

Oxidation of Ethyl Benzene over Mesoporous Ceria Modified with Chromium

Rose Philo.K.J, Sugunan S.

Abstract

Supported metals are used in large scale in heterogeneous catalysis. Highly efficient heterogeneous catalysts consisting of mesoporous ceria modified with different weight% of Cr successfully oxidized ethylbenzene to acetophenone using Tert-Butyl Hydroperoxide (TBHP) with acetonitrile as solvent. Chromium containing mesoporous ceria ($\text{CeCr}(x\%)$) were synthesized by templated method using neutral surfactant Hexadecylamine (HDA) followed by wet impregnation method. The catalytic activities of the newly developed chromium modified samples were evaluated in the liquid phase oxidation of ethylbenzene using TBHP as an oxidant. The kinetic parameters of the catalyst were also calculated for the reaction.

Index Terms: Mesoporous ceria, Neutral surfactant, Ethyl benzene, Oxidation, Heterogeneous catalyst

1. Introduction

Selective oxidation reaction of relatively inert C–H bond of hydrocarbons is one of the most desirable and challenging reactions, since the obtained products are itself important or act as valuable intermediates for industrial organic chemicals [1]. Liquid-phase oxidations of hydrocarbons are potentially very attractive reactions for the preparation of intermediates and fine chemicals [2]. In this work we tried to prepare mesoporous ceria using a neutral surfactant hexadecyl amine (HDA) at a lower calcination temperature, and to modify it with chromium by wet impregnation method. The catalytic activities of the samples were tested in the oxidation reaction of ethyl benzene. We also tried to correlate the conversion with the acidities of the samples. The kinetic parameters were also calculated.

2. Experimental

2.1 Materials and Methods

Chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Alfa 98.5%), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (IRE), and ammonia were used as sources for chromium, cerium and alkali respectively. Hexadecyl amine (HDA; Aldrich 98%), was used as a surfactant for the synthesis. Chromium-containing mesoporous ceria was synthesized, according to

literature procedure [3] and characterized by various analytical and spectroscopic techniques, viz., powder X-ray diffraction (XRD; Rigaku D MAX III VC), thermogravimetry-differential thermal analysis (TGDTA; Perkin Elmer TG analyzer), inductively coupled plasma - atomic emission spectroscopy (ICP-AES; Labtam Plasma 8440), diffuse reflectance ultraviolet-visible (DRUV-Vis; Shimadzu UV-2101 PC spectrometer); FT-IR spectra (Shimadzu FTIR 8201); SEM analysis (JEOL JSM-840 A (Oxford make) model 16211) and N_2 adsorption-desorption studies (Micromeritics Tristar 3000 surface area and porosity analyzer). The acidity measurements of the prepared samples were done by Temperature Programmed Desorption (TPD) of ammonia [4] and tested by vapour phase cumene cracking reaction [5].

2.2. Synthesis and characterization

In a typical synthesis procedure, 0.5M aqueous cerium nitrate solution was added with constant stirring to 6 g of HDA in 1:1 ethanol – water mixture (98%, Aldrich) at a precursor to surfactant ratio of 2. The pH was maintained above 10 by adding ammonia solution. After stirring for a predefined time, the precipitate was aged for 3 days at 70°C. Then washed several times with water – ethanol mixture and deionised water. Since the neutral surfactant – inorganic interaction is due to weak hydrogen bonding the removal of most of the surfactant can be done by washing/solvent extraction. The filtered precipitate is dried and then precalcined at 250°C for 6 hours to make the calcination effective at lower temperature. The sample is then calcined at 350°C for 4 hrs. Mesoporous ceria thus obtained was modified with different weight% (2, 4 & 10) of chromium by wet impregnation method.

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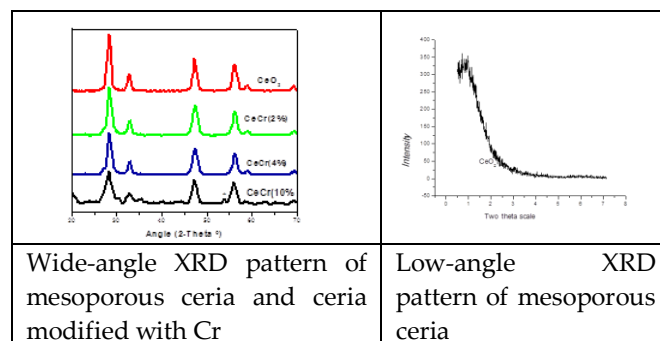
2.2.1 Characterization

