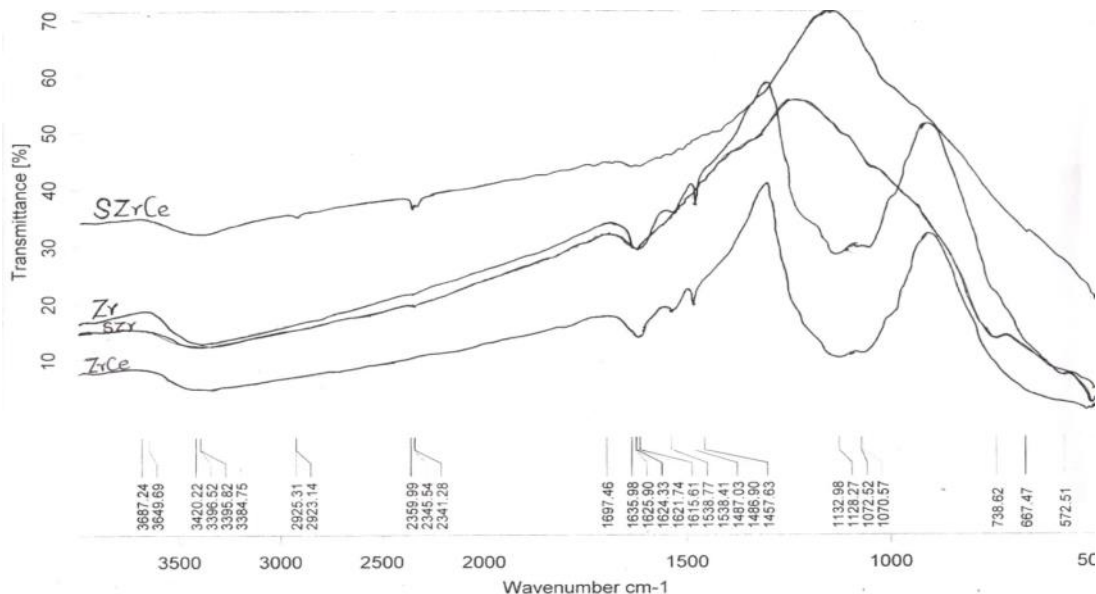


Figure 4. FTIR of Zr, ZrCe, SZr and SZrCe

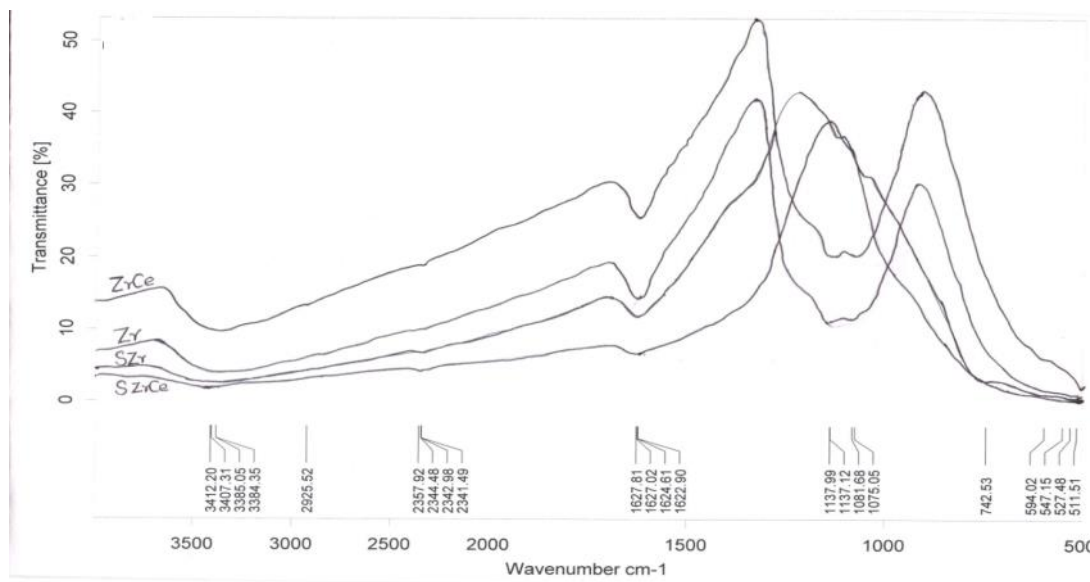


Figure 5. Pyridine adsorbed IR of Zr, CeZr, SZr and SZrCe

capability of holding sulphuric acid to prevent its diffusion.

