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Catalytic activity of ratio-dependent SBA-15 supported zirconia catalysts for highly selective oxidation of benzyl alcohol to benzaldehyde and environmental pollutant heavy metal ions detection

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Highlights

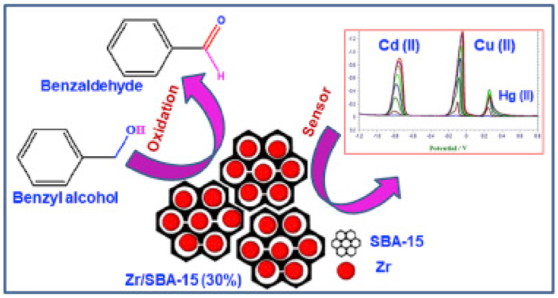
- Zirconium substituted mesoporous SBA-15 molecular silica with different Si/Zr ratios of 10, 20, 30 & 40% have been successfully synthesized by simple hydrothermal method.
- The catalytic activity of the SBA-15/ZrO_2 (30%) samples were using benzyl alcohol converted in to benzaldehyde at 90 °C with higher conversion and selectivity.
- The used SBA-15/ZrO_2 (30%) catalyst was reused and regain several times without significant loss in activity.
- The GCE/SBA-15/ZrO_2 (30%) modified electrode was used for the selective detection of environmentally pollutant metal ions such as Cd^{2+}, Cu^{2+} and Hg^{2+} with excellent selectivity, reproducibility and repeatability.

Abstract

Zirconium incorporated mesoporous SBA-15 silica with Si/Zr ratios of 10, 20, 30 and 40 have been synthesized under hydrothermal conditions. The prepared mesoporous materials were characterized by suitable physical and chemical characterization technique. Besides, the catalytic activity of the prepared SBA-15/ZrO_2 (10–40%) catalyst was used for benzyl alcohol oxidation with tertiary-butyl hydrogen peroxide as the oxidant at 90 °C. The prepared SBA-15/ZrO_2 (30%) catalyst is to facilitate the higher conversion and selectivity. Moreover, the catalyst was regained and reused many times without significant loss in catalytic activity. Furthermore, the SBA-15/ZrO_2 (30%) catalyst modified GCE electrode was used for the determination of environmentally hazardous pollutant metal ions such as Cd^{2+}, Cu^{2+}, and Hg^{2+}. Besides, the proposed modified sensor exhibited excellent selectivity, reproducibility, and repeatability. Thus, the GCE/SBA-15/ZrO_2 (30%) modified electrode as a suitable electrode material for rapid monitoring of these heavy metal ions from the environmental pollutant water samples. Eventually accepted, the SBA-15/ZrO_2 (30%) can be regarded as an effective catalyst to enhance the catalytic activity towards the oxidation of benzyl alcohol and heavy metal ions detection.

Graphical abstract

TOC Graphic, SBA-15 supported zirconia (ZrO_2) catalysts for highly selective oxidation of benzyl alcohol to benzaldehyde and heavy metal ions detection.



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Introduction

A combination of supported metal or metal oxide catalyst with mesoporous silica materials has shown an increased the catalyst surface area and formation of Bronsted acid sites [[1], [2], [3], [4], [5]]. Recent studies on heterogeneous catalysts for oxides supported microporous silica materials are used as catalysts due to the well-ordered networks with a larger size than those in zeolites. In the catalysts conversion, zeolites may increase the active surface area of the supported oxide, which can be harmful to selective properties in the transformation of these catalysts [[6], [7], [8], [9]]. Therefore, the size of the molecules involved in conversion placed as a restriction on the porosity and pore size distribution of the metal oxides used as the catalyst. But, the catalysts need the active sites, which are accessible by the reactant and reaction intermediates for effective conversion. Nowadays, high value-added chemicals produced in these procedures including sugars, alcohols, polyols, toluene, and HMF. The conversion reaction has been recognized as a possible approach to utilize the abundant and the renewable processes [10].

The SBA-15/zirconia (SZ) possesses both strong Brønsted and the Lewis acid sites depending on the preparation condition. Also, zirconium-substituted mesoporous silica materials have learned great applications attributing to the reasonable acidity and the basicity. The isomorphous substitution of Si^{4+} for Zr^{4+}in SBA type materials has been described to generate Lewis acid sites [11,12]. The SZ finds in many industrial application reactions, such as hydrocarbon isomerization, alkylation, oxidation and etherification due to its strong acidic nature [13]. Remarkably, Zr-SBA-15 samples with a high content of zirconium species frequently provided excellent catalytic properties in benzyl alcohol to benzaldehyde conversion. Moreover, the selective oxidation is also the key to starting green and sustainable chemical processes. Currently, the heterogeneous catalytic reaction using O_2 or air as an oxidant, which is cheap and safe. Besides, this process produces water, would give to establishing the maintainable chemical processes. Furthermore, the strongly acidic environment upon in the mixture of SBA-15 also obstructs the precipitation of metal-oxides. Therefore, previously developed an environmentally friendly method for synthesizing metal-incorporated SBA-15 have the well-ordered mesoporous structure [14,15]. In this study, the first time we have demonstrated the formation of Lewis acid species on the surface of Zr-SBA-15 materials with uniform mesoporous structure via simple hydrothermal synthesis and used for catalytic reactions.