Powder X-ray diffractograms of the materials were recorded on a Rigaku D MAX III VC Ni-filtered Cu K α radiation, $\lambda = 1.5404 \text{ \AA}$, 2θ range $10-80^\circ$ at a speed of $1^\circ/\text{min}$. The crystalline phases were identified by comparison with standard JCPDS (Joint Committee on Powder Diffraction Standards) data file [6]. Low angle XRD was also done to confirm the mesoscopic nature of the sample. N_2 adsorption-desorption isotherms, pore size distributions as well as the textural properties of the materials were determined at -196°C by a Micromeritics Tristar 3000 surface area and porosity analyzer. Prior to the measurements the samples were degassed for 1h at 90°C followed by 200°C overnight. Pore size distribution and average pore size of the samples were obtained from the adsorption branch of the isotherms using the Barrnet-Joyner-Halenda (BJH) method. FT-IR spectra of the solid samples were taken in the range of $4000-400 \text{ cm}^{-1}$ on a Shimadzu FT-IR 8201 instrument by diffuse reflectance scanning disc technique. Diffuse reflectance UV-Vis spectra were recorded in the range $200-600 \text{ nm}$ with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment, using BaSO_4 as the reference. SEM analysis of the samples was done using JEOL JSM-840 A (Oxford make) model 16211 scanning electron microscope analyzer with a resolution of 13 eV . The HR-TEM of the sample was carried out in ultrahigh resolution analytical electron microscope JEOL 3010. Perkin Elmer TG analyzer instrument was used for carrying out thermo gravimetric studies. About 20 mg of the sample was used at a heating rate of 20°C per minute in nitrogen atmosphere. The TG data were computer processed to get thermograms.

3. Results and discussions

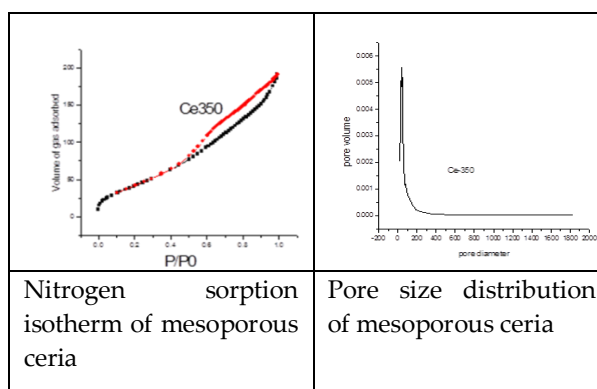
Wide angle XRD analysis clearly shows peaks corresponding to the crystalline cubic fluorite ceria phase (PDF-ICDD34-0394). A peak in low-angle region is due to mesoporosity (Fig.1).

Fig. 1 XRD patterns



The appearance of low-angle diffraction peaks indicates that mesoscopic order is preserved in the calcined metal oxide materials. The sample exhibits N_2 adsorption-desorption of Type IV isotherm with steps between partial pressures P/P_0 of 0.3 to 0.8, and a hysteresis loop, due to capillary condensation in the mesoporous channels and/or cages (Fig.2).

Fig. 2 Nitrogen sorption isotherms & pore size distribution curves



The H3 hysteresis loop is characteristic of mesoporous materials with narrow slit-like pores. Narrow BJH pore size distribution suggests an open pore channel. It also shows a regular mesopore structure. The pore volume, pore diameter & surface area are calculated by desorption studies are given in (Table1).

Table.1 Surface area, Pore measurements

sample	BET S.A (m^2g^{-1})	Average Pore Diameter (nm)	Cumulative Pore Volume (cm^3g^{-1})
CeO_2	164	4.19	0.29
CeCr (2%)	123	5.26	0.20
CeCr (4%)	120	5.26	0.18
CeCr (10%)	96	3.62	0.14

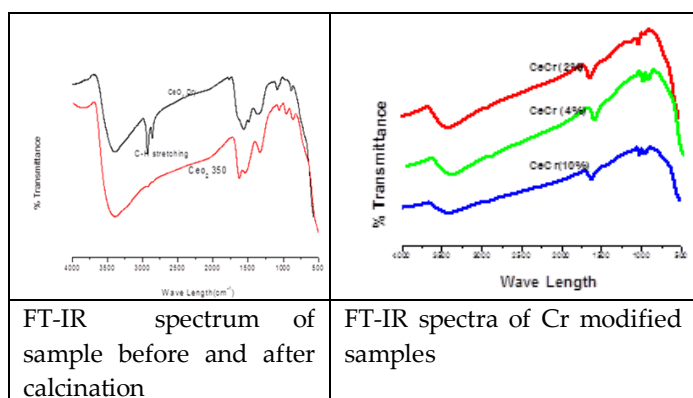
Surface area decreases with metal loading. Crystallite size and lattice parameters are calculated by XRD data. (Table2).