Industrial aromatic nitrations are achieved by employing a mixture of nitric and sulphuric acids. The mixed acid process poses a major problem of spent acid disposal. All these considerations urge the development of solid acid catalysts for the process. Solid acids effectively play the role of sulphuric acid in the reaction, assisting the formation of nitronium species. Vassena et al. demonstrated the nitration of toluene to nitrotoluene and dinitrotoluene in liquid phase at ambient temperature using silica supported sulphuric acid and 65 % nitric acid [42].

Kemdeo et al. reported mixed oxide supported MoO<sub>3</sub> Catalyst for the nitration of *o*-xylene and explained that *para* selectivity increases with the increase in calcination temperature of the catalyst [43]. Mixed metal oxides treated with sulphuric acid were found to be efficient for the nitration reaction [41]. The increase in the activity was attributed to the increase in the Brönsted acidity created by the high temperature treatment with sulphuric acid. Nitration of toluene was carried out under different experimental conditions with the prepared catalysts and is given below.

### 3.2. Process Optimization

#### 3.2.1. Effect of concentration of nitric acid

The catalytic activity of SZr was tested by varying the percentage of nitric acid as 60 and 80. An increase in the percentage of nitric acid (80 %) used as nitrating agent resulted in an enhancement in the catalytic activity as expected. The toluene conversion and product selectivities are given in Fig. 6.

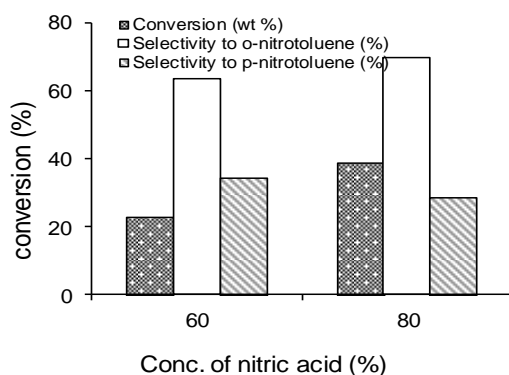
#### 3.2.2. Influence of reaction temperature

The influence of reaction temperature on the catalytic activity and product selectivity was examined taking SZr as representative system. The results are furnished in Table 3. At low temperature the conversion was negligible. Even after 6 hours only 5% of conversion was observed at the reaction temperature of 333 K. An increase in the temperature resulted in a gradual rise in the percentage conversion. At 363 K conversion was found to be 58.2%.

**Table 3.** Effect of reaction temperature on conversion and product selectivity

Temp (K)	Time (h)	Conversion (%)	Selectivity (%) of nitro toluene		
			<i>ortho</i>	<i>para</i>	<i>meta</i>
333 K	6	6	64	33	3
353 K	6	44	65	32	3
363 K	6	58	66	32	2

Note: Toluene:HNO<sub>3</sub> -1:1, conc. of HNO<sub>3</sub> -80%, catalyst amount - 0.1 g SZr



**Figure 6.** Influence of conc. of nitric acid on conversion and product selectivity (Toluene:HNO<sub>3</sub> - 1:1, Time - 4 h, catalyst amount - 0.1 g of SZr, temperature - 363 K)

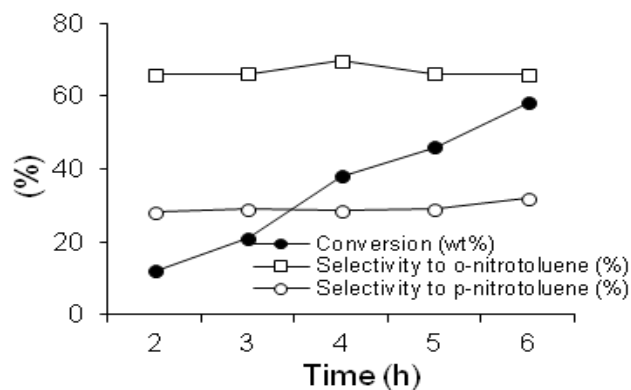
#### 3.2.3. Effect of reaction time

The reaction was done at 363 K with 80 % nitric acid concentration and extracted the products at different time. The results are furnished in Fig.7. As the time increases from 2 to 6 h there is an increase in the conversion. The selectivity to *o*-nitrotoluene remains as such in the initial period, but decreases slightly after 4 h.

