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Ce Dispersed Al-MCM-41: A Photocombinate for Phenol Degradation Activity

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Abstract Al-MCM-41 supported ceria samples of various cerium content (0.2, 0.3, 0.5, 0.8 and 3.0 wt.%) were prepared by impregnation and are characterized by BET, XRD, UV–VIS DRS, XPS and ESR techniques. At lower cerium contents the DRS clearly shows a blue shift of 50 nm in the absorbtion edge of CeO_2 indicating the size quantization and high dispersion of cerium particles. The XPS analyses of Ce–Al-MCM-41 samples revealed the interaction of cerium with Al-MCM-41 in Ce^{3+} state and at higher loadings in $Ce^{3+/4+}$ states. ESR studies also further substantiated this observation. These catalysts when subjected to photo degradation activity of phenol, 0.3 wt.% Ce–Al-MCM-41 is showing maximum degradation among all the catalysts tested. The present study highlights that cerium at lower loadings is in +3 oxidation state and is dispersed highly showing good photocatalytic activity in comparison with pure ceria.

Keywords Ce-Al-MCM-41 · Ce (III) dispersed · Photocatalytic activity · Phenol degradation

1 Introduction

Organic compounds are widely used in industry and daily life and they are common pollutants in water bodies. As they are known to be noxious and carcinogenic, an effective and economic treatment for eliminating these from water is in high demand. Photocatalytic processes are found to be active in the treatment of wastewater for the destruction of several organic pollutants [1–3]. Generally heterogeneous mediated photocatalysis has gained considerable interest for the treatment of wastewater. Many semiconductor oxides like TiO_2, Fe_2O_3, ZnO, CdSe, ZrO_2, Nb_2O_5, WO_3, SnO_2, etc. have been employed as photocatalysts [4–6]. Zeolite based photocatalysts are also studied for the effective photocatalytic degradations [7, 8]. The most abundant rare earth oxide like ceria also is used for wet catalytic oxidation of organic pollutants and for the removal of total organic carbon from the wastewater [9–11]. Coronado et al. have reported that CeO_2 with a wide band gap of 2.9 eV can be photoexcited by absorbing the energy higher than that of band gap energy and it can be used as photocatalyst [2]. Cerium oxide has been employed as a photocatalyst in some of the reactions like water splitting, toluene oxidation and waste water treatment [12–15]. Yuliati et al. reported that cerium oxide in Ce^{4+} state is not able to show the photocatalytic activity and silica based ceria catalysts showed photocatalytic activity [16]. In rare earth ions (Ce^{3+}, Pr^{+3} etc.) photoexcitation is generally caused due to f–d orbital transitions [16]. In the present investigation an attempt has been made to study the photoactivity of highly dispersed cerium on a mesoporous Al-MCM-41 support wherein Ce shows variable oxidation states on photoexcitation. Our earlier studies also reported the photoactivity of Fe (III) immobilized on HY wherein Fe (III) on photoexcitation changes to Fe (II) [17]. The present paper describes the preparation, characterization of dispersed cerium on Al-MCM-41 support and its effective participation in the photodegradation activity by varying its oxidation states.

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2 Experimental

2.1 Chemicals and Materials

Phenol (purity grade (98%) was obtained from S.D. Fine chemicals (India). Tetra ethyl ortho silicate (TEOS), Cetyl trimethyl ammonium bromide (CTAB), Tetra ethyl ammonium hydroxide (TEAOH) and Aluminium isopropoxide were procured from Aldrich. Cerium (III) nitrate was obtained from Loba Chemie (India) and sodium hydroxide was from S.D. Fine chemicals.

2.2 Preparation of Al-MCM-41

Al-MCM-41 molecular sieve was prepared with Si/Al ratio (15.5) in the laboratory as per the procedure reported in the literature [18]. An aqueous solution of aluminum isopropoxide (0.76 g) and sodium hydroxide were taken in a beaker containing water and stirred while heating till a clear solution is obtained. An amount of 9.3 g of TEAOH was added to the solution while cooling under stirring (solution A). Simultaneously, 25 g of tetraethyl ortho silicate was taken in another beaker in 50 mL water (solution B) and then solution A was slowly added to solution B with stirring. After stirring for 2 h, CTAB 10.55 g was added slowly to the above mixture. Finally the gel mixture arrives the molar composition as $1SiO_2$:$0.312Al_2O_3$:0.23CTAB: 0.3TEAOH:$0.26Na_2O$:$125H_2O$ (Si/Al=15.5) is transferred to an autoclave and heated at 100 °C for 24 h. The recovered product was calcined at 500 °C in air for 12 h to expel the imprisoned template.

