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Article

Vapor phase methylation of phenol on Fe-substituted ZrO₂ catalyst

Celia F. Braganza, A. V. Salker *

Department of Chemistry, Goa University, Goa-403206, India

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ABSTRACT

Fe-doped ZrO₂ compounds were prepared by a co-precipitation method. The compounds were characterized by X-ray diffraction, N₂ adsorption-desorption, ultraviolet diffuse reflectance infrared Fourier transform spectroscopy, scanning electron microscopy–energy-dispersive X-ray spectroscopy, transmission electron microscopy, NH₃ temperature-programmed desorption, X-ray photoelectron spectroscopy, and in situ Fourier transform infrared spectroscopy. The incorporation of Fe into ZrO₂ lattice favored and effectively stabilized the formation of purely ZrO₂ tetragonal phase. Subsequently, the catalytic activity of the Fe-doped ZrO₂ compounds was evaluated toward vapor phase methylation of phenol. The catalytic activity was governed by Fe content and related to the Lewis acidity of the prepared catalyst.

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1. Introduction

The alkylation of phenolic compounds is an important process as the resulting products are essential intermediates involved in the chemicals industry. Specifically, alkylated phenolic compounds are widely used in the pharmaceutical and agrochemical industries. Di-alkylated phenols, such as 2,6-xylenol, are used in the synthesis of polyphenylene oxide [1]. Several catalysts such as zeolites, mixed metal oxides, and ferrosinels have been investigated for catalyzing this reaction to date [2–10]. However, the high reaction temperatures involved, poor catalyst selectivity, and coking limit the application of such catalysts, hence the search for new efficient catalysts is desirable.

As an option, Fe-incorporated ZrO₂ solids, prepared by different routes and with various compositions, show potential owing to their diverse applications, as demonstrated in the literature. For example, nitrite photo-oxidation, ethylenediaminetetraacetic acid oxidation, and chromium (VI) reduction have been conducted over these catalysts [11]. Electrochemical studies have shown that these catalysts can promote electro-

chemical oxygen reduction [12]. The enhanced photocatalytic visible light-driven H₂ evolution over these catalysts was also demonstrated [13]. Furthermore, the magnetic properties of Fe-doped ZrO₂ thin films were investigated [14].

In the present study, the catalytic methylation of phenol in vapor phase over Fe-doped ZrO₂ (at varying Fe contents) is investigated for the first time. The catalytic results of the prepared Fe-doped ZrO₂ compounds were compared with those of pristine ZrO₂.

2. Experimental

2.1. Catalyst preparation

A series of Fe-doped ZrO₂ catalysts were prepared by the simple co-precipitation method, wherein known amounts of ferric nitrate (Thomas Baker) and zirconyl nitrate (Sigma-Aldrich) were dissolved in distilled water. Precipitation was instigated upon dropwise addition of NH₄OH with constant stirring until a pH of ~8.5 was attained. The resulting brownish white precipitate was then aged for 18 h. The aged precipitates

* Corresponding author. Tel: +91-832-6519315; E-mail: sal_arun@rediffmail.com

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were filtered and washed with doubly distilled water until the filtrate pH was 7. The resulting product was oven dried at 75 °C for 12 h and subsequently calcined at 500 °C for 5 h. The prepared products with compositions of $\text{Zr}_{1-x}\text{Fe}_x\text{O}_2$, where $x = 0.0, 0.02, 0.05$, and 0.1 , were respectively denoted as Z, ZF1, ZF2, and ZF3.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using $\text{Cu K}\alpha$ radiation and a Ni filter.

The morphology and elemental composition of the samples were determined by scanning electron microscopy (SEM) on a JEOL 5800LV microscope equipped with an energy-dispersive X-ray spectroscopy (EDX) unit (Oxford Instruments, UK). Transmission electron microscopy (TEM) images were taken on a Phillips CM 200 electron microscope.

