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RECOVERY OF HYDROGEN FROM HYDROGEN SULPHIDE USING GAS PHASE PHOTOCATALYTIC REACTOR

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ABSTRACT

A highly photoactive Ti-containing Cr-modified MCM-48 photocatalyst was prepared by a facile one-step method at room temperature. A combination of various physicochemical techniques such as X-ray diffraction (XRD), diffuse reflectance UV–vis spectra (DRS) and scanning electron microscopy (SEM) were used to characterize the properties of the synthetic catalysts. The characterization and experimental results indicated that tetrahedral Ti oxide moieties as dominant Ti oxide were loaded into the mesoporous structure and there was a synergistic interaction between the Ti species anchored on the walls and the Cr ions presented in the MCM-48 framework, which was considered to be directly correlated to the photoactivity. The optimized for maximum hydrogen production of 333.41 mL was found to be 2 g catalyst dosage, 722 W/m^2 light intensity and 60 min of irradiation

INTRODUCTION

Occurrence of Hydrogen sulphide (H_2S) in small quantities is quite common in the environment. Hydrogen sulphide is harmful to environment and human beings (Abel, *et al.* 2011). It is abundant in natural gas and petroleum (Gargurevich, 2005). Hydrogen sulphide is an obnoxious gas, it is commonly found in nature as a by-product of anaerobic metabolic processes (Clovis *et al.* 2004). It is a toxic chemical generated in large quantities from both natural sources and industrial processes (Subramanian *et al.*, 2007). Hydrogen sulphide in excess concentration can cause adverse effect on the human body. Conventional technologies for the degradation of H_2S are not efficient.

The growing concern about the environment and resource utilization have resulted in a need for research in novel technologies to convert hydrogen sulphide to hydrogen and sulphur using solar energy (Morton, 2006). Several problems are related to sulphide build up, which include corrosion of concrete sewer pipes, release of obnoxious odours to the urban atmosphere, safety hazards to sewer workers due to the toxicity of sulphide gas and negative impacts on the subsequent wastewater treatment (Nielsen *et al.*, 2005). Photocatalytic decomposition of H_2S or sulphide ion was done by Ti-Cr-MCM-48. In this study, 92% conversion was observed (Zhen Wang *et al.*, 2012).

A range of technologies are available to treat

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odorous air stream, such as chemical scrubbing, incineration and adsorption. Disadvantage of these technologies are treatment of scrubbing unit discharge, requirement of large surface area and regular replacement of media. Biological treatment of contaminated air is an emerging technology for air pollution control (Moosavi *et al.* 2005) and it is proved to be efficient only in lower concentrations. Nowadays, Photocatalytic method of H_2S treatment is a cleaner technology, non-toxic and has the higher oxidation potential to decompose the obnoxious gas. Hydrogen is an excellent energy carrier and can be produced from any source by using solar, hydro biomass, wind, geothermal, and boron compounds, etc. Moreover, another important source for hydrogen is hydrogen sulfide that is abundantly found in many industries as waste gas. The study was done to recover hydrogen from hydrogen sulfide in gas phase using Ti-Cr-MCM-48 photocatalyst in a packed bed photoreactor.

Reactor design and catalyst required for photocatalyst H_2 production

Materials

The chemicals used in preparing the reagents were Sodium Thiosulphate ($Na_2S_2O_3$, Merck), Sodium Hydroxide (NaOH, Merck), Potassium iodine (KI, Merck), Hydrochloric acid (HCl, Merck) and Iodine (Merck). The reagents were prepared by dissolving required quantity of chemicals of analytical grade.

Synthesis of photocatalysts

The photocatalysts of Ti-containing Cr-modified MCM-48 mesoporous material were prepared by a facile one step method at room temperature. The preparation procedure for 50 mL ethanol is first dissolved in 100 mL deionized water, then 2.4g N-hexadecyltrimethylammonium bromide (CTAB) and 0.128g $Cr(NO_3)_3 \bullet 9H2O$ were added under stirring till dissolved.

In stirring conditions, 3.4g tetraethoxysilane (TEOS) is introduced to the solution after 12 mL aqueous ammonia is joined. After stirring the mixture for 2h, 1.46 mL titanium isopropoxide is added drop wise to the milky solution, stirring violently. Then the final gel is stirred for another 8 h. The pH of the mixture measured before and after the reaction varied between 10 and 12. To remove the template, the powder is subjected to calcination in air for 10 h at 823 K (Zhen Wang *et al.*, 2012).