2.3 Preparation of Ce–Al-MCM-41

Ce doped Al-MCM-41 photocatalyts are prepared by impregnating cerium salt followed by calcination at 450 °C for 5 h. Ce doping over Al-MCM-41 was maintained to obtain 0.2, 0.3, 0.5, 0.8, and 3 wt.% in the finished catalyst.

2.4 Catalyst Characterization

Powder XRD patterns were recorded with a Siemens D-5000 X-ray diffractometer using Cu Kα radiation. UV–VIS DR spectra were recorded on Cintra 10e spectrophotometer using pellets of 50 mg sample ground with 2.5 g of KBr. XPS were recorded on a KRATOS AXIS 165 photoelectron spectroscopy using the Mg Kα radiation (150 W) anode, taking C 1s level as internal standard. The specific surface area of the samples was determined using Micromeritics Pulse Chemisorb 2700 instrument. ESR spectra of the calcined samples were recorded on a Bruker EMX-X with band frequency of 9.1546 GHz at 20 °C and the spectra were calibrated with ER 035M NMR Gauss meter.

2.5 Photocatalytic Experiments

In a typical experiment a phenol solution of 40 mL (10^{-4} M) was taken in a quartz reactor and 120 mg of catalyst (3 gL^{-1}) was added. An UV source of 250 W mercury vapor lamp of wave lengths greater than 254 nm is used for irradiation. Prior to start of light experiment dark adsorption experiments were carried out for 1 h under continuous stirring. Samples were analyzed by HPLC at regular intervals.

2.6 Analyses

The concentration of phenol was determined by HPLC with C-18 Phenomenex (5 μm), 250 × 4 mm column using1:1 ratio of methanol/water mobile phase at λ_{max} 220 nm.

3 Results and Discussion

3.1 BET Surface Area

The surface area, 902 $m^2\ g^{-1}$ of Al-MCM-41 is decreased on impregnation of cerium ion as seen from Table 1 and it is due to the increased number of particles with loading.

3.2 XRD

The XRD patterns of Al-MCM-41 and Ce modified Al-MCM-41 are shown in Fig. 1. The Al-MCM-41 show a strong peak in the 2θ range 1.5–2.6 due to 100 reflection line and small peaks due to higher order 110, 200 and 210

Table 1 Physical characterization of Ce loaded Al-MCM-41 catalysts

S.No.	Ce wt.% Al-MCM-41 catalysts	Surface area (m^2g^{-1})
1.	0.0	902.0
2.	0.2	883.0
3.	0.3	872.5
4.	0.5	860.7
5.	0.8	800.2
6.	3.0	750.0

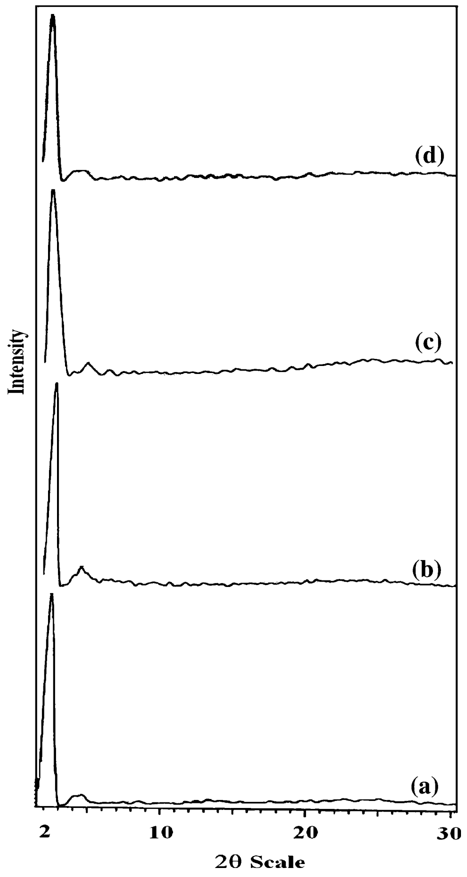


Fig. 1 XRD patterns of (**a**) Al-MCM-41 and Ce wt.% loaded: (**b**) 0.3 (**c**) 0.8, and (**d**) 3.0

reflections (2θ (5) indicating the well ordered mesoporosity of the material [19]. Further the peak appearance in the Ce modified Al-MCM-41 catalysts suggests that the hexagonal array of Al-MCM-41 is retained after incorporation of the metal. However, the intensity of 100 peak is decreased with increasing Ce content and this indicates the slight reduction of hexagonal symmetry of Al-MCM-41 in view of the metal ion incorporation [20]. No characteristic peak of crystalline CeO_2 phase is observed (2θ (25) even at 3 wt.% loading of cerium indicates that metal ions were either dispersed in the mesopore or interacted with the walls of the Al-MCM-41.