N_2 adsorption-desorption studies were performed on a Quantachrome Autosorb surface and porosity instrument using N_2 as a probe molecule at -196 °C. Prior to the measurements, the samples were degassed at 300 °C for 3 h to remove any adsorbed moisture and volatiles. The Brunauer-Emmett-Teller (BET) model was used to determine the specific surface area of the metal oxide samples. The pore size and pore volume of the samples were measured using the Barrett-Joyner-Halenda (BJH) method.

Ultraviolet-visible (UV-vis) spectra were recorded in the range of 200–800 nm in air at room temperature using a Shimadzu spectrophotometer equipped with a diffuse reflectance accessory. The reflectance was converted using the Kubelka-Munk function and the results were plotted against wavelength.

X-ray photoelectron spectroscopy (XPS) studies were conducted on a VSW Scientific Instrument using $\text{Mg K}\alpha$ as the incident source with an energy of 1253.6 eV and a resolution of 0.9 eV. A vacuum of 10^{-8} Torr was maintained in the sample analyzer chamber.

Pyridine adsorption analysis was conducted to determine the nature and amount of acidic sites on the surface of the metal oxide samples. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Nicolet IS-50 FTIR spectrometer fitted with a praying mantis DRIFTS accessory. A small amount of sample was compacted into the high-temperature vacuum cell of the instrument. The cell was then evacuated and heated to 300 °C for 2 h to remove any adsorbed gases. After cooling to 25 °C, the sample was spiked with pyridine vapors. The cell was then gradually heated under vacuum, and spectra were recorded as a function of temperature. The degree of acidity of the samples was determined by temperature-programmed desorption (TPD) using NH_3 as probe molecule.

2.3. Catalysis study

For the catalysis studies, the vapor phase alkylation of phenol over the prepared samples was assessed. The reaction was

conducted in a vertical fixed bed reactor (internal diameter of 1.5 cm and length of 30 cm) at 300 °C under atmospheric pressure and flowing dry N_2 . The catalyst sample (1 g) was packed between glass wool, and the upper portion of the reactor was filled with ceramic beads, which served as pre-heating devices. Before the reaction, the catalyst was activated at 350 °C in flowing dry N_2 for 1 h. Then, the reaction temperature was set and allowed to equilibrate. A mixture of phenol and methanol at a molar ratio of 1:12 (unless specified otherwise) was then introduced into the reactor using a syringe pump (Miclins, India) at a rate of 1.5 mL/h. The formed liquid products were condensed and collected in a chill trap and subsequently analyzed by gas chromatography (Nucon 5765) using a flame ionization detector and an OV101 column.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the prepared samples. As observed from Fig. 1, pristine ZrO_2 featured a monoclinic structure. In contrast, all the Fe-doped ZrO_2 samples displayed a tetragonal phase structure only except for ZF1, which additionally displayed minor features of the monoclinic phase.

SEM-EDX analysis were performed and the results were matching well with the calculated and observed elemental composition of the samples.

The representative TEM image showed that the particle size ranged from 10 to 20 nm. The particles were highly agglomerated and formed discrete clusters. The N_2 adsorption-desorption isotherms revealed the mesoporous nature of the prepared catalysts with pore diameters in the range of 4–10 nm. Specifically, the isotherms were identified as type IV isotherms with a type H2 hysteresis loop, which is characteristic of ink-bottle pores [15]. The N_2 sorption studies additionally revealed that the N_2 uptake decreased as the Fe content increased, and smaller pore sizes and lower pore volumes were observed with increasing Fe doping contents as seen in Table 1.

The Tauc's plots of the samples, obtained from the

Fig. 1. XRD patterns of ZrO_2 and Fe-doped catalysts.

Table 1

BET surface area, pore data and activity of the catalysts.

