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Influence of reactor geometry on the yield of CO_2 photocatalytic reduction

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ABSTRACT

The effect of reactor geometry on the photocatalytic reduction of CO_2 employing ZnS-MMT (ZnS nanoparticles deposited on MMT) suspension was studied in two annular batch photoreactors. Reaction products in liquid phase (methanol) and in gas phase (methane, carbon monoxide, oxygen and hydrogen) were analyzed by GC/TCD/FID. The dependence of products yields on the reactor diameter and on the volume of the liquid phase confirmed the fact that the requirement of perfect mixing is difficult to fulfill in the annular configuration of the reactor. The highest yields of the photocatalytic reduction were achieved in a configuration where the lamp just touches the surface of the liquid in the reactor and the configuration of the reactor was not annular.

1. Introduction

Photocatalytic reactions, in which both the gas phase and the liquid phase participate, are from the point of possible macroscopic phenomena more complex than reactions proceeding in only one phase. The reaction rate and selectivity can be influenced by a mass transport from the bulk of gas to the gas–liquid interface, by the dissolved gas diffusion through the liquid to an external catalyst surface, by an internal mass transfer in the catalyst pores or agglomerates; further by a phase equilibrium and by the transfer of light radiation. The problem of mass transfer limitations in slurry photocatalytic reactors employing titanium dioxide was discussed in the comprehensive works of Ballari [1–3].

A batch photoreactor using a suspended catalyst must meet two important requirements. It has to utilize the expensive UV energy as efficiently as possible and at the same time maintain the highest possible reaction yields throughout the whole reactor volume. This can be a difficult task as it is often necessary to meet conflicting requirements; e.g. due to scattering effect high concentration of catalyst is not possible to use [4–9].

The photocatalytic reduction of CO_2 by water in the gas–liquid slurry batch reactor with the ZnS-MMT catalyst [10] is the subject of this study. This reaction is one of the most promising methods to reduce CO_2 emitted e.g. from fossil fuel combustion to useful compounds (methane, methanol, carbon monoxide, formic acid, formaldehyde, etc.) by UV light irradiation. Although many works have been written on this topic, CO_2 photocatalytic reduction is still far from its practical application. The aim of this work is to study the effect of reactor geometry and the volume of the reactant solution on the yields of CO_2 photocatalytic reduction employing ZnS-MMT suspension.

2. Experimental part

The catalyst was prepared by adding 50 ml of the aqueous solution of Na_2S and cethyltrimethyammonium (CTA) drop wise to aqueous solution of zinc acetate ($Zn(AcO)_2$) under vigorous stirring. This suspension was then shaken with 0.5 g MMT for 24 h. The resulting ZnS-MMT was filtered, washed and dried. The detailed preparation procedures together with basic characteristics of the ZnS-MMT nanocomposite were described in our previous paper [10]. The characteristics can be summarized as follows: The diameter of the ZnS nanoparticles ranged from 3 nm to 5 nm (determined from HRTEM and calculated from UV–Vis). The band gap energy was found to be 3.89 ± 0.03 eV by the Tauc's plot from UV–Vis spectra. Romboedric ZnS exhibited the vacant structure demonstrated by the strong photoluminescence band between 300 nm and 600 nm [10].

The photocatalytic reduction of carbon dioxide was carried out in a homemade apparatus. Two stirred batch annular reactors with three quartz glass tubes of different diameters (3.5, 4.0 and 4.5 cm) situated inside the reactors were tested. The ZnS-MMT catalyst ($1\ g\ l^{-1}$) was suspended in the 0.2 M NaOH solution and after saturation of the solution by CO_2, the reaction was started by illumination

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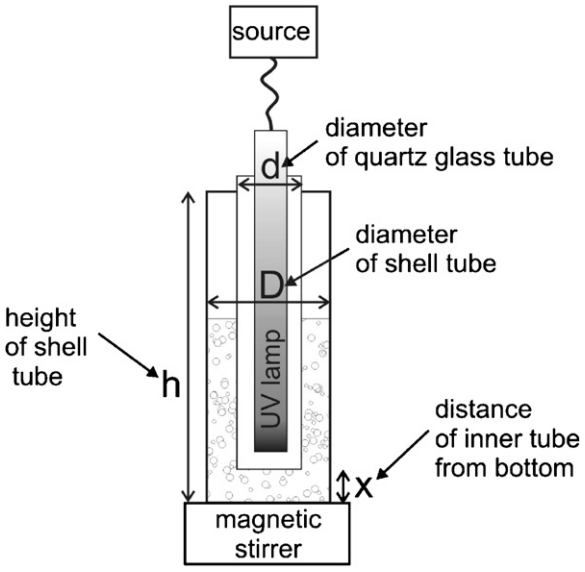

Fig. 1. Schema of basic dimensions of stirred batch annular photoreactor used in this study.

with an UV 8 W Hg lamp (254 nm). GC/FID/TCD was used for the analysis of gas and liquid reaction products. Details of the CO_2 photocatalytic reduction experiment and the analytical methods were described in our previous publication [11].

