Photocatalytic activity of Ce-modified SBA-15 for the degradation of isoproturon

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Abstract. Cerium (Ce)-modified SBA-15 and Al-grafted SBA-15 are prepared and compared their photocatalytic activity for isoproturon degradation. The Al-SBA-15 is prepared by postsynthetic grafting method and cerium-modified samples are prepared by the impregnation technique. All the samples are characterized by X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (UV-vis DRS), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and N₂ adsorption/desorption analysis. The samples show well-ordered mesoporous structure and it is confirmed by XRD. The UV-vis DRS of Ce-modified sample shows a red shift compared to SBA-15 and the cerium species are stabilized in +3 oxidation state at lower cerium contents. The presence of Ce³⁺ species is also substantiated by XPS analysis. The higher amount of Ce³⁺ species are accompanied by oxygen vacancies which are formed due to the contact of ceria with the support. The N₂ adsorption/desorption analysis of the samples show type-IV isotherms characteristic of mesoporous materials. Photocatalytic activity evaluation studies are made on all the samples for the degradation of isoproturon. Among them, 0.3 (wt%) Ce-modified Al-SBA-15 catalyst has shown a maximum activity in comparison with Ce-modified SBA-15. The better activity is attributed to the synergistic effect of mesoporosity and the presence of Ce³⁺ species along with oxygen vacancies.

Keywords. Cerium; SBA-15; photocatalytic degradation; isoproturon.

1. Introduction

Photocatalytic processes are found to be active in the treatment of wastewater for the destruction of several organic pollutants.^{1,2} Heterogeneous mediated photocatalysis has gained considerable interest for the treatment of wastewater. Generally, semiconductor oxides like TiO₂, ZnO, Bi₂O₃, etc. are employed as photocatalysts with and without supported material.^{3–11} Porous material such as ordered mesoporous silica is widely used as support in catalyst preparations due to their high thermal and chemical stability, as well as tunable pore-size and specific surface area. In this investigation, SBA-15 has been chosen as a support as it is used in many catalytic reactions owing to its high surface area and larger pore diameter. These support materials with various transition metals are used as heterogeneous catalysts for many organic transformations.^{12–14} In recent times, attention has been paid to the combination of the rare earth metals with the mesoporous materials in which the rare earth metals are used as the active catalyst component.^{15–17} Ceria is one of the most reactive rare earth metal oxide and it is having growing importance due to its chemical versatility in adjusting valence states (+3 and +4) resulting in the generation of oxygen vacancies. These properties of ceria

are crucial for the potential application including fast ion conductors, oxygen storage capacitors, catalysts, UV blockers, polishing materials and electrolytes for solid oxide fuel cells. CeO₂ or CeO₂-based materials have also been found to be very important under environmental protection materials family. In particular, supported CeO₂ and CeO₂-based mixed oxides are effective catalysts for the oxidation of different hydrocarbons and for the removal of organics from polluted water.^{7,8,18} Existence of different sites of cerium ions and capability of one-electron oxidations, oxygen storage/release properties made the cerium containing materials important for many catalytic reactions like oxidation of CO¹⁹ water-gas shift reaction²⁰ elimination of CO and NO_x contaminants from automotive exhaust gases and combustion reaction of hydrocarbons.²¹ In this study, Ce-SBA-15 and Ce-Al-SBA-15 are prepared and their performance towards photocatalytic degradation of isoproturon in aqueous solution is evaluated.

2. Experimental

2.1 Chemicals and materials

Isoproturon (analytical standard), Pluronic P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)), cetyltrimethyl ammonium bromide (CTMABr), tetraethyl orthosilicate (TEOS) and aluminum isopropoxide

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$\text{Al}(\text{OC}_3\text{H}_7)_3$ were obtained from Sigma-Aldrich (India). Ammonium cerium (IV) nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was purchased from Merck (India). HCl, ethanol, 1-propanol and KBr were procured from Rankem (India).

2.2 Preparation of Al-SBA-15

SBA-15 was prepared by procedure adopted by Zhao *et al*²² using tri-block copolymer (Pluronic P123) template. Aluminum was introduced into the SBA-15 *via* post-synthetic alumination using a grafting procedure to obtain Al-SBA-15. The procedure adopted for the grafting method has been reported elsewhere.²³ Aluminum isopropoxide (70 wt% solution in 1-propanol) was used as the aluminum source, and absolute ethanol was used as the solvent. SBA-15 was made slurry in ethanol containing aluminum isopropoxide for 8 h at room temperature. The filtered material was then washed with ethanol and the solid was dried in air at room temperature and calcined at 823 K for 5 h. The amount of aluminum was added such that the atomic ratio of Si to Al would be 40 and this material now referred as Al-SBA-15.