Catalyst	BET surface area (m ² /g)	Pore diameter (nm)	Pore volume (mL/g)	Conversion ^a (%)	
				1:6	1:12
Z	118	9.6	0.25	7	13
ZF1	82	8.5	0.18	12	36
ZF2	79	6.2	0.12	25	56
ZF3	78	4.5	0.09	57	70

^a Conversion at phenol/methanol molar ratios of 1:6 and 1:12.

UV-DRIFTS measurements, revealed that doping caused narrowing of the band gap relative to that of pristine ZrO₂, similarly to the results observed by Xiao et al. [12]. The band gap (E_g) values of Z, ZF1, ZF2, and ZF3 were 6.54, 4.00, 3.94, and 3.87 eV, respectively, with corresponding wavelengths ($\lambda = 1240/E_g$) of 189, 310, 314, and 320 nm.

The surface acidity and reactivity of a catalyst for the present target reaction (methylation of phenol in vapor phase) can be explained by the formation of selective *ortho* products in vapor phase as the reaction is influenced by the presence of active acid–base pair sites. The reaction mechanism was discussed by Chary et al. [1]. Hence, FTIR and TPD studies were conducted to assess the presence of acid sites on the prepared catalysts. The in situ FTIR spectra of ZF3 samples in Fig. 2 featured intense IR bands at 1445 and 1605 cm^{−1}, which could be attributed to strong Lewis acid sites. The small weak band observed at 1492 cm^{−1} could be referred to a Lewis–Brønsted combined peak [4,16], which could be due to the disappearance of surface hydroxyls at higher temperatures. Based on the peak intensity calculations, it could be inferred that the catalyst is predominantly Lewis acidic in nature. The NH₃-TPD profiles revealed the increasing presence of strong acidic sites with increasing Fe contents as shown in Fig. 3.

The chemical states of the prepared catalysts were assessed by XPS. Fig. 4 shows the XPS spectra of representative sample ZF2. All spectra were deconvoluted using a peak-fitting software. XPS peaks of Fe 2p, O 1s, and Zr 3d were distinctly visible, confirming the presence of these elements. The XPS spectrum of Fe 2p is shown in Fig. 4(a); two signals corresponding to Fe

Fig. 2. Pyridine adsorbed IR spectra of ZF3 catalyst. **Fig. 3.** NH₃-TPD profiles of Fe-doped catalysts.

2p_{1/2} and Fe 2p_{3/2} were observed. The peaks at 722.7 and 710.3 eV are representative of Fe³⁺. A satellite peak at 717.8 eV was also observed. These results confirmed the presence of Fe³⁺

Fig. 4. XPS spectra of ZF-2 catalyst. (a) Fe 2p; (b) Zr 3d; (c) O 1s.

oxidation state [17]. In Fig. 4(b), the peaks corresponding to Zr $3d_{3/2}$ and Zr $3d_{5/2}$ were observed at 183.8 and 181.5 eV, respectively; these are characteristic Zr^{4+} [18]. The O 1s XPS spectrum is presented in Fig. 4(c). The peak observed at 531.6 eV was attributed to lattice oxygen. The additional peak at 531.6 eV could be attributed to defect oxygen [19].

3.2. Catalytic activity

Fig. 5(a) shows the effect of temperature on the catalytic activity of the prepared samples. No activity was observed at temperatures of less than 300 °C. Hence, subsequent studies were performed at 300 °C. The performance results of the prepared catalysts with respect to phenol conversion are listed in Table 1. As observed, increased activity towards the formation of 2,6-xyleneol was observed with increasing Fe contents.

Additionally, to study the effect of feed concentration, mixtures of phenol and methanol at molar ratios of 1:6 and 1:12 were examined. By doubling the methanol content, a consider-

able increase in the conversion of phenol to 2,6-xyleneol was observed (Fig. 5(b) and (c)). Additionally, a higher activity was observed. In contrast, a greater selectivity toward *o*-cresol was observed when a 1:6 phenol/methanol mixture was employed. The increase in the conversion of phenol at the higher molar ratio (1:12) was attributed to the greater availability of alkylating methyl groups, thereby rationalizing the propensity for the formation of higher alkylated product 2,6-xyleneol [9]. ZF3 showed the highest conversion of 70% at 300 °C. However, further increases in the reaction temperature led to a slow decline in activity. The reduced performance of the catalysts at the higher reaction temperatures could be attributed to catalyst sintering or coke formation and fouling.