Table2.XRD data

Sample	Average crystallite size (nm)	Lattice parameter (nm)	d-spacing (nm)
CeO ₂	12.8	0.545	3.15
CeCr (4%)	9.9	0.543	3.13
CeCr (10%)	8.86	0.546	3.13

In FT-IR spectrum (Fig3) for the calcined materials, bands related to the template are removed which shows the successful removal of surfactant at a lower calcination temperature (350°C) which is effective for a high surface area for the calcined sample free of surfactant. No peaks corresponding to the C-H bands are seen in calcined sample.

Fig. 3 FT-IR spectrums



In (Fig.3) peaks at 3400 cm⁻¹ correspond to the OH stretching vibration, the peak at 1630 cm⁻¹ corresponds to the H₂O bending vibration, Peak at 1380 cm⁻¹ to Ce-OH stretching vibration, Peaks 1075 cm⁻¹ & 860 cm⁻¹, are attributed to the stretching and bending vibrations of M-O-M bonding 500 cm⁻¹ corresponds to the CeO₂ stretching vibration. (Fig 4) represents the SEM pictures of the samples. The HR-TEM and SAED of mesoporous ceria are given in (Fig.5). The TG curves of pure ceria (Fig.5a) show weight loss near 100°C which is due to the loss of physisorbed water as well as water held on surface of the catalyst. The second weight loss around 125-315°C could be due to the elimination of surfactant which is occluded in the mesopores through

oxidation process. No phase transition is observed indicating the stability of cerium oxide fluorite phase.

Fig.4 SEM Images

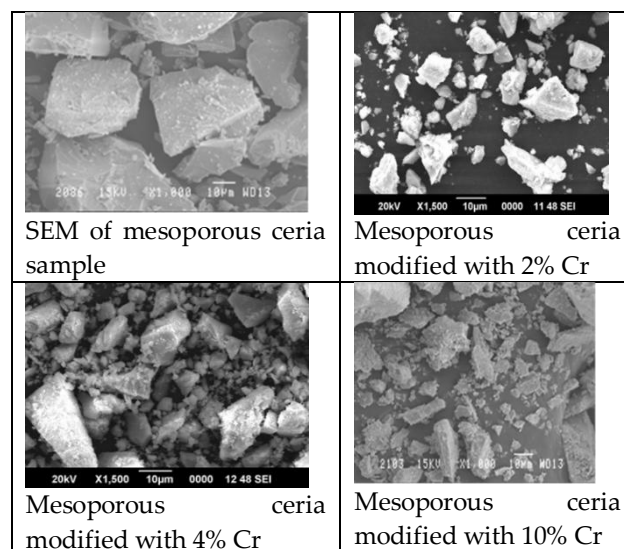


Fig5. TEM images of mesoporous ceria

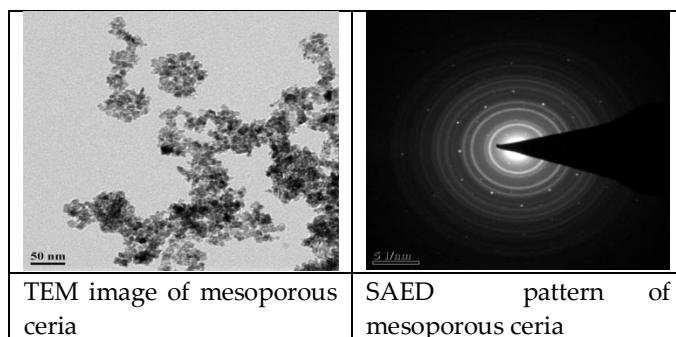
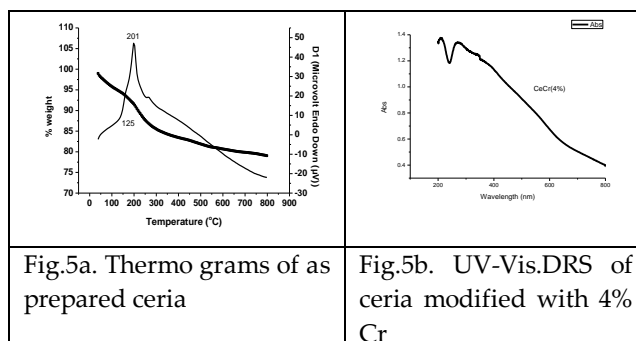


Fig.5a & b Tg/DTA curves and UV-Vis.DRS spectrum of samples



UV-Vis.DRS spectrum (Fig.5b) clearly shows that a single band arising from ceria species around 270 nm is found which shows that the Ce⁴⁺ species are in the tetra co-

coordinated environment. The acidities of the samples measured by TPD of ammonia indicate an increase in the total acidity with the Cr loading in the sample (Table 3).