Photoreactor

The packed bed photocatalytic reactor was made of quartz tube with a length of 50 cm and a height of 3 cm. Vermiculite material coated with Ti-Cr-MCM-48 powder was packed inside the quartz tube as photocatalysts. The photocatalytic reactor was illuminated by visible lamps with a maximum emission spectrum at 270 nm. The experimental test was performed in a laboratory. Gas samples were collected and analyzed by gas chromatography (TCD). The H_2S gas sample is allowed to enter into the reactor. The reactor is allowed to run for recovery of hydrogen from hydrogen sulfide. The maximum hydrogen production of 333.41mL was achieved at the catalytic dosage of 2 g under visible light (Chung

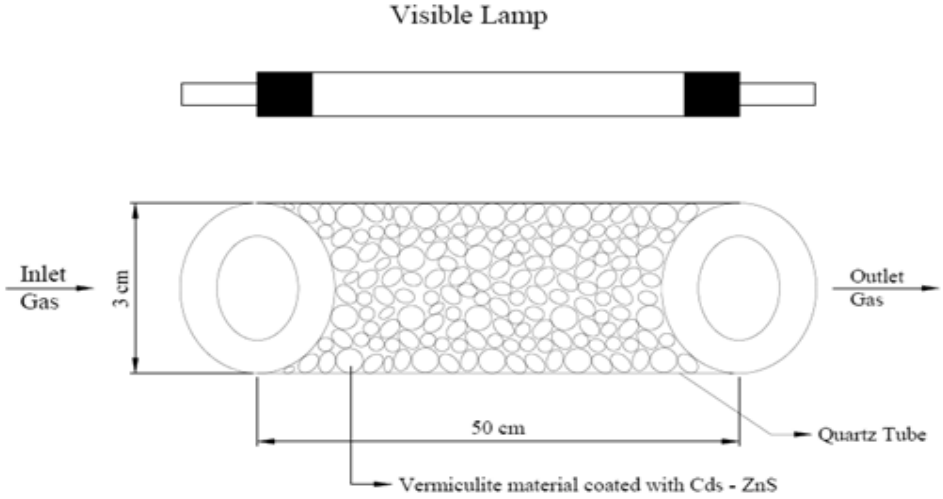

Fig. 1 Schematic diagram of packed bed Photoreactor

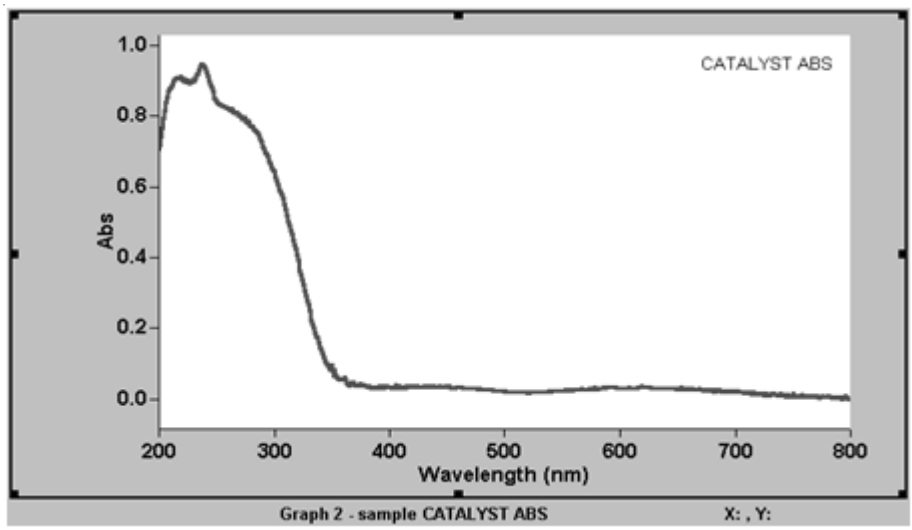

Fig. 2 UV-DRS of Ti-Cr-MCM-48

hsuang hung *et al*., 1998).