The present reaction was believed to proceed via the Langmuir–Hinshelwood mechanism, wherein alkylation of phenol proceeds by adsorption of the phenyl ring and methanol on the acidic centers because of the –OH groups (Scheme 1). The phenol ring undergoes a double bond rearrangement, the –H breaks away at the *ortho* site and is adsorbed on the lattice. The –OH group breaks away from the CH_3OH group to supply –H to the lattice at the basic sites. The CH_3^+ carbocation, which is subsequently formed, attacks the phenolic nucleophile in adsorbed state, forming products *o*-cresol and water. Then, the adsorbed products are desorbed. The *o*-cresol formed in Step 1 is subsequently adsorbed along with methanol on the acidic sites of the catalyst because of the –OH groups. The cresol ring undergoes a double bond rearrangement, the –H breaks away at the second *ortho* position and is adsorbed on the lattice. The –OH of CH_3OH breaks away, supplying –H to the lattice. The CH_3^+ carbocation attacks the cresol nucleophile (*ortho*) in ad-

Fig. 5. Catalytic activity profile over a temperature range (a) for phenol to methanol ratio (b) 1:6 and (c) 1:12.

Scheme 1. Possible catalytic reaction mechanism for vapour phase phenol alkylation with methanol.

sorbed state, forming the products 2,6-xyleneol and water. Subsequently, the adsorbed products are desorbed.

4. Conclusions

A series of Fe-doped ZrO_2 compounds were successfully prepared by co-precipitation method. Fe doping in the ZrO_2 lattice caused structural modification, which was clearly observed from the XRD analysis. The oxides were mesoporous in nature; they exhibited type IV N_2 sorption isotherms with an H2-type hysteresis loop. The amount of strong acidic sites increased with increasing Fe doping contents. XPS analysis confirmed the presence of Fe^{3+} . The prepared compounds were successfully employed as catalysts in the vapor phase methylation of phenol and were highly selective toward the formation of *ortho* products. The incorporation of Fe into the zirconium oxide increased the activity of the catalyst. Higher conversion rates and greater amounts of higher alkylated products were obtained when higher concentrations of alkylating agents were introduced in the feed. ZF3 showed the best activity with a 74% selectivity toward 2, 6-xyleneol.

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Graphical Abstract

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Vapor phase methylation of phenol on Fe-substituted ZrO_2 catalyst

Celia F. Braganza, A. V. Salker *
Goa University, India

Mixtures of phenol and methanol were introduced into a reactor in vapor phase. The vapors adsorbed and reacted at 300 °C over nano Fe-doped ZrO_2 catalyst to generate highly selective *ortho* alkylated products.

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Fe掺杂ZrO₂催化剂上苯酚气相甲基化

Celia F. Braganza, A. V. Salker *

果阿大学化学系, 果阿-403206, 印度

摘要: 采用共沉淀法制备了Fe掺杂的ZrO₂样品, 并采用X射线衍射、N₂吸附-脱附、紫外漫反射光谱、扫描电镜-电子能谱、氨程序升温脱附、X射线光电子能谱和原位红外光谱进行了表征. 结果表明, Fe进入ZrO₂晶格中有效稳定了其晶相结构为单一的四方相. 这些样品可很好地催化苯酚气相甲基化反应, 其催化活性取决于Fe含量, 并与样品中L酸有关.

关键词: 氧化锆; 铁掺杂; 甲基化; 苯酚; 二甲苯酚

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*通讯联系人. 电话: +91-832-6519315; 电子信箱: sal_arun@rediffmail.com

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