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AgBr/Al-MCM-41 visible-light photocatalyst for gas-phase decomposition of CH_3CHO

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Abstract

AgBr/Al-MCM-41 catalyst was active for the photooxidation of acetaldehyde in the gas phase under visible and UV light. Upon visible light illumination, continuous production of CO_2 with a decrease in CH_3CHO concentration was observed without the destruction of AgBr. The crystallite sizes of AgBr increased, as seen from powder X-ray diffraction after photocatalytic reaction under both visible and UV irradiation. It appears that AgBr together with Ag^0 is the photoactive species in the decomposition of CH_3CHO, and the high-surface-area Al-MCM-41 helps in high dispersion of AgBr on the support.

Keywords: Mesoporous; Photocatalyst; Acetaldehyde; AgBr/Al-MCM-41; Visible-light irradiation; UV irradiation

1. Introduction

The cleanup of polluted air has required the development of numerous technologies. Treatment of polluted air or gas by catalytic treatment is a well-established process. Catalytic combustion or catalytic incineration processes require temperatures of 473–1273 K for efficient operations and hence are energy intensive. Furthermore, these traditional methods of treatment are not economically feasible at lower pollutant concentrations. Hence, extensive research is under way to find processes and technologies that operate under ambient conditions of temperature and pressure to treat low pollutant levels. Photocatalysis has attracted the attention of some research scientists for several years and has recently emerged as an advanced oxidation process (AOP) [1,2]. Gas-phase heterogeneous photocatalysis is an AOP that could be successfully used for improving indoor air quality. The discovery of mesoporous materials by Mobil scientists in 1992 attracted the attention of several research workers [3,4]. One form of mesoporous material, MCM-41, has been a focus of attention in the field of catalysis. MCM-41 possesses a uniform arrangement of hexagonally ordered pores of diameters ranging from 20 to 100 Å. Such large pore systems are useful in the selective conversion of bulky molecules in the refining industry (for upgrading of heavy fractions of crude oil) and in the manufacture of fine chemicals and pharmaceuticals. Transition-metal-incorporating mesoporous materials with high surface areas have been examined as photocatalysts [5–8]. We have recently reported that Cr–Al-MCM-41 is active as a visible-light photocatalyst for the decomposition of trichloroethylene in the gas phase [9]. Acetaldehyde, a toxic compound, forms in considerable amounts inside of buildings upon oxidation of organic compounds released by furniture and carpets by incoming ozone [10]. A number of remediation processes have been suggested for this. Deep photocatalytic oxidation of organic compounds and acetaldehyde, particularly over TiO_2 nanoparticles [11–17], has received perhaps the greatest attention so far. Indeed, in this process the oxidation can proceed at atmospheric concentrations of oxygen at room temperature.

The importance of silver halides in the photographic process [18] and in photoelectrochemistry has shown how these materials are unique. In the photographic process the

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absorption of a photon liberates an electron and a positive hole. The electron then combines with the interstitial silver ion, thus leading to the formation of a silver atom. Upon repeated absorption of photons, silver clusters are formed. This reflects the fact that silver halides are unstable under irradiation with light leading to a color change after photoreaction. Silver chloride-coated electrodes have been used for photocatalytic oxidation of water to O_2 under UV–vis illumination in aqueous solution in the presence of an excess of Ag^+ ions [19]. The light sensitivity in the visible range is due to self-sensitization caused by reduced silver species. Calzafeeri et al. reported that thin silver chloride layers on SnO_2-coated glass plates evolved O_2 in the presence of a small excess of Ag^+ ions in aqueous solution under near-UV illumination [20]. The role of Ag^+ ions was to supply AgCl species in order to perform continuous photooxidation of water. However, a suitable condition must be chosen to avoid the photodecomposition of the silver halides. A silver bromide emulsion dispersed on silica substrate has been studied by Noriyoshi et al. in the CH_3OH/H_2O system for H_2 evolution under UV illumination [21]. Silver deposition on titania has been used for reduction [22,23] and oxidation [24–29] reactions and has been proved to increase photocatalytic activity, especially if it is present in the form of nanoparticles [30]. Recently, thin mesoporous titania films incorporating silver nanoparticles have been reported to have an increased effect on the photocatalytic degradation of steric acid under UV irradiation [31].

In the present study, AgBr was well dispersed on an Al-MCM-41 support and was studied as a visible-light photocatalyst for the decomposition of acetaldehyde in the gas phase for the first time without involving self-sensitization. So far the reports in the literature pertain only to studies of silver halides as UV photocatalysts in aqueous solutions [20–31].