Experiment

The catalyst was mixed with vermiculite material and then dried for 30 minutes on hot air oven temperature at 107°C. Synthetically prepared H_2S was decomposed by using Round bottom flask. N_2 gas was purged inside the reactor for 30 mins before starting the experiment. The reactor was swept with N_2 gas for 30 min to flush out air completely prior to each irradiation. A gas mixture of H_2S/N_2 was flowed continuously through each of the reactor tunnel at a rate of 20 mL/min. The reactor is allowed to run for about 60 mins. After reaction, H_2S in the mixed gas was eliminated by purging in NaOH solution. For every 5-10 minutes the H_2+N_2 gas produced was measured and gets collected in an inverted measuring jar. Finally the collected hydrogen gas is analyzed by Gas Chromatograph (TCD). The total amount of H_2 production was found at by following calculation.

Characterization methods

The Diffusion reflection spectrum of the photocatalyst was measured by UV-DRS method. Morphology of the photocatalyst was measured by scanning electron microscopy (SEM, S3400N, HITACHI) (LEO Stereo Scan 440). It was used for studying the dispersion of all the catalytic material in the particulate mixture. The diffraction study revealed the particle size and structure of the photocatalyst was studied using X-ray diffractometer (XRD, CuKα1, λ= 1.54 nm, PANalytical, Netherlands).

RESULTS AND DISCUSSION

Characterization of photocatalyst (Ti-Cr-MCM-48)

The visible photocatalyst Ti-Cr-MCM-48 was prepared by a rapid one step method at room temperature. Diffuse reflectance UV–vis spectra of Ti-Cr-MCM-48 mesoporous materials were given in Figure 2. Ti-Cr-MCM-48 was transparent in the wavelength range 200–800 nm. In the case of Ti-Cr-MCM-48, the spectrum can be distinguished to one band at 350 nm. This closely matches the diffuse reflectance UV-vis spectra as reported in the literature (Zhen Wang *et al.*, 2012).

The scanning electron microscope of the catalyst is shown in Figure 3. Widely varying morphologies were observed. The catalyst was a mixture made of different components with different morphologies. The particles with nano dimensions appeared as round shaped agglomerated particles. The average diameter of the particles was equal to 84.7nm.

The visible photocatalyst Ti-Cr-MCM-48 was prepared by a rapid one step method at room temperature. The XRD measurements was performed using a powder diffractometer operating in the reflection mode. The XRD pattern for Ti-Cr-MCM-48 was given in Figure 4. The particle size was obtained as 5.90 nm. The pattern was corresponding to Ti-Cr-MCM-48 was clearly evident from the Figure in comparison with standard XRD patterns (Zhen Wang *et al.*, 2012).

Effect of operating variables

Effect of catalyst dosage

The effect of catalyst dose on recovery of hydrogen from hydrogen sulfide was studied by varying catalyst dose by 1 g to 3 g at an irradiation period of 60 minutes. Ti-Cr-MCM-48 catalyst was coated on the vermiculite material and dried for the catalyst to fix the vermiculite material. The vermiculite material with catalyst was placed in the packed bed photocatalytic reactor. The H_2S/N_2 mixed gas was passed into the reactor and collected at the outlet. 6 samples were collected at the interval of 10 minutes. The samples were analyzed to calculate its H_2 production efficiency. From the Figure 5, it was observed that the effect of catalyst dosage on recovery of hydrogen from hydrogen sulphide (H_2S/N_2 gas Cylinder).

Table 1. Effect of catalyst dosage on recovery of hydrogen from hydrogen sulfide (H_2S/N_2 gas Cylinder)

Sample No	Catalyst dosage (g)	H_2 production (mL)
1	1	77.13
2	2	333.41
3	3	209.25

The results indicate that optimum dosage played an important role in photocatalytic production of hydrogen from hydrogen sulphide. The photocatalytic splitting method can be used to efficiently produce hydrogen from hydrogen sulfide. The optimum experimental conditions the maximum hydrogen production of 333.41mL was achieved at the catalyt dosage of 2g.

Effect of light intensity

In order to study the effect of light intensity on hydrogen production, experiments were conducted in room temperature. The graph was plotted between visible light intensity (W/m^2) and production of hydrogen (mL). The effect of light intensity was studied for the photocatalytic splitting by various research (Clovis*et al.* 2004). From the results, it was observed that the rate of reaction linearly with light intensity and it was illustrated in Figure 6.

