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The Photocatalyzed Reduction of Aqueous Sodium Carbonate Using Nano $SrFeO_3$

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Abstract: Heterogenous photocatalyzed reduction of aqueous Na_2CO_3 has been carried out by using nano $SrFeO_3$ semiconductor powders. Formic acid, formaldehyde and methyl alcohol were identified as photoproducts, and were measured spectrophotometrically. The effect of the variation of different parameters such as sodium carbonate concentration, amount of photocatalyst and different light sources on the yield of photoproducts was also investigated. It shows that nano $SrFeO_3$ has photocatalytic activity. Irradiation leads to the production of electrons in the conduction band of the $SrFeO_3$ semiconductor. It is likely that the photoproduced electrons reduce CO_3^{2-} initially to $HCOO^-$, and then to HCHO and CH_3OH.

Keywords: Photocatalysed reduction, sodium carbonate , $SrFeO_3$.

The increase in carbon dioxide has resulted in some serious environment hazards which have already alarm for future generations. Hence, attention has been raised to carry out an intense search of an alternate environmental friendly technology for energy production .

The reduction of carbon dioxide using semiconducting powders as photocatalysts has been reported[1], TiO_2 and $SrTiO_3$ are known for their high stabilities towards photo corrosion and their favorite band energies[2]. Possible ways to extend the semiconductor photo response to light absorption involve doping with suitable foreign cations[3] and sensitizing by coating with photoactive dyes[4].

A detailed survey of literature reveals that little attention has been paid to the use of nano complex oxides $SrFeO_3$ semiconductor in aqueous media for the reduction of carbon dioxide, the present work was therefore undertaken.

Experimental

All the reagents were analytic grade and the $SrFeO_3$ were prepared by the citrate method as follows.

50 mL 0.1 $mol{\cdot}L^{-1}$ strontium nitrate and 50 mL 0.1 $mol{\cdot}L^{-1}$ iron nitrate were mixed with 60 mL 0.5 $mol{\cdot}L^{-1}$ citric acid (mole ratio of La: Co: citric acid =1∶1∶6) under magnetic stirring. The mixture was evaporated under infrared lamp (250 W) to

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become a viscous liquid. The next drying was carried out at 368 K in a vacuum of 79~80 Pa for 6-8 h to produce the required pink foamy precursors. The precursors were decomposed in air at 400 ^{o}C for 4 h. The minimum calcination temperature for obtaining phase-pure crystalline sample of $SrFeO_3$ was 700 ^{o}C. The product was black powder.

The photocatalyzed reduction of aqueous Na_2CO_3 was carried out in a 250 mL tapered bottle containing 100 mg $SrFeO_3$ and 50 mL 0.01 mol·L^{-1} Na_2CO_3. The bottle was set on a vibrator operated at 120 times per minute. The whole reaction mixture was exposed to light of different intensity. For this purpose a 450 W fluorescent Hg lamp or sunlight 9:00~10:00 Am in the mid-September of Tianjin were used as the irradiator. The distance between the bottle and lamp was 25 cm. Low temperature was attained by a bath cooler to prevent evaporation of the photo reduced products.

The amount of formaldehyde and formic acid were estimated spectrophotometrically using Nash reagent at λ_{max} 410 nm. Methyl alcohol was detected spectrophotometrically using ammonium cerium nitrate.

Results and Discussion

According to the XRD spectrum of prepared $SrFeO_3$ the crystal lattice parameters of $SrFeO_3$ were calculated. Compared to the theoretical values of crystal lattice parameters, we can find the experimental value which well consisted with the theoretical value, suggesting the prepared $SrFeO_3$ was a pure phase compound.

Observing the TEM photography the particle size of $SrFeO_3$ is 40~50 nm, hence, it belongs to nano particles.

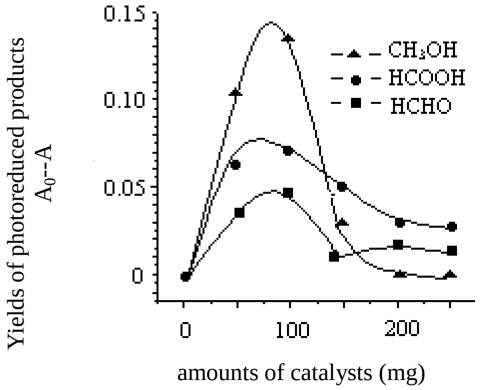
Effect of amount of photocatalyst

The dependence of the yields of CH_3OH, HCHO and HCOOH on the amount of $SrFeO_3$ was investigated and the results are shown in **Figure 1.** It can be seen that an increase in the yields of CH_3OH, HCHO and HCOOH was observed with an increase in the amount of photocatalyst. This may be attributed to the exposed surface area of the reaction vessel, which was completely covered by a specific number of $SrFeO_3$ particles. However, there was a certain limit, if the amount of photocatalyst is more than 100 mg there is no further increase in the exposed surface area, hence no increase in the yield.

Effect of different light sources

The effect of light sources on the formation of HCHO and HCOOH was also investigated using high pressure mercury lamp and solar irradiation. The result are given in **Table 1.**

Figure 1 Effect of amount of catalyst on yield of reduced products



A_0---absorbance of reaction solution, A----absorbance of blank test solution

Table 1 Effect of different irradiator on yields of reduced products

light sources	HCHO ($\times 10^4$) $molL^{-1}$	HCOOH ($\times 10^4$) $molL^{-1}$	CH_3OH ($\times 10^3$) $molL^{-1}$
solar	9.2	1.36	1.74
mercury lamp	0.93	0.64	0.94

* Illuminating time 5h; amount of catalyst 100mg; 0.01mol • L^{-1} Na_2CO_3

It was also observed that higher yields of CH_3OH, HCHO and HCOOH were obtained under solar irradiation than the mercury lamp. This may be explained that the range of wavelength of solar light is larger than mercury lamp (>410 nm), while absorption peak of $SrFeO_3$ situated in ultraviolet region and visible light region (according to the photoacoustic spectrum of $SrFeO_3$). When the suspensions are irradiated with sunlight, the number of photons per unit area striking catalyst molecules increases and therefore the photoreduction of carbonates increases.

It is known that irradiation of semiconductor with light of energy greater than the band gap of the semiconductor causes excitation of an electron of the conduction band of semiconductor. This leaves a hole in the valence band. The fate of the photogenerated holes was not investigated in the present study, but it is believed that the photogenerated holes were reacted with the hydroxylated semiconductor surface, producing photoadsorbed oxygen. Peroxo species and H_2O_2 have also been reported as the products of the reaction of photo-holes with hydroxylated catalyst surfaces[5].

It is likely that on migrating to the surface, the electrons photoproduced in the conduction band reduce carbonate ions initially to formate ions[6] according to:

$$CO_3^{2-} + 2H_2O + 2e^- \rightarrow HCOO^- + 3OH^-$$

It is worth mentioning that the electrochemical reduction of CO_2 in aqueous solution is also known to produce formate ions. This is in agreement with the above reaction. The reduction of formate ions to formaldehyde and then methyl alcohol, by the photo-produced electrons, can be represented by similar reaction.

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