2. Experimental

2.1. Synthesis of mesoporous AgBr/Al-MCM-41

The co-assembly process for forming mesopores can involve surfactant cations, aluminosilicate species, and an ammonia-coordinated metal complex, $M(NH_3)_n{}^{2+}$, where $M = Ag$. The gel has a molar composition of 1 SiO_2:x_1 Al_2O_3:2.5 x_2 Ag^+:20 x_1 NH_4OH:0.14 CTAB:2.4 Et_2NH: 100 H_2O. AgBr/Al-MCM-41 was prepared by a method reported earlier in the literature [32]. Briefly, 10 ml of diethylamine solution (Et_2NH) was added to a solution containing 72 ml of deionized water, 2.04 g of cetylmethylammonium bromide (CTAB), and 0.6 g of $Al(NO_3)_3 \cdot 6H_2O$ and stirred vigorously. Then 0.339 g of $AgNO_3$ in 3.6 ml of NH_4OH (25 wt% NH_3) was quickly added to the above mixture. The resulting solution was stirred, and 8.9 ml of tetraethylorthosilicate (TEOS) was added to this solution dropwise over a minute. Finally the mixture was stirred at room temperature for 4 h followed by static heating at 110 °C for 4 days in a 250-ml polypropylene container. The product was filtered, washed with water, and dried overnight at room temperature. The samples were calcined in air at 630 °C at a heating rate of 1°/min. The resulting product was pale yellow in color.

2.2. Characterization

Powder X-ray diffraction of AgBr/Al-MCM-41 was recorded on a Scintag Diffractometer with a Cu-K_α radiation of wavelength 1.5418 Å. XRD was used to identify the crystal phase of the AgBr/Al-MCM-41. AgBr/Al-MCM-41 powders were analyzed from 2° to 7° (2θ) and from 20° to 68° with a step size of 0.01° to assess the crystallinity of the samples under study. N_2 adsorption–desorption isotherms were obtained at liquid nitrogen temperature (77 K) on a Nova 1000 Series apparatus. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. Visible absorption spectra of the samples were recorded on a Cary 500 Scan UV–vis NIR spectrophotometer with an integrating sphere attachment for their diffuse reflectance in the range of 200–800 nm.

2.3. Quantitative and qualitative analysis

A gas chromatograph equipped with a mass selective detector (GCMS-QP5000 from Shimadzu) was used for qualitative and quantitative analysis. The following method was used for qualitative identification and quantification of analyzed gaseous reaction products in the present study. Thirty-five microliters of the gaseous mixture to be analyzed was injected into the GCMS injection port that was maintained at 150 °C. The column temperature was maintained at 40 °C. We identified the separated products by comparison of experimental and reference mass spectra, by following the characteristic masses and making a comparison of retention times of reaction products with the retention times of pure compounds. Photocatalytic testing of acetaldehyde was carried out with the combination of two vis–NIR long pass filters (400 nm) and a colored glass filter (>420 nm) to eliminate ultraviolet radiation during visible light experiments. The reaction temperature was maintained at 298 K. The UV source was a 1000-W high-pressure mercury arc lamp (Oriel Corp.). Broadband illumination was used in all of the UV experiments.

3. Results

3.1. XRD, N_2 adsorption, and UV–vis studies

A powder X-ray diffraction pattern of the catalyst from 2° to 7° (2θ) exhibited the same location of peaks as siliceous MCM-41 [33], with the higher angle peaks assigned to AgBr [34], along with the formation of Ag^0 in smaller

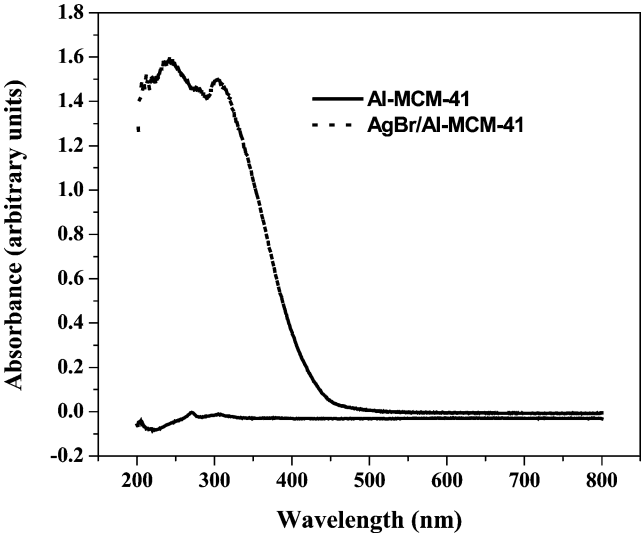

Fig. 1. UV–vis diffuse reflectance spectra of Al-MCM-41 in solid line and AgBr/Al-MCM-41 in dotted lines after calcination at 630 °C.

amounts. The reflections at 100, 110, 200, and 210 indicate a hexagonal structure for the mesoporous materials. The surface area of the AgBr-containing Al-MCM-41 sample was 1150 m^2/g, which is comparable to the surface area of pure Al-MCM-41 (1200 m^2/g). The UV–vis spectrum of the AgBr/AlMCM-41 (Fig. 1) has an absorption band around 303 nm corresponding to the direct band gap of AgBr (290 nm), whereas the Al-MCM-41 mesoporous material is transparent in the wavelength range of 200–800 nm [35].