From the illustrations, it was evident that the maximum production of hydrogen was observed at visible light intensity at 722 W/m^2. The production of hydrogen decreased with decrease of visible light intensity.

Table 2. Effect of visible light intensity on production of hydrogen

S.No	Visible light intensity(W/m^2)	Hydrogen production (mL)
1.	246	10.97
2.	482	187.85
3.	722	333.41

Effect of irradiation period

The effect of irradiation period was investigated at optimum catalyst dosage of 2 g for production of hydrogen from hydrogen sulfide. Maximum hydrogen production occurred in a period of 60 minutes. After 60 minutes the hydrogen production rate is decreased. As long as the irradiation period was long enough the hydrogen sulphide was almost completely degraded. From the results, it was observed that the rate of reaction linearly with irradiation period and it was illustrated in Figure 7.

Table 3. Period on Effect of irradiation hydrogen production

S.No.	Irradiation period (mins)	Hydrogen production (mL)
1.	5	11.92
2.	15	15.81
3.	25	82.39
4.	35	216.39
5.	45	15.78
6.	55	10.23
7.	60	5.23

From the results, it was observed that the maximum production of hydrogen (333.41 mL) was observed at 60 minutes of irradiation period.

CONCLUSION

The prepared photocatalyst Ti-Cr-MCM-48 was characterized for structure and particle size, morphology and bandgap energy. The photocatalyst was found to be round shaped agglomorated particles of 5.9 nm diameter. Its bandgap was 3.5eV. The gas phase tubular photocatalytic reactor was fabricated. The optimized for maximum hydrogen production of 333.41 mL was found to be 2 g catalyst dosage, 722 W/m^2 light intensity and 60 min of irradiation period in gas phase photocatalytic splitting of hydrogen from hydrogen sulfide.