#### 3.2.4. Comparison of toluene nitration over different catalysts

The results of toluene nitration over different catalytic systems at 363 K are tabulated in Table 4. At the same reaction conditions, a maximum conversion of less than 3 % was achieved in the blank reaction and the mononitration products were almost not detected (1%). On the contrary, a significantly higher selectivity to mononitration products was obtained over various different catalysts, indicating the substantial effect of catalysts on the toluene nitration reaction. Besides, in comparison with blank experiment and pure zirconia, the toluene conversion increased remarkably over SZrCe and SZr catalysts. Pure zirconia gives very low conversion. In all cases, nitrotoluenes were formed exclusively with no trace of dinitration. The selectivity being around 61-66 % *ortho* and 28-35 % *para* and 1-3 % *meta* isomers. Nitration of toluene was found to proceed with predominant formation of *ortho* isomer. Purely statistical analysis without consideration of the electron donating inductive effect of the methyl group would predict 67% *ortho* and 33% *para* products. In our case also preference to the *ortho* isomer was observed in spite of the steric factor.

The metal doping and sulfation has considerably



**Figure 7.** Influence of Time on conversion and product selectivity (Toluene:HNO<sub>3</sub> - 1:1, Conc. of HNO<sub>3</sub> - 80 %, Temperature- 363 K, Amount of the catalyst-0.1 g SZr)

Table 4. Nitration of toluene over various catalysts

Catalyst	Time (h)	Conversion (%)	Selectivity (%) of nitrotoluene		
			<i>ortho</i>	<i>para</i>	<i>meta</i>
Blank	4	-	-	-	-
Zr	4	6.7	62.4	34.1	3.5
SZr	4	38.4	69.7	28.5	1.8
ZrCe	4	28.2	64.3	33.4	2.3
SZrCe	4	57.8	66.5	30.7	2.8

Note: Toluene: HNO<sub>3</sub>: 1:1, conc. of HNO<sub>3</sub>– 80 %, temperature - 363 K, catalyst amount- 0.1 g

increased the conversion of toluene. The product selectivity remained almost constant immaterial of the nature of the catalyst used.

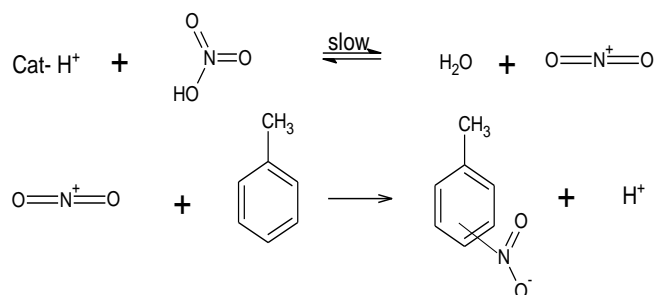
### 3.2.5. Catalyst reusability

The reusability of the catalyst systems was also subjected to investigation. The catalyst, SZr was removed by filtration from the reaction mixture, washed thoroughly with acetone, dried and activated at 823 K. It was used in the nitration reaction with a fresh mixture and only a slight decrease in the conversion was observed for three cycles. This suggests the resistance to rapid deactivation. But from the fourth cycle onwards the decrease in conversion was much higher. The catalyst crystals adsorb water (obtained during the reaction) and this causes dilution of the nitric acid used in the next nitration. The dilution can result in decreasing the conversion. To prove the heterogeneous character of the reactions; the catalyst was removed by filtration after a particular time (4 h) from the reaction mixture. The filtrate was subjected to qualitative analysis for testing the presence of Ce ion. From the results, it is clear that cerium ions are not leaching from the metal oxide surface during the reaction.