3.3 UV–VIS DRS

The DRS of ceria and cerium doped Al-MCM-41 catalysts are shown in Fig. 2. The ceria shows an absorption band edge around 420 nm and a band at 370 nm that may be due to the charge transfer from O (valence band) to Ce (conduction band) [16]. The Al-MCM-41 shows an absorption band below 210 nm due to the presence of Al in tetrahedral coordination [21]. Ce doped Al-MCM-41 develops a band around 300 nm and further increase in cerium loading this band is shifted towards of pure ceria. Earlier reports on dispersion of ceria at lower loadings confirmed the presence of bands (290–300 nm) due to 4f–5d transition of the Ce^{3+} ion [22].

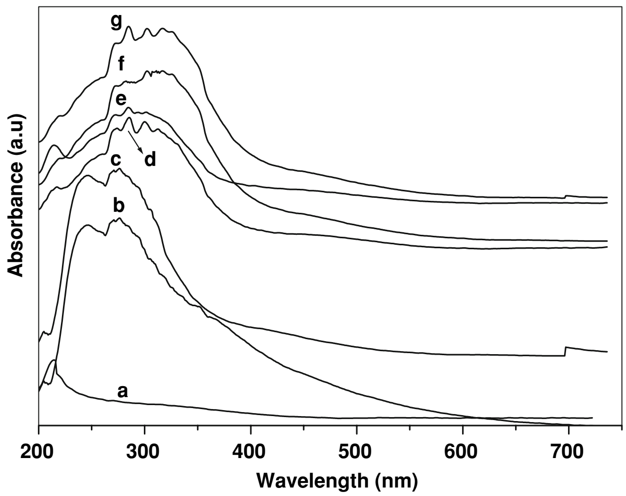


Fig. 2 UV–VIS DRS of (**a**) Al-MCM-41 and Ce (wt.%) loaded Al-MCM-41 catalysts: (**b**) 0.2, (**c**) 0.3, (**d**) 0.5, (**e**) 0.8, (**f**) 3.0 and (**g**) Bare CeO_2

3.4 XPS

XPS of Ce loaded Al-MCM-41 catalysts are shown in Fig. 3. The peaks between 880–895 eV correspond to Ce $3d_{5/2}$ and 895–910 eV correspond to Ce $3d_{3/2}$ and peak at 916 eV is a characteristic one that indicate the presence of Ce^{4+} [23]. Generally eight distinct peaks can be seen in the spectra of ceria that are raised from the +3 and +4 oxidation states of cerium. The peaks that can differentiate clearly Ce^{3+} and Ce^{4+} [24] are seen in the Fig. 3. In the samples at low loadings of Ce (0.2–0.5 wt.%), high intense peaks at 885.9 and 904.2 eV are observed and they are attributed to Ce^{3+}. No characteristic peaks of Ce^{4+} are observed for low loading samples indicating that Ce exists in +3 oxidation sate only. At higher loadings (0.8, 3.0 wt.%) of Ce and for pure ceria high intense peaks at 882.2, 898.4 eV are observed which are attributed to Ce^{4+}. The presence of Ce^{4+} in high Ce containing sample also is supported by characteristic peak of Ce^{4+} that observed at 916 eV. From the observed XPS results it is understood that when ceria is loaded in small amounts on Al-MCM-41, the particles show oxygen vacancies which are highly dispersed and interacted with the support wherein most of the cerium is present in +3 oxidation state.