2.3 Preparation of Ce-SBA-15 and Ce-Al-SBA-15

Ce-modified SBA-15 sample was prepared by the impregnation method. Required amount of ammonium cerium (IV) nitrate was dissolved in deionized water and added 0.5 g SBA-15. The mixture was kept under stirring with constant slow heating till the excess water was evaporated. The samples were oven dried at 373 K overnight and calcined at 723 K for 5 h with a temperature ramping of 2 K min⁻¹. Cerium (wt%) content over SBA-15 was maintained to get 0.1, 0.3, 0.6, 1.0 loaded samples. The same procedure was followed for the preparation of Ce-Al-SBA-15 samples using 0.1, 0.3, 0.6, 1.0 cerium (wt%) over Al-SBA-15 support material.

2.4 Catalyst characterization

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a KRATOS AXIS 165 equipped with MgK α radiation (1253.6 eV) at 75 W apparatus using MgK α anode and a hemispherical analyzer, connected to a five-channel detector. The analysis was performed at room temperature. Prior to the analysis, the samples were evacuated at high vacuum and then introduced into the analysis chamber. The C 1s line was used as an internal standard for the normalization of binding energies.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using CuK α radiation (0.1540 nm), operated at 40 kV and 40 mA.

Surface properties of the catalysts were measured by N₂ adsorption in Autosorb 1C Quantachrome physical adsorption apparatus. The specific surface area and pore volume of

the samples were calculated by applying Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

UV–vis DRS measurements were performed over the wavelength range 200–800 nm using a GBC UV-Visible Cintra 10e spectrometer with an integration sphere diffuse reflectance attachment. Barium sulfate was used as standard for recording the spectra.

Fourier transform infrared (FTIR) spectra of the catalysts were recorded on a Nicolet 740 FTIR spectrometer (USA) using KBr self-supported pellet technique in the frequency range of 400–4000 cm⁻¹.

For scanning electron microscopy (SEM) analysis, samples were mounted on an aluminum support using a double adhesive tape, coated with gold in HUS-SGB vacuum coating unit and observed in Hitachi S-520 SEM unit.

2.5 Photocatalytic experiments

Isoproturon solution (1.14×10^{-4} M) was always freshly prepared by dissolving the required herbicide in deionized water. Prior to light experiments, dark (adsorption) experiments are carried out for monitoring the adsorption extent of the herbicide on the catalyst. For photoexperiments, 50 ml isoproturon solution was taken in a quartz reactor along with 50 mg of the added catalyst (1 g l⁻¹). The solution was illuminated under 250 W Mercury lamp.

2.6 Analysis

The isoproturon degradation was monitored by Shimadzu SPD-20A HPLC using C-18 phenomenex reverse phase column (250 $\times$ 4.6 mm²–5 μ m) with acetonitrile/water (50/50 v/v%) as the mobile phase at a flow rate of 1 ml min⁻¹. The wavelength of the LC detector was set at 254 nm for the detection of isoproturon. The samples collected at regular intervals are filtered through millipore microsyringe filters (0.2 μ m).

3. Results and discussion

3.1 Characterization

3.1a XRD: The high-angle XRD patterns of SBA-15 and Al-SBA-15 samples are shown in figure 1A. The wide-angle patterns show a broad diffraction peak at $2\theta = 23^\circ$, which is of amorphous silica. It is seen that there are no diffraction lines due to crystalline Al₂O₃ reflections in Al-SBA-15 sample. The low-angle XRD patterns of SBA-15 and Al-SBA-15 are shown in figure 1B. Low-angle well-resolved diffraction peaks that can be indexed as (100), (110) and (200) reflections are indicating the mesoporosity of the prepared materials. The diffraction peaks are related to long-range 2D hexagonal ordering in the *P6mm* space group. Furthermore, the appearance of the same peaks in

Figure 1. (A) High-angle XRD of (a) SBA-15 and (b) Al-SBA-15. (B) Low-angle XRD of (a) SBA-15, (b) 0.3 (wt%) Ce-SBA-15, (c) Al-SBA-15 and (d) 0.3 (wt%) Ce-Al-SBA-15.

the cerium-modified SBA-15 and Al-SBA-15 catalysts suggest that the hexagonal array of parent samples are retained after incorporation of the cerium metal. However, the diffraction intensity of (110) and (200) planes decreased with cerium loading. This can be illustrated to a slight decrease of the mesoporosity due to the pore-filling effect of CeO_2 particles.

