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Photocatalytic Synthesis of Oxygenates from Gaseous CO_2 and CH_4 over Semiconductor

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Abstract: Photoinduced synthesis of CO_2 and CH_4 was investigated using a batch reaction system on several photoactive materials supported on silicon dioxide. Single semiconductor showed higher selectivity to C1 compounds. The production of C2-C3 oxygenates took place preferentially on composite semiconductor photocatalysts. In particular, it was found that acetone was the primary product over Cu / CdS –TiO_2 / SiO_2.

Keywords: Methane, carbon dioxide, oxygenates, photocatalysis.

The direct conversion of CO_2 and CH_4 into useful chemicals is a desirable process, many approaches have been investigated for this reaction, such as direct synthesis of acetic acid by means of homogeneous[1] and heterogeneous[2, 3] catalysis, producing of oxygenated compounds on Cu-Co-based catalysts in two-step method[4], dielectric-barrier discharge plamas technology[5] *etc*. However, it is very difficult to achieve high yield in such reaction, since CO_2 and CH_4 have low reactivity because of their thermodynamic stability.

Photocatalytic reactions are one of the most available reactions at low temperature, because they can promote the thermodynamically unfavorable reaction under mild conditions. We previously reported that CO_2 is reduced to methanol by H_2O under irradiation on Cu / TiO_2 – NiO[6]. In a later study, we showed that CH_4 reacted with H_2O under irradiation at surface of TiO_2 – MoO_3 / SiO_2[7]. The illuminating light supplies the large energy required to activate CO_2 and CH_4 , so that the highly endothermic reaction proceeds at low temperature.

In the present study, SiO_2 supported TiO_2, CdS and CdS – TiO_2 samples with or without Cu-loading were manufactured as photoactive materials and photocatalytic reaction of CO_2 and CH_4 over them was examined in a batch reactor. composite semiconductor catalyst Cu / CdS – TiO_2 / SiO_2 exhibited the highest photocatalytic activity for this reaction.

The catalysts were prepared with impregnation method. The metal or semiconductor was firstly supported on silicon dioxide carrier, then were dried and calcined, at last reduced with hydrogen.

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Table 1 Contrast of conversion of CO_2 and CH_4, selectivity of products [a]

Run	Samples	X_{CH4} (%)	X_{CO2} (%)	S_x (%)					
				CO	CH_3OH	HCOOH	CH_3CH_3	CH_3COOH	CH_3COCH_3
1[b]	-	-	-	-	-	-	-	-	-
2	SiO_2	-	-	-	-	-	-	-	-
3	Cu/SiO_2	-	-	-	-	-	trace	-	-
4	TiO_2/SiO_2	-	-	trace	-	trace	trace	-	-
5	$Cu/TiO_2/SiO_2$	0.3	0.25	34.3	-	55.6	trace	10.1	-
6	CdS/SiO_2	-	-	trace	-	-	-	-	-
7	$Cu/CdS/SiO_2$	-	-	trace	-	trace	trace	-	trace
8	$CdS\text{-}TiO_2/SiO_2$	0.07	0.057	29.4	trace	27.2	-	32.8	10.6
9	$Cu/CdS\text{-}TiO_2/SiO_2$	1.47	0.74	4.6	-	-	3.1	trace	92.3
10[c]	$Cu/CdS\text{-}TiO_2/SiO$	-	-	-	-	-	-	-	-

[a] Reaction temperature = *ca*. 393K, reaction time = 2 h, CO_2 = 20 μmol, CH_4 = 20 μmol. X_{CH4}: Conversion of methane. X_{CO2}: Conversion of carbon dioxide. S_x (%): selectivity of the product. [b] A blank test. [c] Reaction at 473 K without UV-irradiation.

The reactions were carried out with an innovative experimental apparatus as previously described [8]. The closed fixed-bed reactor was made of a jacketed quartz tube (15 cm^3). The sample (5.0 g) was inserted. CO_2 and CH_4 were mixed and then introduced into the reactor. The initial pressure of mixed gas in the reactor is 100 KPa avoiding air introduction. The sample was irradiated with a 125 W Hg lamp for 2 h, the temperature of the sample bed was controlled at *ca.*393 K. The products were analyzed by quadrapole mass spectrograph and gas chromatograph.

In the blank test (run 1) and silicon dioxide sample (run 2), no products were formed upon irradiation. Over the semiconductor samples, the conversion was obviously much higher than that over silicon dioxide. For single semiconductor, a large amount of C1-C2 oxygenates was obtained while C3 compound was trace. On composite semiconductor, C2-C3 oxygenated compounds were the major products. The selectivity of formic acid was higher at $Cu / TiO_2 / SiO_2$ than that at others. The highest selectivity of acetic acid was found on $CdS – TiO_2 / SiO_2$. On $Cu / CdS – TiO_2 / SiO_2$, the conversion rate of CO_2 was 0.74% and CH_4 at 1.47%, the selectivity of acetone was 92.3%, the by-products were ethane and carbon dioxide 3.1% and 4.6%, respectively. In the dark (run 10) at 473 K, no products were detected, which clearly indicated that irradiation is necessary for the above reaction.

Table 1 showed that the conversion of CO_2 and CH_4 was higher with copper-loading catalyst than without Cu-loading. This indicated that the photocatalytic conversion of CO_2 and CH_4 could be improved by Cu-loading. The reason was that Cu was able to increase the absorption of CO_2 and CH_4. **Table 1** also showed the catalytic activity of coupled semiconductors was higher than that of single semiconductors. This conclusion was consistent with UV-Vis test results. The UV-Vis spectra measurements showed that the UV-absorption character of coupled semiconductor was better than that of single semiconductor. TiO_2 catalysts showed more activity on conversion of CO_2 and CH_4 than CdS catalysts.

In conclusion, the synthesis of oxygenated compounds from gaseous CO_2 and CH_4 can be proceeded under irradiation at SiO_2 supported TiO_2, CdS and CdS – TiO_2 with or without copper-loading. A remarkable amount of oxygenates products was obtained on Cu / TiO_2 / SiO_2, CdS –TiO_2 / SiO_2 and Cu / CdS –TiO_2 / SiO_2. Specially, Cu / CdS –TiO_2 / SiO_2 sample exhibited highest activity of acetone producing.

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