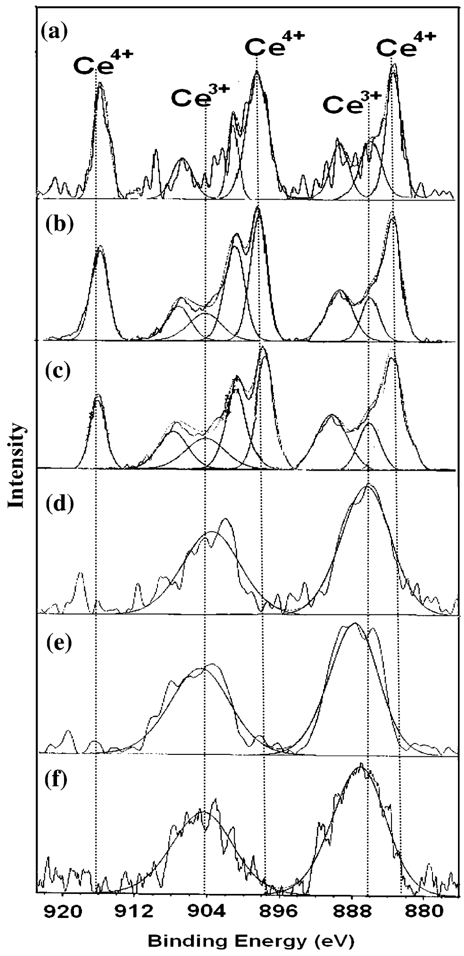


Fig. 3 XPS of (**a**) Ceria and Ce wt.% loaded Al-MCM-41 catalysts (**b**) 3.0, (**c**) 0.8, (**d**) 0.5, (**e**) 0.3 and (**f**) 0.2

3.5 ESR

ESR analyses was performed at room temperature to obtain the oxidation state of cerium ion for 0.3 wt.% Ce–Al-MCM-41 and also higher cerium containing (0.8 and 3.0 wt.%) samples calcined at 450 °C. It is observed that paramagnetic signals are clearly obtained in 0.3 wt.% Ce–Al-MCM-41 at $g_{\perp} = 1.967$ and $g_{\parallel} = 1.948$ (Fig. 4). Earlier ESR studies on ceria supported systems reported such signals are observed due to the presence of coordinately unsaturated cerium ions in contact with oxygen vacancies $[Ce^{3+} - V_o]$ formed on high temperature calcinations [25, 26]. Such paramagnetic signals are not seen with increasing cerium loading on Al-MCM-41 indicating that the chemical environment of cerium at low loadings is different from that of cerium at higher loadings. Thus the formation of Ce^{3+} species at lower cerium loading is in agreement with the earlier report [16].

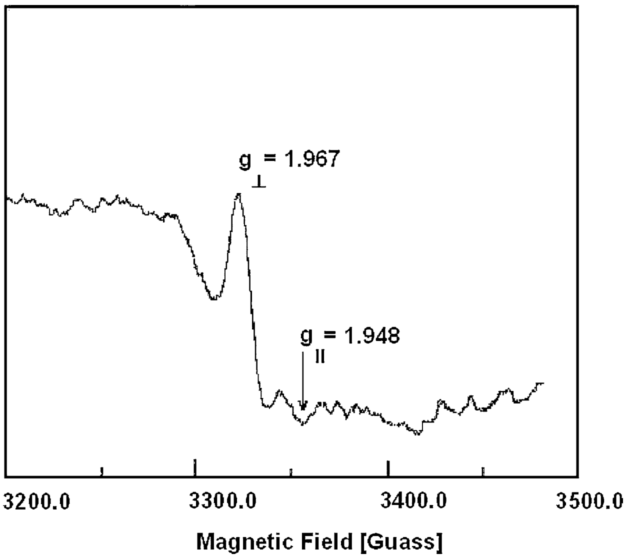


Fig. 4 ESR spectra of 0.3 wt.% Ce–Al-MCM-41 calcined at 450 °C

3.6 Photocatalytic Activity

The effect of cerium loading (wt.%) on Al-MCM-41 for the photocatalytic degradation of phenol is shown in Fig. 5. The catalyst containing 0.3 wt.% cerium is showing good photo catalytic activity. This is observed within 4 h of irradiation as seen from HPLC chomatograms in Fig. 6. However, the total organic carbon left over in the fourth hour sample of the active catalyst is 19%. Also it is noted that Ce based catalysts photocatalytic activity is slightly low in comparison with P-25 Degussa titania as shown in Fig. 7. The Al-MCM-41 support absorbs about 20% phenol in dark and on illumination undergoing photolysis of 7%.