### 3.3. Mechanism of toluene nitration

The nitration reaction is an electrophilic substitution reaction where Brønsted acidic sites are responsible for the generation of nitronium ion (NO<sub>2</sub><sup>+</sup>) from nitric acid. It is assumed that the reaction may take place between nitric acid and the Brønsted acid sites of the catalyst, forming nitronium ion. Then electrophilic attack of nitronium ion on the aromatic ring (toluene) takes place, resulting in the formation of nitro toluene. Brei *et al.* also explained that strong Brønsted sites are necessary for an effective formation of intermediate NO<sub>2</sub><sup>+</sup> ions from nitric acid [10]. The reaction may be considered to proceed *via.* a carbocation mechanism, in which the nitronium

ion is generated by the interaction of nitric acid with the Brønsted acid sites. The *ortho* and *para* attack of the nitronium ion is favored due to the stabilization of the specific *ortho* and *para* resonance structures *via.* an electron-donating inductive effect of the methyl groups. A plausible mechanism for nitration of toluene is given in scheme 1. Nitric acid was used as a nitrating agent without the use of sulfuric acid, which makes this process environmentally benign.



Scheme 1. Plausible mechanism of nitration of toluene over zirconia catalyst.

## 4. Conclusions

Liquid phase nitration of toluene was investigated on modified zirconia catalysts. The results indicated that Brønsted acid sites increases with sulfate modification, leading to enhanced catalytic activity. SZrCe shows the maximum conversion at 363 K. The crystallite size of the modified ceria was calculated from the Scherrer's equation to be 4-8 nm. No characteristic peaks of ceria are observed in the modified ceria, confirming that CeO<sub>2</sub> is well dispersed on zirconia surface. FTIR results confirm the sulfate modification by asymmetric and symmetric stretching of S=O in sulfated samples. The surface area of zirconia has been increased after sulfate modification. The onset of sulfate decomposition is



observed around 923 K for SZr and SZrCe while Zr and ZrCe are stable up to 1173 K. The metal doping and sulfation has considerably increased the conversion of toluene. The nitration proceeds via nitronium ion mechanism and the increase of nitration activity can be attributed to the increase of Brønsted acidity by the sulfation of metal oxides.

### Acknowledgement

Authors gratefully express sincere gratitude to Bangalore University, St. Joseph's College, Bangalore and Indian Institute of Science, Bangalore for various spectral analysis.