3.1b N_2 adsorption/desorption analysis: In order to find out the effect of cerium modification on the surface area and porosity of the SBA-15 samples, N_2 adsorption studies are employed for the bare SBA-15, Al-SBA-15 as well as Ce-modified samples. The N_2 adsorption/desorption isotherms of the samples shown in figure 2 are of type IV with a H1 type hysteresis loop. Three different regions can be seen on these isotherm plots: (i) a linear region due to monolayer-multilayer adsorption in mesopores; (ii) a steep region due to capillary condensation within these mesopores; (iii) a second linear region due to multilayer formation on the external surface of the grains. SBA-15, Al-SBA-15 and the corresponding Ce-modified samples show a hysteresis loop. For the Ce-modified samples, the shape of the hysteresis closely resembles that of the parent SBA-15 sample. The pore volume, pore size and surface area of the samples are provided in table 1. A small decrease in the surface area for the cerium-modified samples may be due to the formation of CeO_2 nanocrystals within the mesopores of SBA-15.

3.1c SEM–energy-dispersive X-ray analysis (EDAX): The surface morphology of 0.3 wt% Ce containing SBA-15 and Al-SBA-15 samples are studied by SEM and the corresponding micrographs are presented in figure 3. EDAX data of 0.3 and 1.0 wt% Ce–Al-SBA-15 are provided in table 2. Both the samples have Si/Al ratios higher than the actual

Figure 2. N_2 adsorption/desorption isotherms of (a) SBA-15, (b) Al-SBA-15, (c) 0.3 (wt%) Ce-SBA-15 and (d) 0.3 (wt%) Ce-Al-SBA-15.

Table 1. Physicochemical properties of SBA-15, Al-SBA-15 and their cerium-modified materials.

Sl. no.	Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore diameter (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
1	SBA-15	715.32	6.13	0.98
2	Al-SBA-15	692.58	6.05	0.92
3	0.3 wt% Ce-SBA-15	680.41	5.95	0.86
4	0.3 wt% Ce-Al-SBA-15	663.70	5.85	0.82

Figure 3. SEM images of (a) 0.3 (wt%) Ce-SBA-15 and (b) 0.3 (wt%) Ce-Al-SBA-15.

Table 2. Elemental analysis of Ce-Al-SBA-15.

Element	Atomic % by EDAX	
	0.3 wt% Ce-Al-SBA-15	1.0 wt% Ce-Al-SBA-15
Si	30.10	29.11
Al	0.28	0.21
Ce	0.10	0.17

amount ($\text{Si}/\text{Al} = 40$). The increase in Si/Al ratio suggests that the aluminum present on the surface of the material is less than the actual amount of added aluminum. These results describe that small amount of Al is either entered into the framework of silica or exists in the mesopores of SBA-15.

3.1d UV-vis diffuse reflectance spectroscopy (UV-vis DRS): UV-vis DRS measurements evidences the charge transfer processes and electronic states of the species. The DRS of cerium-modified SBA-15 and Al-SBA-15 catalysts are provided in figure 4. The cerium-modified samples exhibit three characteristic bands at 250, 300, and 350 nm corresponding to O^{2-} to Ce^{3+} , O^{2-} to Ce^{4+} charge transfer and interband transitions, respectively.²⁴ The former band is observed because of the oxygen defects formed in ceria due to the interaction of ceria with the support SBA-15 or Al-SBA-15. The 0.1 and 0.3 wt% Ce-modified samples show more intensity of the former band than the later one. However, with the increase in cerium content the intensity of O^{2-} to Ce^{3+} charge transfer band is suppressed and O^{2-} to Ce^{4+} charge transfer band is increased and the band is shifted towards the bulk ceria. Although, the same pattern is observed for both Ce-SBA-15 and Ce-Al-SBA-15 samples the presence of more number of Ce^{3+} species are observed for Ce-Al-SBA-15 samples compared to Ce-SBA-15 sample. This observation is further confirmed in the XPS data provided.