Table 3. Acidity values obtained from TPD of ammonia, & vapour phase cumene cracking reaction

Sample	Acidity (mmol g ⁻¹) ^a				Lewis/ Bronsted acidity ^b	Cumene Conv. (%) ^c
	weak	Medium	strong	Total		
CeO ₂	0.1036	0.0207	0.0148	0.1391	1.380952	3.5
CeCr(2%)	0.1098	0.0498	0.0398	0.1994	1.48139	31.6
CeCr(4%)	0.1364	0.0226	0.0226	0.1816	1.380952	22.5
CeCr(10%)	0.3756	0.0214	0.0107	0.40774	2.04878	31.8

^aThe acidity values equivalent to desorbed ammonia. ^bThe ratio of Lewis to Bronsted acidity obtained from the cumene cracking test reaction for acidity; ^cIn vapour phase cumene cracking test reaction.

Vapour phase cumene cracking reaction is a model reaction for identifying the Lewis to Brønsted acid ratio of a catalyst. The major reactions taking place during the cracking of cumene are dealkylation to give benzene and propene over Bronsted acid sites (BAS) and dehydrogenation to give α -methyl styrene over Lewis acid sites (LAS). A comparison of the amount of dealkylated products and α -methyl styrene gives an idea about the (BAS) and (LAS) possessed by the catalyst [6].

3.2 Oxidation Reactions

Catalytic oxidation of ethylbenzene was carried out in acetonitrile solution (5.0 mL) with ca. 5 mg of catalyst, 1 mL of substrate, and 4 mL of TBHP. The reactions were performed at 70 °C in a two-neck roundbottom reactor fitted with a reflux condenser, and aliquots were taken at regular intervals and analysed by gas chromatograph Chemito GC1000. The reaction parameters like temperature, time, ratio of substrate to oxidant, weight of catalyst, solvent volume are optimised before the reaction was done using different catalysts. Under optimised condition, an 88.7% conversion of ethylbenzene was achieved (Table 4), with the major product being acetophenone (93% selectivity). The results show correlation between the % conversion, % selectivity of the major product and total acidity. The kinetic parameters (Table 5) and different plots are also shown (Fig. 6).

Table 4. Oxidation of ethyl benzene with TBHP using mesoporous ceria and ceria modified with Cr catalysed

sample	Conversion (%)	Major product ^a (% selectivity)	TON ^b	TOF (h ⁻¹) ^c
Ce	4.7	74.1	-	-
CeCr(2%)	26.2	78.6	7700	282
CeCr(4%)	63	80	13600	344
CeCr(10%)	88.7	93	11300	226

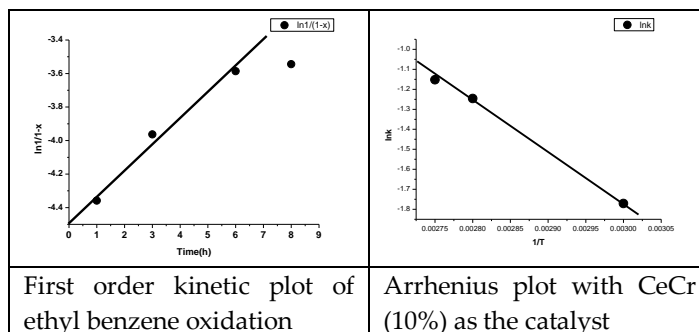
(70 °C, reaction time: 6 h, wt of catalyst: 0.05g, solvent: acetonitrile (5 mL))

^a- Acetophenone; ^b- turnover Number = (moles of ethyl benzene consumed / moles of metal loaded in the catalyst) $\times 100$; ^c- Turn over Frequency = moles of products / wt of the catalyst / time

Table 5. Kinetic parameters

Kinetic parameters	Values
Activation energy E_a	21.37 kJ/mol
Frequency factor A	15.3×10^8 (kg of catalyst) ⁻¹ h ⁻¹
Enthalpy of activation ΔH^\ddagger	18.52 kJ/mol
Entropy of activation ΔS^\ddagger	- 206.4 J/Mol /K

Fig. 6. Kinetic plots



The reaction is found to be pseudo first order with respect to the conversion of ethyl benzene.

4. Conclusion

Neutral surfactant route using HDA as surfactant is effective for the preparation of mesoporous ceria with high surface area and pore volume at a lower calcination temperature. Mesoporous ceria modified with Cr can be successfully utilized for the selective oxidation of ethyl benzene to more desirable product acetophenone with 93% selectivity in 6 hours using only 0.05g of the catalyst under milder condition. In addition to the redox properties of Ce & Cr the conversion is found to be correlated to the total acidity of the samples. The reaction is proved to be pseudo first order with respect to the conversion of ethyl benzene.

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5. References

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