In the synthesis of AgBr/AlMCM-41, Et_2NH is basic enough to form MCM-41 while also permitting the dissolution of the aluminum source, thus readily allowing the incorporation of Al^{3+} into the framework. It is this feature in the synthesis that allows the introduction of metal cation into the reaction media. The use of ammonia in the procedure is for the formation of complex cations with the metal ions, thus preventing precipitation under basic conditions. The amount of bromide ion from CTAB is more than sufficient to precipitate AgBr from the added $AgNO_3$ during the synthesis. On calcination, the surfactant molecule is eventually removed, and formation of a well-dispersed AgBr on Al-MCM-41 occurs. The Ag^0 could have formed during carbonization and removal of surfactant since, under these conditions, a reducing environment could be present in the pores. The choice of Al-MCM-41 as the support was based on the fact that Al-MCM-41 exhibits higher hydrothermal stability compared with pure siliceous MCM-41. We are also interested in the use of these Al-MCM-41 supports as photocatalysts for remediation of dyes and surfactants (reactions to be carried out in aqueous medium), and hence Al-MCM-41 was chosen as the support. In addition, the incorporation of Al into the framework of MCM-41 generally improves the acidity and ion-exchange capacity of MCM-41, which are crucial properties for catalysts.

3.2. Photocatalysis

Photocatalytic experiments were carried out in a cylindrical air-filled static reactor (305 ml total volume). This reactor is made of glass and has a quartz window. The AgBr-containing Al-MCM-41 sample (50 mg) was placed in a circular glass dish to have a uniform surface and then mounted in the reactor. The reactor was cooled by circulating water, and experiments were performed at 298 K under constant stirring. One hundred microliters of liquid acetaldehyde was added to the reactor containing the sample. Before irradiation, the reaction was equilibrated for 30 min to allow vaporization of the aldehyde and monitored for change in the amount of acetaldehyde consumed or evolved CO_2. Gaseous samples (35 µl) were periodically extracted and analyzed by GC-MS (Shimadzu GCMS-QP 5000). Gaseous samples were injected into the GC-MS injection port, which was maintained at 473 K. The column temperature was maintained at 313 K. We identified the products by making a comparison of experimental and reference mass spectra, by following the characteristic masses, and by making a comparison of retention times of reaction products with retention times of pure compounds. The UV source was a 1000-W high-pressure mercury arc lamp (Oriel Corp.) with a 420-nm cutoff filter for visible-light experiments. Upon visible-light illumination (>420 nm) and in the presence of the catalyst (Fig. 2a) there was a decrease in the concentration of acetaldehyde and a subsequent increase in the production of CO_2, which is the product of oxidation of acetaldehyde. The reaction was also carried out under UV illumination (320 nm to 400 nm) (Fig. 2b). Photocatalytic reaction under UV irradiation was examined with the use of a Pyrex glass cell with a quartz lid. A 1000-W Hg lamp was used as a light source, and the cell was maintained at a constant temperature of 298 K. A 300-nm cutoff filter was used during the experiments. The initial reaction rates are comparable (within a factor of 3) under visible-light and UV illumination. That the reaction rates were comparable confirmed the excellent catalytic performance of AgBr/Al-MCM-41 as a visible photocatalyst, and this is the first example we have seen where such high activities under visible light have been observed. A balance between the consumed acetaldehyde concentration and the amount of CO_2 formed could not be achieved since, although CO_2 was the only dominant gaseous product, often less volatile products were also formed. Acetic acid was one of these other products, but most of this remained strongly adsorbed to the surface of the catalyst. The reaction is photocatalytic in nature. Indeed, as determined from separate experiments, the turnover number, calculated as a ratio of the carbon dioxide molecules formed to the number of silver ions present in the sample, exceeded 100 during the course of the experiment.