3.1e FTIR: FTIR spectra of the samples are provided in figure 5. The bands at 1085 and 802 cm^{-1} are assigned to

asymmetrical and symmetrical stretching vibrations of Si-O-Si and tetrahedron Si-O groups, respectively. The band at 965 cm^{-1} is caused by the Si-O stretching vibrations of Si-OH group present in the framework of SBA-15. In general, the IR weak characteristic band at 971 cm^{-1} for V_{as} (Si-O-Ce) overlapped with band at 965 cm^{-1} for Si-OH group. Hence, it is difficult to distinguish the effect of cerium loading on the structure of SBA-15. However, the increase in the intensity of peaks at 802 and 970 cm^{-1} with cerium amount suggests that cerium atoms are in interaction with the support SBA-15. To confirm this, we study the influence of cerium content on the nature of OH-groups in Ce-SBA samples at 3000–3800 cm^{-1} range (the O-H stretching region). Three types of bands at 3240, 3450 and 3620 cm^{-1} are observed in IR spectra of all the samples. The band at 3620 cm^{-1} is attributed to the stretching vibration of isolated silanol groups and the band 3450 cm^{-1} is likely ascribed to the isolated silanol groups that slightly interact with the walls of SBA-15. The band 3240 cm^{-1} is attributed to the stretching vibration of hydrogen bonded Si-OH and Ce-OH groups. The increase in intensity of these bands with cerium loading confirms that more number of OH groups available on the surface of catalysts which are responsible for the photocatalytic oxidation reaction.^{25,26}

3.1f XPS: XPS has been utilized to obtain information about the chemical composition of the surface of the material. The core level spectra of the cerium-modified samples are shown in figure 6A and B corresponding to Ce 3d and O 1s, respectively. The Ce 3d spectrum is composed of five spin-orbit doublets due to two multiplets, 3/2 (u) and 5/2 (v). Here, v/u , v''/u'' , and v'''/u''' are attributed to Ce^{4+} : v/u and v''/u'' are due to a mixture of $(5d\ 6s)^0\ 4f^2\ \text{O}\ 2p^4$ and $(5d\ 6s)^0\ 4f^1\ \text{O}\ 2p^5$ configurations, and v'''/u''' is due to the $(5d\ 6s)^0\ 4f^0\ \text{O}\ 2p^6$ final state. While, v_0/u_0 and v'/u' are due to $(5d\ 6s)^0\ 4f^2\ \text{O}\ 2p^5$ and $(5d\ 6s)^0\ 4f^1\ \text{O}\ 2p^6$ corresponding to Ce^{3+} . A significant increase in the u_0/v_0 and u'/v' with simultaneous decrease in the u/v , u''/v'' and u'''/v''' peak intensities

Figure 4. (A) UV-vis DRS of (a) SBA-15 and cerium, (b) 0.1, (c) 0.3, (d) 0.6 and (e) 1.0 (wt%) modified SBA-15. (B) (a) Al-SBA-15 and cerium, (b) 0.1, (c) 0.3, (d) 0.6 and (e) 1.0 (wt%) modified Al-SBA-15.

Figure 5. FTIR spectra of (a) SBA-15, (b) 0.3 (wt%) Ce-SBA-15, (c) 1.0 (wt%) Ce-SBA-15, (d) Al-SBA-15, (e) 0.3 (wt%) Ce-Al-SBA-15 and (f) 1.0 (wt%) Ce-Al-SBA-15.

is observed for 0.3 wt% Ce-SBA-15 compared to 1.0 wt% cerium supported SBA-15. Therefore, an increase in Ce^{3+} amount can be noted for 0.3 wt% cerium supported SBA-15 sample. Interestingly, for 0.3 wt% Ce-Al-SBA-15 only peaks corresponding to Ce^{3+} are observed and no characteristic peaks of Ce^{4+} are noted. This might be due to the fact that at lower loadings, cerium interacted with the support mainly present as Ce^{3+} . This illustrates the perturbation of the electronic structure of the Ce ion brought out by a change

Figure 6. (A) Ce 3d XPS of (a) 0.3 (wt%) Ce-Al-SBA-15, (b) 0.3 (wt%) Ce-SBA-15 and (c) 1.0 (wt%) Ce-SBA-15, CeO_2 (inset). (B) O 1s XPS of (a) 0.3 (wt%) Ce-Al-SBA-15, (b) 0.3 (wt%) Ce-SBA-15 and (c) 1.0 (wt%) Ce-SBA-15.

in the coordination of the Ce and oxygen ligands when ceria is in contact with the support.