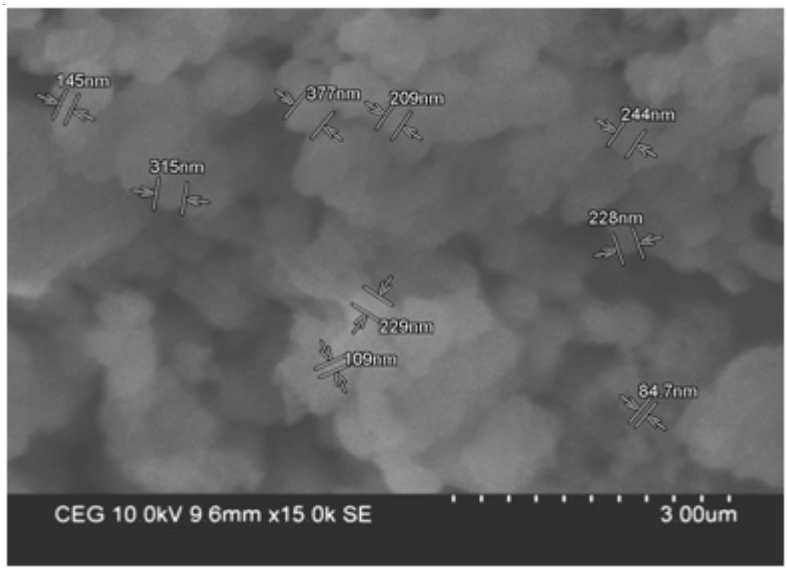

Fig. 3 SEM of Ti-Cr-MCM-48

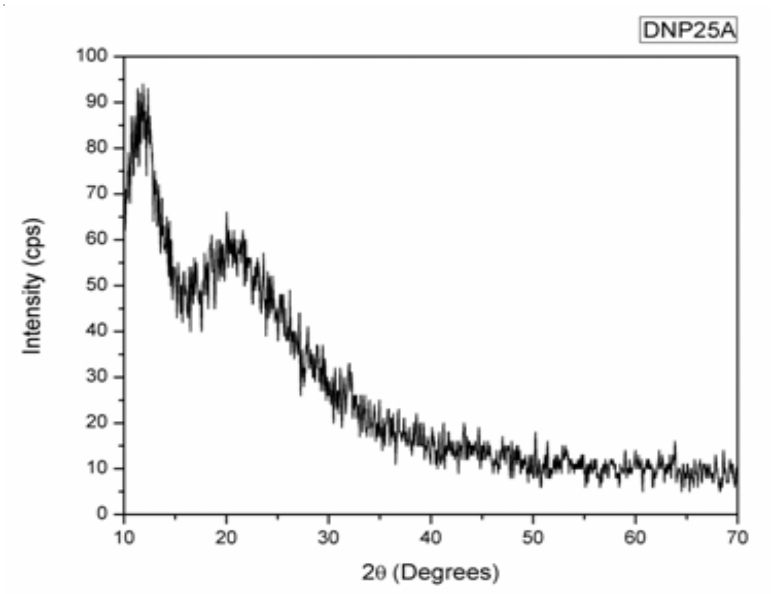

Fig. 4 XRD image of Ti-Cr-MCM-48

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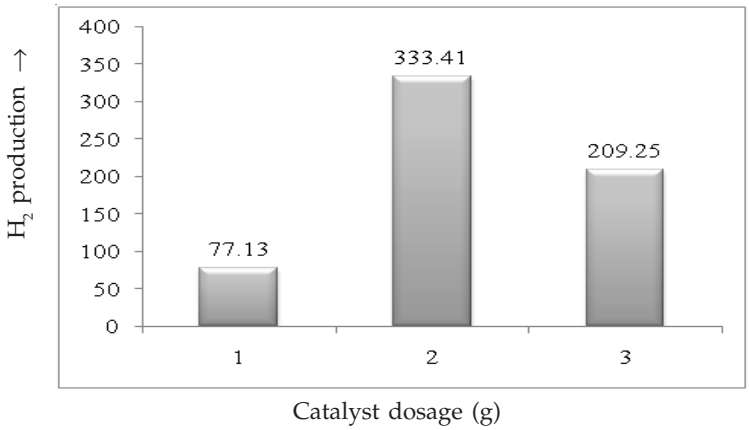

Fig. 5 Effect of Ti-Cr-MCM-48 Dosage on recovery of hydrogen from hydrogen sulphide

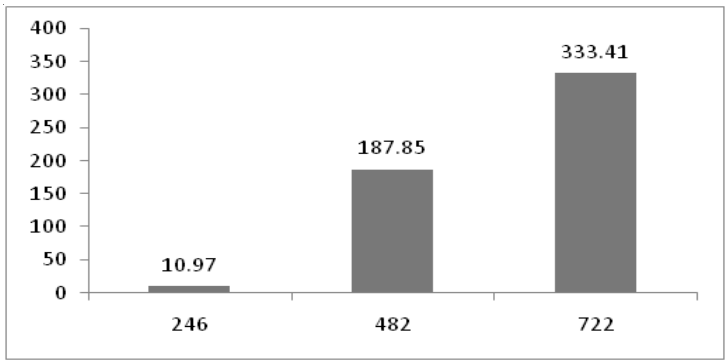

Fig. 6 Effect of visible light intensity on production of Hydrogen

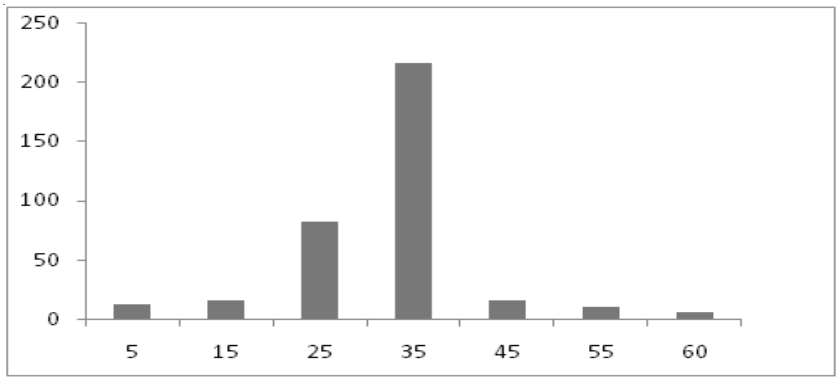

Fig. 7 Effect of Irradiation period on hydrogen production

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