### References

- [1] Olah, G.A., Malhotra, R., Narang, S.C. (1989). *Nitration: Method and Mechanisms*: VCH publisher Inc-New York 1989: 5-15.
- [2] Winnacker, K., Kuchler, L., Harnisch, H., Steiner R., Winnacker, K. (Eds.), *Chemische Technologie (Band 6): Organische Technologie II*, 4<sup>th</sup> Edition, Carl Hanser Verlag, Munchen, (1982), pp. 169.
- [3] Glushko, V.P., (Ed.), *Thermodynamic Properties of Individual Substances*, Nauka, Moscow, (1978). Vol. 1.
- [4] Kalbasi R.J., Ghiaci, M., Massah, A.R. (2009). Highly selective vapor phase nitration of toluene to 4-nitro toluene using modified and unmodified H<sub>3</sub>PO<sub>4</sub>/ZSM-5. *Applied Catalysis A: General*, 353: 1-8.
- [5] Dagade, S.P., Waghmode, S.B., Kadam, V.S., Dongare, M.K. (2002). Vapor phase nitration of toluene using dilute nitric acid and molecular modeling studies over beta zeolite. *Applied Catalysis A: General*, 226: 49-61.
- [6] Dagade, S.P., Kadam, V.S., Dongare, M.K. (2002). Regioselective nitration of phenol over solid acid catalysts. *Catalysis Communications*, 3: 67-70.
- [7] Patil, P.T., Malshe, K.M., Dagade, S.P., Dongare, M.K. (2003). Regioselective nitration of o-xylene to 4-nitro-o-xylene using nitric acid over solid acid catalysts. *Catalysis Communications*, 4: 429-434.
- [8] Parida, K.M., Pattanayak, P.K. (1997). Sulphated zirconia: An efficient paraselective catalyst for mononitration of halobenzenes. *Catalysis Letters*, 47: 255 - 257.
- [9] Yadav, G.D., Nair, J.J. (1999). Sulfated zirconia and its modified versions as promising catalysts for industrial processes. *Microporous and Mesoporous Material*, 33: 1-48.
- [10] Brei, V.V., Prudius, S.V., Melezhyk, O.V. (2003). Vapour-phase nitration of benzene over superacid WO<sub>3</sub>/ZrO<sub>2</sub> catalysts. *Applied Catalysis A: General*, 239(1-2): 11-16.
- [11] Sunajadevi, K.R., Sugunan, S. (2005). Sulfated titania mediated regioselective nitration of phenol in solid state. *Catalysis Communications*, 6(9): 611-616.
- [12] Mao, W., Ma, H., Wang, B. (2009). A clean method for the solvent-free nitration of toluene over sulfated titania promoted by ceria catalysts. *Journal of Hazardous Materials*, 167: 707-712.
- [13] Wright, O.L., Teipel, J., Thoennes, D. (1965). The Nitration of Toluene by Means of Nitric Acid and an Ion-Exchange Resin. *Journal of Organic Chemistry*, 30: 1301-1303.
- [14] Shi, M., Cui, S.C. (2002). Perfluorinated rare earth metals catalyzed nitration of aromatic compounds *Journal of Fluorine Chemistry*, 113: 207-209.
- [15] Shi, M., Cui, S.C. (2002). Electrophilic aromatic nitration using perfluorinated rare earth metal salts in fluoruous phase. *Chemical Communications*, 7(9): 994-995.
- [16] Shi, M., Cui, S.C. (2003). Electrophilic Aromatic Nitration Using a Mixed Catalyst of Lithium, Molybdenum, Ytterbium on Silica Gel. *Advanced Synthesis & Catalysis*, 345: 1329 - 1333.
- [17] Heravi, M.M., Bakhtiari, K., Benmorad, T., Bamoharram, F.F., Oskooie, H.A., Tehrani, M.H. (2006). H<sub>3</sub>PMo<sub>12</sub>VO<sub>40</sub>(heteropolyacids)-catalyzed regioselective nitration of phenol to o-nitrophenol in heterogeneous system. *Journal of Molecular Catalysis A: Chemistry* 264: 318-321
- [18] Zhao, X.Q., Han, Y.T., Sun, X.L., Wang, Y.J. (2007). Structure and Catalytic Performance of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> Prepared by Several Methods. *Chinese Journal of Catalysis*, 28: 91-95.
- [19] Choudary, B.M., Sateesh, M., Kantam, M.L., Rao, K.K., Ram, K.V. (2000). Selective nitration of aromatic compounds by solid acid catalysts. *Chemical Communications*, 1: 25-26.
- [20] Akolekar, D.B., Lemay, G., Sayari, A., Kaliaguine, S. (1995). High-pressure nitration of toluene using nitrogen dioxide on zeolite catalysts. *Research on Chemical Intermediates*, 21: 7-16.
- [21] Sakhivel, R., Prescott, H.A., Deutsch, J., Lieske, H., Kemnitz, E. (2003). Synthesis, characterization, and catalytic activity of SO<sub>4</sub>/Zr<sub>1-x</sub>Sn<sub>x</sub>O<sub>2</sub>. *Applied Catalysis A: General*, 20: 237-247.
- [22] Escribano, V.S. (2003). Characterization of cubic ceria-zirconia powders by X-ray diffraction and vibrational and electronic spectroscopy. *Solid State Sciences*, 5: 1369-1376.
- [23] Yamaguchi, T. (1994). Application of ZrO<sub>2</sub> as a catalyst and a catalyst support *Catalysis Today* 20: 199-217.