The O 1s XP spectrum of the samples is shown in figure 6B. The O 1s core level peak is mainly composed of two characteristic peaks. The first peak at a lower binding energy of 533.0 ± 0.6 eV is attributed to lattice oxygen of silica. Appearance of the peak at higher binding energy at 534.5 ± 0.3 eV corresponds to mixed contribution from oxygen defects and surface hydroxyl groups at the surface. The hydroxyl groups are also confirmed from the FTIR study. Existence, of more number of oxygen vacancies on the surface permits more amounts of chemisorbed OH groups on the surface which are very crucial in the photocatalytic oxidation of pollutant molecules on the surface of the catalyst.^{24,27}

3.2 Photocatalytic activity studies

The photocatalytic activities of Ce-modified SBA-15 and Al-SBA-15 catalysts are shown in figures 7 and 8, respectively. The catalyst containing 0.3 wt% cerium showed good photocatalytic activity. The photocatalytic activity of Ce-modified SBA-15 sample with increase of cerium loading found to have a decrease in activity (figure 7). A sharp decrease in the photocatalytic activity of 1.0 wt% cerium Al-SBA-15 may be due to the formation of agglomerated cerium crystallites that behaves as bulk ceria. This is substantiated by the XPS of 1.0 wt% Ce-Al-SBA-15 that shows spectra similar to bulk ceria (inset figure 6A). The 0.3 wt% Ce-SBA-15 sample contains most of the cerium species in +3 oxidation state. This might be the reason for high photocatalytic activity of cerium-modified samples at lower loadings. The same was observed in the case of cerium-modified Al-SBA-15 sample (figure 8).

The comparison of photocatalytic activities of SBA-15, Ce-modified support and CeO₂ are shown in figure 9. Among

all the catalysts, 0.3 wt% Ce-Al-SBA-15 has shown better activity. The enhanced photocatalytic activity of Ce-Al-SBA-15 is due to highly dispersed and interacted nano-sized ceria particles on the support. Also they show oxygen vacancies and establish a strong interaction with the support wherein, cerium is in Ce³⁺ form. Dispersion of ceria over alumina containing SBA-15 would permit in improving the redox performance of ceria. Due to dispersion, the close contact between the ceria and the alumina may facilitate the formation of cerium aluminum composite. This formation is generally expected to affect the Ce³⁺ and Ce⁴⁺ species composition as it fixes a single oxidation state, i.e., Ce³⁺. However, in high cerium loaded samples the features

Figure 8. Photocatalytic activity of cerium (♦) 0.1, (●) 0.3, (▲) 0.6, (■) 1.0 (wt%) loaded Al-SBA-15 for the degradation isoproturon.

Figure 7. Photocatalytic activity of cerium (♦) 0.1, (●) 0.3, (▲) 0.6, (■) 1.0 (wt%) loaded SBA-15 for the degradation isoproturon.

Figure 9. Photocatalytic activity comparison of (▲) SBA-15, (●) 0.3 (wt%) Ce-SBA-15, (■) 0.3 (wt%) Ce-Al-SBA-15 and (♦) CeO₂ for the degradation of isoproturon.

Scheme 1. Photocatalytic degradation pathway for isoproturon.

Figure 10. Recycling activity studies of 0.3 (wt%) Ce-Al-SBA-15 catalyst for the degradation of isoproturon: (■) Fresh, (●) 1st cycle and (▲) 2nd cycle.

of bulk ceria is visualized in which cerium is in +3 and +4 oxidation states which are evidenced by XPS and UV-vis DRS techniques. This might be the reason for low activity at higher loadings of ceria. Ce^{3+} on irradiation becomes Ce^{4+} with a release of electron and this electron combines with oxygen forming a per-oxide that oxidizes the organic pollutant (scheme 1). From these, it is clearly understood that aluminum is playing a vital role in stabilizing the cerium species in +3 oxidation state resulting good photocatalytic activity. As 0.3 wt% Ce-Al-SBA-15 is showing better photoactivity, it is further tested for sustainability of phenol photo-degradation and the results obtained indicate that the catalyst can be reused without losing the photocatalytic activity (figure 10).

4. Conclusions

The present study described the preparation of Ce-modified SBA-15 photocatalyst and their photocatalytic activity for the degradation of isoproturon. The results illustrated that 0.3 wt% Ce-Al-SBA-15 was efficient catalyst for the photocatalytic degradation of isoproturon. The higher activity of 0.3 wt% Ce-Al-SBA-15 compared to bare CeO_2 -modified SBA-15 and this may be due to the presence of aluminum in Al-SBA-15 that stabilizes cerium in +3 oxidation states. From this study it is found that Ce at lower loadings over Al-SBA-15 exists in +3 oxidation state rather than +4. The $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox chemistry results in the degradation of isoproturon.

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