3. Results and discussion

3.1. The photocatalytic reduction of CO_2

The difference between the reactors used in this study is in their basic dimensions as summarized in Table 1. These basic dimensions are showed in Fig. 1. The R1 reactor has smaller volume and the distance of the inner tube from the bottom is higher compared to the R2 reactor.

The effect of different geometries on the formation of CO_2 photocatalytic reduction products was investigated on the ZnS-MMT catalyst after 24 h of irradiation. The used photocatalyst was chosen for its great photocatalytic efficiency reported in our previous publication [10]. In all photocatalytic experiments performed here, two main products of CO_2 photocatalytic reduction were determined by GC: methane in the gas phase and methanol in the liquid phase. A low amount of carbon monoxide and a large amount of hydrogen, which originated from photocatalytic water splitting, were also measured. The observed order of yields ($\mu mol/g_{cat}$) $H_2 > CH_4 > CH_3OH \geq CO$ was in agreement with our previous works [10–13]. However, quite different yield values were obtained in different reactor configurations in this work.

First, the experiments in R1 and R2 reactors equipped with the inner quartz tube of the same diameter of 3.5 cm and different volumes of the liquid phase were performed. The dependence of the product yields on the volume of the liquid phase for R1 and R2 reactors is depicted in Fig. 2A and B, respectively. It is clear that the ratio of the liquid and gas phase volumes and the width of the annular space in the reactor influenced the yields of the gas and liquid products.

The yields of all products in both reactors increased by lowering the volume of the liquid phase until the volume of 100 ml was reached. The proposed reason for this is insufficient mixing of the liquid phase at its higher volumes, especially in the narrow annular space. As a consequence of better mixing, the mean trajectories for photons were also changed, which led to an abundance of photons being created and available for reaction. The thinner annular space in R1 caused the lower yields because the same volume of liquid reached higher than in R2. In this case, the catalyst in annular space was not maintained in uplift, so its particles gradually fell down to the bottom part of the reactor and the catalyst concentration was not uniform, which could cause a scattering effect. Ballari et al. [2] concluded that perfect mixing is one of the most important prerequisites to avoid transport phenomena in the TiO_2 slurry photocatalytic reactor. This requirement is often not fulfilled in a laboratory reactor equipped with a magnetic stirrer even though the stirrer operates at high speeds. Surprisingly, the liquid volume of 100 ml in R1 reactor corresponded to the situation when the end of the pen UV lamp was just touching the surface of the liquid solution. This means that the configuration of the reactor was not annular anymore. Further decreasing of the liquid volume led to a sharp decrease in yields, due to a higher distance between the lamp and the solution, which caused less intensive irradiation. The number of available photons decreased exponentially with increasing distance from UV lamp: 9.2×10^{15}, 4.4×10^{15}, 3.7×10^{15} photons for 0 cm, 2 cm and 5 cm distance, respectively.

It was found out from the first experiment that the highest yields of the photocatalytic reduction in R1 were achieved in a configuration where the lamp just touches the surface of the liquid in the reactor. It was decided to confirm this conclusion in the R2 reactor as well. The volume of 40 ml of the reaction suspension was chosen, which corresponded with the situation when the end of the lamp is just touching the liquid surface during the stirring. Two

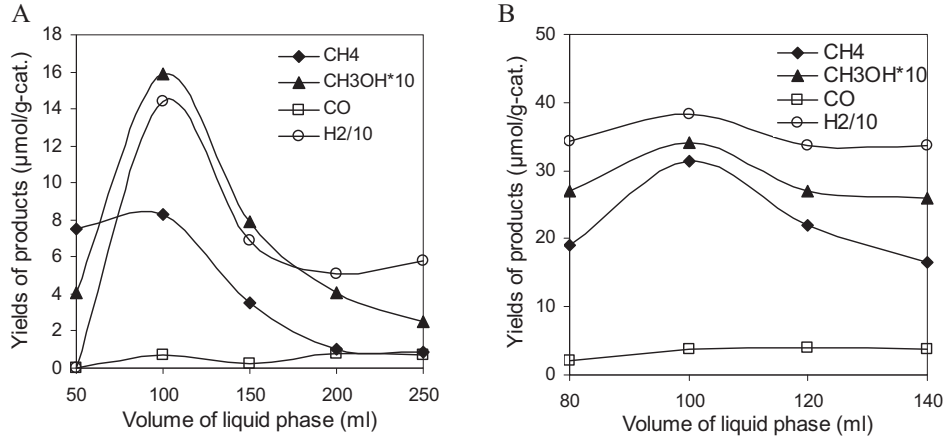

Fig. 2. Dependence of product yields on the volume of liquid phase in the R1 reactor with diameter $D = 5.0$ cm and quartz glass tube $d = 3.5$ cm (A) and in the R2 reactor with diameter $D = 6.2$ cm and quartz glass tube $d = 3.5$ cm (B).