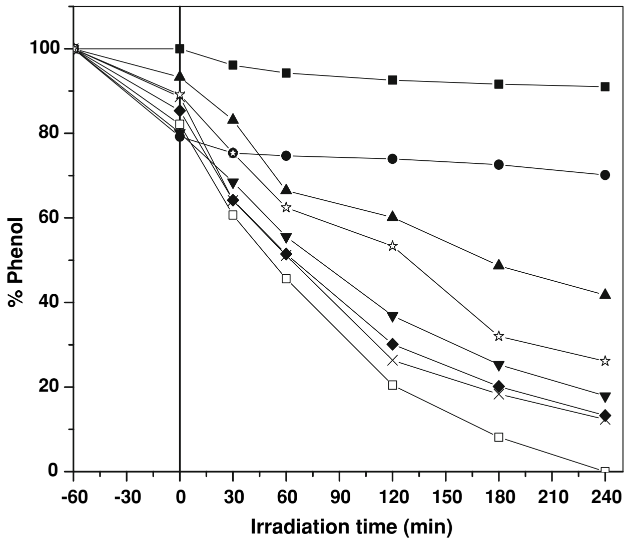


Fig. 5 Degradation of phenol (10^{-4} M) over Ce (wt.%) loaded Al-MCM-41 catalysts: (•) Al-MCM-41, (▼) 0.2, (□) 0.3, (×) 0.5, (♦) 0.8, (✯) 3.0, (▲) Bare CeO_2 and (■) Photolysis

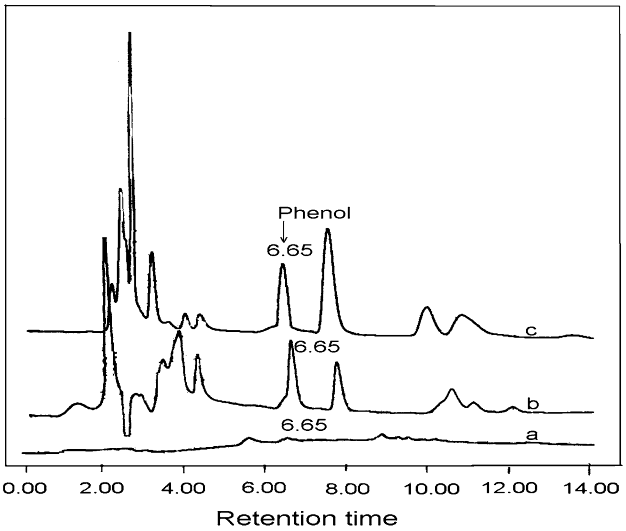


Fig. 6 HPLC-Chromatogram of the phenol degradation over Ce wt.% Loaded Al-MCM-41 catalysts after 4 h: (**a**) 0.3, (**b**) 0.8 and (**c**) 3.0

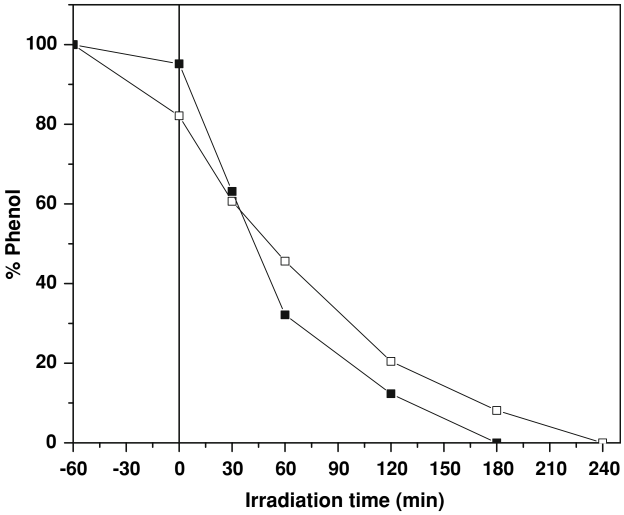


Fig. 7 Degradation of phenol (10^{-4} M) over (□) 0.3 wt.% Ce–Al-MCM-41 and (■) Titania P-25