It is generally reported in the literature that silver halides decompose rather easily with absorption of UV light to form silver metal. Thus, we were interested in the fate of our dispersed AgBr and used XRD as a probe of the samples

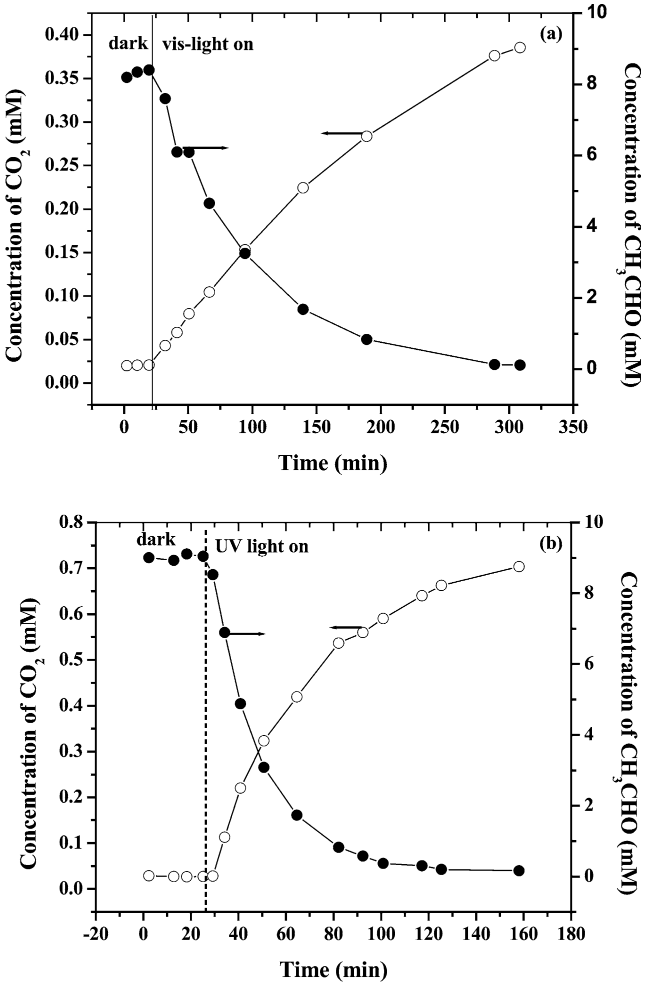

Fig. 2. Graph of concentration vs. time for evolution of CO_2 and decrease in concentration of CH_3CHO using AgBr/Al-MCM-41 under (a) visible light irradiation and (b) UV irradiation.

before and after they were subjected to photocatalysis under visible light (Fig. 3). Initially the peaks were assigned to AgBr with crystallite sizes of ∼4 nm, whereas after the photocatalytic reaction the peaks became sharp, indicating the crystalline growth of AgBr (22 nm) (calculated with the Debye–Scherrer equation from the linewidth of the XRD data), along with Ag^0 formation in smaller amounts. The low angle peaks of Al-MCM-41 and high angle peaks of AgBr were still intact. The presence of AgBr peaks after the reaction suggests that AgBr is not destroyed by exposure to visible light. In addition to the crystalline growth of AgBr, we were able to more clearly identify the formation of Ag^0 in the XRD pattern after the photooxidation reaction. Ag^0 formation has been reported in the literature for H_2 production from water with the use of Ag/TiO_2 [36] and $AgBr/SiO_2$ [21]. Now for the first time Ag^0 has also been observed during a gas-phase photooxidation experiment under visible-light irradiation. So it is possible that either AgBr or Ag^0 is the active component of the catalyst, and this will be explored further in our future work.

The high-surface-area silica seems to have two functions: (1) the facile sorption of CH_3CHO for better adsorption of CH_3CHO, and (2) enabling and stabilizing the high dispersion of AgBr crystallites during visible-light or UV exposure. However, the stabilization mechanism of AgBr is not very clear, and further experiments are needed to better understand the photocatalytic behavior in gas-phase reactions. We do know that irradiation of the sample under vacuum, rather than in air, with visible light also caused Ag^0 formation.