Table 1
Comparison of photoreactor geometry used for CO_2 photocatalytic reduction.

Reactor	R1	R2		
	d = 3.5 cm[a]	d = 3.5 cm	d = 4 cm	d = 4.5 cm
Diameter of shell tube D (cm)	5	6.19	6.19	6.19
Height of shell tube h (cm)	34.5	34.5	34.5	34.5
Max. liquid volume of reactor with immersed tube (ml)	380	725	630	520
Volume V_0[b] (ml)	98	40[c]	40[c]	40[c]
Distance of inner tube from bottom x (cm)	5	2	2	2

[a] d is diameter of the inner tube.
[b] V_0 is volume of liquid phase when the lamp just touched the liquid surface.
[c] After the insertion of the magnetic stirrer into the shell tube and switching it on.

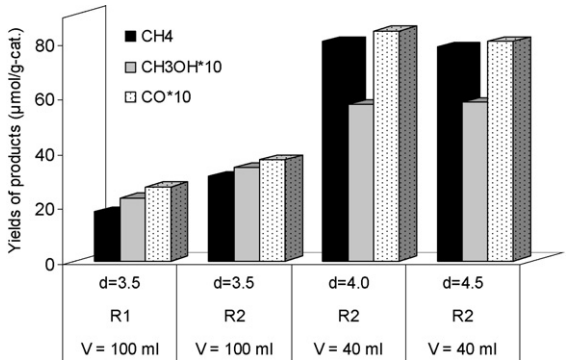

Fig. 3. Dependence of product yields on the volume of liquid phase in the different reactor configurations.

quartz tubes with diameters d = 4 and d = 4.5 cm were used. The results were compared with those obtained in R1 and R2 reactors in Fig. 3. Compared to the R1 reactor, the yields of CO_2 photocatalytic reduction in the R2 reactor were much higher. The reason is that the space between the end of the quartz tube with the UV lamp and the bottom of the reactor was smaller (5 cm in the R1 reactor and 2 cm in the R2 reactor). This caused more intensive irradiation of the reaction mixture (with increasing distance from the UV lamp, the intensity of the light decreased).

Fig. 3 also shows that using the same volume of the liquid phase (100 ml), the same quartz tube diameter (3.5 cm) but different shell tube diameters, the yields of CO_2 photocatalytic reduction are 1.5- to 2-fold higher in R2 reactor than in the R1 reactor due to the above mentioned reasons. If the R2 reactor was used with its optimal volume (40 ml), the yields increased almost 4-fold and 2.5-fold in the gas and the liquid phase, respectively. This data lead to the conclusion that the geometry of the reactor greatly affects the efficiency of CO_2 photocatalytic reduction.

The liquid phase volume of 40 ml in R2 corresponded with the situation when the solution surface is 1.3 cm above the bottom of the shell tube. It is not dependent on the inner tube diameter because the distance of the inner tube from the bottom is 2 cm (x = 2 cm). The lamp just touched the liquid surface after the insertion of the magnetic stirrer into the shell tube and switching it on. When the volume of the liquid phase in R2 was 40 ml, the inner quartz tube was not immersed in the liquid and its diameter played no role. For this reason, the same yields were observed for inner tubes with diameters of 4 and 4.5 cm. This also confirmed the reproducibility of the performed experiments.

4. Conclusion

The effect of reacting phase volume on photocatalysis exemplified by CO_2 photoreduction on suspended nanocrystalline ZnS-MMT was studied in two annular batch reactors with different widths of annular space, different distances of UV lamp from the reactor bottom and different volumes of liquid phase. In the both reactors, the highest yields of the photocatalytic reduction were achieved in a configuration where the lamp just touches the surface of the liquid in the reactor and the configuration of the reactors was not annular. The observed dependence of the product yields on the volume of the liquid phase confirmed the fact that the requirement of perfect mixing is one of the most important factors in photocatalytic slurry reactors and its implementation is difficult in reactors of annular configuration.

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