Dark experiments were carried out on all the Ce based catalysts prior to the light experiments. The difference in the adsorption of phenol with increasing amount of cerium on Al-MCM-41 is nominal and with increase in cerium loading degradation activity is relatively slow as can be seen from (Fig. 5). Only 50% phenol photodegradation is observed on pure CeO_2 and is less in comparison to Ce–Al-MCM-41 catalysts. The enhanced photocatalytic activity of Ce–Al-MCM-41 combinate may seem due to (1) adsorption properties of Al-MCM-41 that pool the phenol molecules in vicinity of the photocatalyst resulting synergistic activity, (2) CeO_2 particles in highly dispersed and interacted are nano-sized with an increased band gap that decreases the rate of electron-hole recombination. This may be facilitating charge transfer from the surface of the catalyst to the substrate molecule and (3) Ceria in lower amounts on the support may be dispersed highly and form nanosized particles. Thus the nanosized ceria show oxygen vacancies [23] and establishes a strong interaction with the support wherein Ce is in Ce^{3+} form [27]. In high Ce loaded samples particles are aggregated showing the features of bulk ceria in which Ce is in both +3 and +4 oxidation states which are evidenced by XPS, ESR and UV–VIS DRS techniques. Ce^{3+} on irradiation becomes Ce^{4+} with a release of electron and this electron combines with oxygen and forms peroxide that oxidizes the organic pollutant molecules. From the above observations, it is clearly understood that cerium at lower loadings is highly dispersed and +3 oxidation state with increased band gap energy is showing good photo-catalytic activity by 4f–5d transitions compared to pure ceria electron-hole recombination may be more. As 0.3 wt.% Ce-Al-MCM-41 is showing better photoactivity, it is further tested for sustainability in photo-degradation of phenol and the results obtained indicate that the catalyst can be reused without losing the photoactivity as shown in Fig. 8. In view of the above observations a plausible mechanism in operation over the Ce–Al-MCM-41 photocatalyst is proposed as shown in Scheme 1.

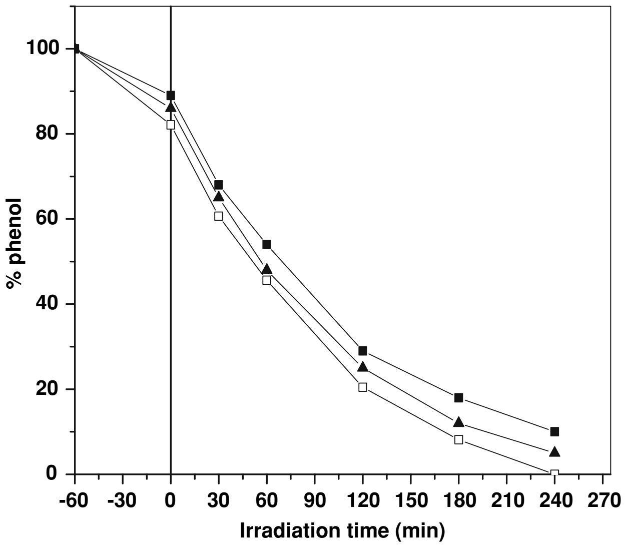
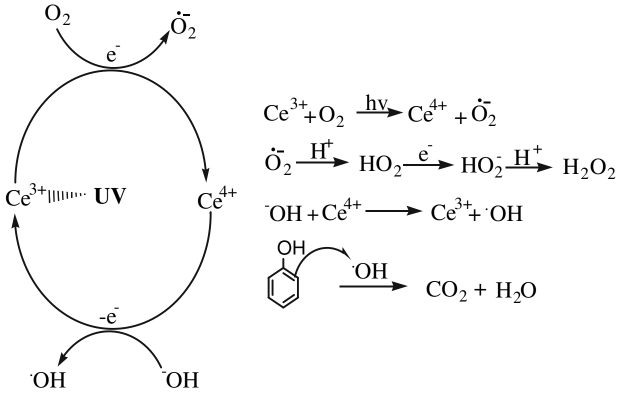


Fig. 8 Degradation of phenol over fresh and recycled 0.3 wt.% Ce–Al-MCM-41 (□) Fresh catalyst, (▲) First recycled catalyst and (■) Second recycled catalyst

4 Conclusions

Cerium in interaction with Al-MCM-41 is in +3 oxidation state and showing the best photocatalytic activity compared



Scheme 1 Plausible photocatalytic mechanism over Ce–Al-MCM-41

to pure ceria. Ce^{3+} on irradiation ($Ce^{3+} \xrightarrow{hv} Ce^{4+} + e^{-}$) generates eletron that participates in effective photodegradation of phenol. The present investigation here on Ce modified Al-MCM-41 as a photocatalyst is reported for the first time.

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