Interestingly, the calcined catalysts that were synthesized with the use of cetylmethylammonium chloride or cetylmethylammonium hydroxide, when subjected to photocatalytic oxidation of CH_3CHO under visible light, did not produce CO_2. We have also carried out the photooxidation of acetaldehyde in the gas phase with AgBr (2 wt%) impregnated on Al-MCM-41 and found that it was not active under visible light, and Ag^0 was not observed on examination of the samples after photooxidation under visible light by XRD. However, these catalysts were photoactive under UV irradiation. The possible explanation for the AgBr/Al-MCM-41 catalyst being active for acetaldehyde photodecomposition under visible light may be the well-dispersed nature of the AgBr along with silver metal formed at the early stages of the reaction, which is detected clearly after photoreaction in the XRD. The silver formation is not observed on the impregnated samples, however. It can be concluded, based on these experimental results, that AgBr/Al-MCM-41 is a visible-light photocatalyst and that both AgBr and Ag metal nanoparticles are necessary. Interestingly, AgCl/Al-MCM-41 and Ag_2O/Al-MCM-41 are only UV photocatalysts. The mechanism of photocatalytic oxidation of acetaldehyde by this AgBr/Al-MCM-41 system is not known at this time but very likely involves an excited-state silver ion (or silver peroxo complex) extracting an electron (and proton) to form an acetyl radical, which then goes on in chain reactions with oxygen to form oxidized products such as acetic acid and carbon dioxide [37].

4. Conclusions

High-surface area-mesoporous AgBr/Al-MCM-41 has been synthesized successfully by the co-assembly process. The catalyst was found to be useful in the photooxidation of acetaldehyde, an indoor air pollutant. For the first time we report here comparable photoactivities for the decomposition of acetaldehyde under visible and UV irradiation. The similarity in rates of the photodecomposition of acetaldehyde under visible and UV light is reported for the first time. Both the fine dispersion of AgBr during the synthesis and the formation of Ag metal nanoparticles during synthesis and upon irradiation appear to be necessary for visible activity.

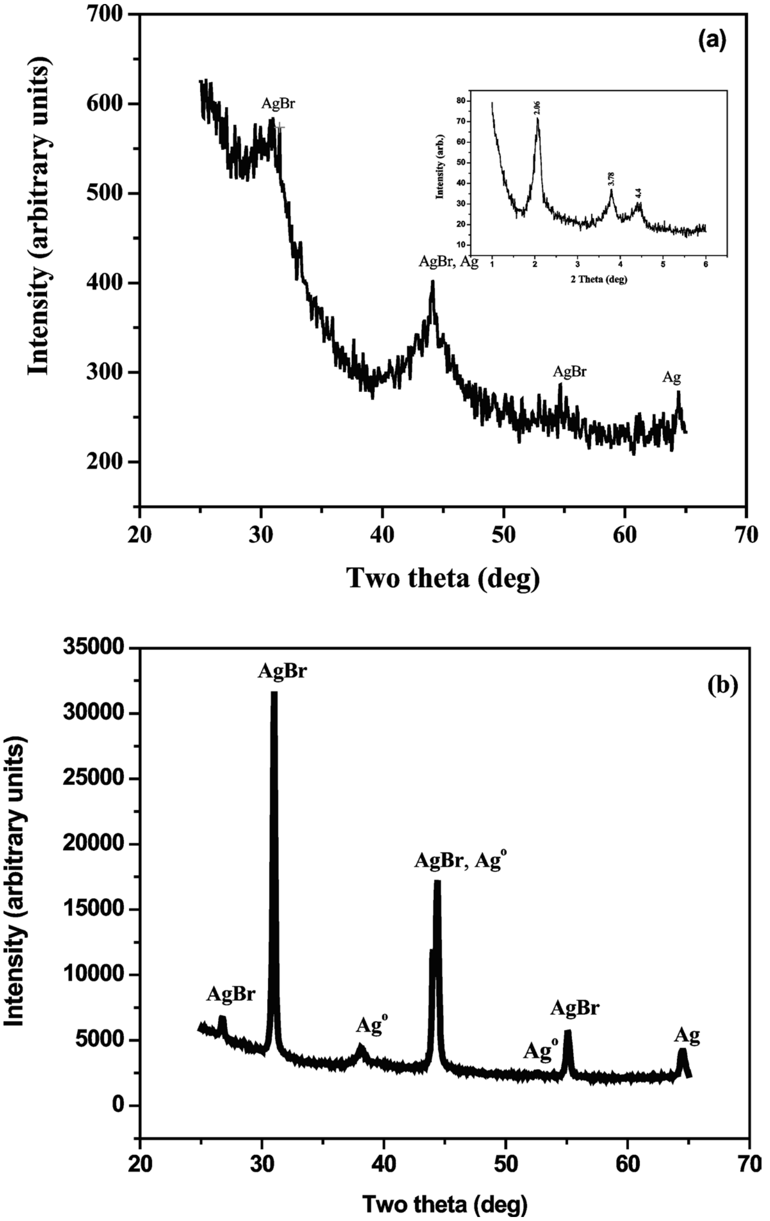

Fig. 3. X-ray powder diffraction pattern of AgBr/Al-MCM-41 (a) before and (b) after photooxidation of CH_3CHO. The insert shows peaks due to the MCM-41 (Al incorporated) structure.

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