Heavy metal ions, such as cadmium (II) (Cd^{2+}), copper (II) (Cu^{2+}) and mercury (II) (Hg^{2+}) pollution is becoming a serious problem due to the environmental toxicity [16,17]. Besides, these heavy metal ions are non-biodegradable and can enter into the food chain, causes serious diseases to both aquatic life and humans [18]. Therefore, it is necessary to develop a highly selective and sensitive method for the identification of heavy metal ions flux in environmental samples [19]. Nowadays, numerous analytical methods utilized for the determination of environmental hazardous heavy metal ions such as atomic fluorescence spectrometry (AFS), atomic absorption spectroscopy (AAS), atomic emission spectrometry (AES), inductively coupled plasma mass spectrometry (ICP-MS) and hyper-Rayleigh scattering. Even though, these methods are widely used in the laboratory and not suitable for in-situ analysis due to the complicated operating procedure [[20], [21], [22]]. Therefore, it is necessary to develop straightforward and sensitive methods for detecting heavy metal ions pollutants. In contrary, the electrochemical technique used for the detection of heavy metal ions with high sensitivity, fast response, straight forward and inexpensive. Among the other electrochemical methods, difference pulse voltammetry (DPV) method used for the sensitive detection of heavy metal ions. Even though, the unmodified bare electrodes have poor sensitivity and selectivity. Therefore, it is important to improve the electrode by the high electrocatalytic material. The GCE/SBA-15/ZrO_2 modified electrode as a suitable electrode material for detecting of heavy metal ions due to their unique chemical, electronic, thermal and mechanical properties [[23], [24], [25], [26]]. In the present study, we have reported the synthesis of a series of SBA-15/ZrO_2 material an applied for both the benzyl alcohol oxidation and heavy metal ion detection.

Section snippets

Materials and methods

All the purchased chemicals used were of analytical grade without further purification. The polymer templates of tri-*block* poly-(ethylene oxide), poly (propylene oxide), poly (ethylene oxide) (P123, EO20PO70EO20, MW = 5800) was purchased from Aldrich. Tetraethylorthosilicate (TEOS), hydrochloric acid (HCl) (37%), zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$), sodium acetate and acetic acid were purchased from Sigma Aldrich. Benzyl alcohol (BzOH), aqueous *tert*-butyl hydroperoxide (TBHP) and ethyl acetate

X-ray diffraction studies

Fig. 1 shows in XRD analysis, it can be observed that pure SBA-15 has amorphous structure, whereas the supported zirconium was represented by monoclinic and tetragonal phases. The compositions of these supports suggest a significant enhancement in the Zr content by hydrothermal synthesis. Furthermore, (a) SBA-15 shows major diffraction peak corresponding to the (100) reflection and two corresponding additional peaks for (110) and (200) reflections. Moreover, the SBA-15 exhibited a broad

Activity of SBA-15/ZrO_2 (10–40%) catalyst towards benzyl alcohol conversion

The selective oxidation of benzyl alcohol (BzOH) was carried out on SBA-15/ZrO_2 with the different ZrO_2 wt. % (10, 20, 30 and 40%) with constant reaction conditions. The optimization for maximum BzOH conversion and benzaldehyde (BzH) selectivity was done by investigating the influence of the variation in reaction parameters, such as catalyst loading (0.02–0.12 g), reaction temperature (60–100 °C) and TBHP/BzOH ratio (0.75–1.75), then the most active sample of SBA-15/ZrO_2 (30%) was identified.

Catalytic activity of pure SBA-15 and Zr-SBA-15 catalyst

Different SBA-15/ZrO_2 (10–40%) modified electrodes for heavy metal ions detection

Under optimum conditions, the electrochemical behavior of different modified GCE was studied by using differential pulse voltammetry studies (DPV) in the presence of heavy metals ions. Fig. 8 presents the DPV responses of (a) bare GCE, (b) GCE/SBA-15/ZrO_2 (10%), (c) GCE/SBA-15/ZrO_2 (20%), (d) GCE/SBA-15/ZrO_2 (30%) and (e) GCE/SBA-15/ZrO_2 (40%) modified electrode. When the accumulation process was carried out for 120 s at 1.0 V in a solution containing 1.0 μM of Cd^{2+}, Cu^{2+}, and Hg^{2+} in 0.1 M

Conclusion

Different wt.% of Zr (10%, 20%, 30% and 40%) on mesoporous SBA-15 molecular silica was successfully synthesized at 373 K under hydrothermal conditions. Besides, the prepared mesoporous silica materials were characterized by suitable physical and chemical characterization technique. On the other hand, the SBA-15/ZrO_2 (30%) mesoporous silica exhibited the selective oxidation of benzyl alcohol to benzaldehyde. Moreover, these SBA-15/ZrO_2 (30%) catalyst gave a higher conversion, selectivity,

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> …The wide-angle XRD patterns of uncalcined and calcined series samples of xCuMn-MS are displayed in Fig. 2a, b, respectively. As observed, all diffraction curves derived from different samples exhibit a broad diffraction peak from 20° to 30° ascribed to amorphous silica carrier [28]. However, regarding uncalcined samples (Fig. 2a), it should be evident that several peaks at 2θ = 12.8°, and 25.7° can be identified obviously and indexed to crystal diffraction of Cu2NO3(OH)3 nanocrystals (PDF#54-0747) introduced in the mesopore of the sample.…

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