- [24] Brei, V.V. (2005). Superacids Based on Zirconium Dioxide. *Theoretical and Experimental Chemistry*, 3(42): 165-175.
- [25] Yu, S., Jiang, P., Dong, Y., Zhang, P., Zhang, Y., Zhang, W. (2012). Hydrothermal Synthesis of Nanosized Sulfated Zirconia as an Efficient and Reusable Catalyst for Esterification of Acetic Acid with n-Butanol. *Bulletin of Korean Chemical Society*, 2(33): 524-528.
- [26] Reddy, B.M., Sreekanth, P.M., Lakshmanan, P. (2005). Sulfated zirconia as an efficient catalyst for organic synthesis and transformation reaction. *Journal of Molecular Catalysis A: Chemical*, 237: 93-100.
- [27] Scherrer, P. (1918). Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen*, 26: 98-100.
- [28] Saravanan, K., Beena Tyagi, Bajaj, H.C. (2012). Synthesis of dypnone by solvent free self condensation of acetophenone over nanocrystalline sulfated zirconia catalyst. *Journal of solgel Science and Technology*, 61: 275-280.
- [29] Angel, J. D., Aguilera, A. F., Galindo, I. R., Martínez, M., Viveros, T. (2012). Synthesis and Characterization of Alumina-Zirconia Powders Obtained by Sol-Gel Method: Effect of Solvent and Water Addition Rate. *Materials Sciences and Applications*, 3: 650-657
- [30] Powers, A., Gray, H.B. (1973). Characterization of the thermal dehydration of zirconium oxide halide octahydrates. *Inorganic Chemistry*, 12: 2721-2726.
- [31] Ranjan Sahu, H., Ranga Rao, G. (2000). Characterization of combustion synthesized zirconia powder by UV-vis, IR and other techniques. *Bulletin of Material Sciences*, 23: 349-354.
- [32] Hao, Y., Li, J., Yang, X., Wang, X., Lu, L. (2004). Preparation of ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite membranes by sol-gel process and their characterization. *Material Science Engineering A*, 367: 243-247.
- [33] Fielicke, A. Von Helden, G., Meijer, G., Pedersen, D.B., Simard, B., Rayner, D.M. (2005). Gold Cluster Carbonyls: Saturated Adsorption of CO on Gold Cluster Cations, Vibrational Spectroscopy, and Implications for Their Structures. *Journal of American Chemical Society*, 127: 8416-8423.
- [34] Saur, O., Bensitel, M., Saad, A.B.M., Lavalley, J.C., Tripp, C.R., Morrow, B.A. (1986). The structure and stability of sulfated alumina and titania. *Journal of Catalysis*, 99: 104-110.
- [35] Morterra, C., Bolis, V., Cerrato, G. (1993). Lewis and Brønsted acidity at the surface of sulfate-doped ZrO<sub>2</sub> catalysts. *Catalysis Today*, 17: 505-515.
- [36] Morterra, C., Cerrato, G., Pinna, F., Signoretto, M. (1994). Brønsted Acidity of a Superacid Sulfate-Doped ZrO<sub>2</sub> System. *Journal of Physical Chemistry*, 47(98): 12373-12381.
- [37] Clearfield, A., Serrete, G.P.D., Khazi-Syed, A.H. (1994). Nature of hydrous zirconia and sulfated hydrous zirconia. *Catalysis Today*, 20: 295-312.
- [38] Kustov, L.M., Kazansky, V.B., Figueras, F., Tichit, D. (1994). Investigation of the Acidic Properties of ZrO<sub>2</sub> Modified by SO<sub>4</sub><sup>2-</sup> Anions. *Journal of Catalysis*, 150: 143-149.
- [39] Sun, Y., Ma, S., Du, Y., Yuan, L., Wang, S. Yang, J., Deng, F., Xiao, F.S. (2005). Solvent-Free Preparation of Nanosized Sulfated Zirconia with Brønsted Acidic Sites from a Simple Calcination. *Journal of Physical Chemistry B*, 109: 2567-2572.
- [40] Li, N., Wang, A.Q., Zheng, M.Y., Wang, X.D., Cheng, R.H., Zhang, T. (2004). Probing into the catalytic nature of Co/sulfated zirconia for selective reduction of NO with methane. *Journal of Catalysis*, 225: 307-315.
- [41] Sato, H.; Nagai, K.; Yoshioka, H.; Nagaoka, Y. (1998). Vapor phase nitration of benzene over solid acid catalysts: III. Nitration with nitric acid (2); mixed metal oxide treated with sulfuric acid and heteropolyacid partially neutralized. *Applied Catalysis A: General*, 175: 209-213.
- [42] Kogelbauer, A., Vassena, D., Prins, R., Armor, J.N. (2000). Solid acids as substitutes for sulfuric acid in the liquid phase nitration of toluene to nitrotoluene and dinitrotoluene. *Catalysis Today*, 55: 151-160.
- [43] Kemdeo, S.M., Sapkal, V.S., Chaudhari, G.N. (2010). Mixed Oxide Supported MoO<sub>3</sub> Catalyst: Preparation, Characterization and Activities in Nitration of o-xylene. *Bulletin of Chemical Reaction Engineering & Catalysis*, 5(1): 39-49.