CERAMIC CORDIERITE/CeO_2 FOR PHOTOCATALYTIC REDUCTION OF CO_2

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Abstract
Photocatalytic reduction of carbon dioxide (CO_2) is a challenging reaction attracting a lot of attention. Finding a novel, efficient and relatively cheap photocatalyst is the goal of many research teams all over the world. Cordierite ceramic materials containing ceria (CeO_2) nanoparticles show interesting photocatalytic properties. Five ceramic cordierite/CeO_2 samples prepared from talc, kaolin, vermiculite/CeO_2 nanocomposite with various amounts of CeO_2 were investigated for the photocatalytic reduction of CeO_2. Samples were prepared and characterized by X-ray diffraction method, specific surface area and nanoparticles CeO_2 using transmission electron microscope. The photocatalytic activity of all samples was investigated in batch reactor irradiated by 8 W Hg lamps (254 nm). The main products of the photocatalytic reduction of CO_2 were methane and carbon monoxide. Hydrogen was also detected, however, it is a product of water splitting, not CO_2 reduction. Nevertheless, the presence of water is necessary for the reaction as water serves as hydrogen source. The cordierite/CeO_2 samples containing CeO_2 from 4 to 9 wt.% showed higher activity of photocatalytic reduction of CO_2 than commercial catalyst TiO_2 P25. The finding that lower CeO_2 amount of 5.1 and 3.9 wt. % produced the highest photocatalytic activity is in an agreement with the literary results.

Keywords: Cordierite ceramics, CO_2, photocatalytic reduction

1. INTRODUCTION
In recent years, the increasing level of carbon footprint has become a severe global environmental issue, because of global warming and energy source depletion. The CO_2 emission can be reduced in different ways. Photocatalytic reduction of carbon dioxide to valuable chemicals or renewable fuel, using solar energy, is still attracting more and more attention [1-3]. Especially, photocatalytic reduction of CO_2 with H_2O is important in the development of solar energy based on the carbon neutral cycle [4].

Cordierite (Mg₂Al₄Si₅O₁₈) is a structural material used as a diesel particulate trap. Cordierite has been chosen for automotive applications because of its low coefficient of thermal expansion and relatively low cost of production compared with other ceramic materials. Automobile exhausts such as NOx, CO and CxHy, affecting the quality of the atmosphere, were reduced by installing the catalytic converters. The converter generally consists of a ceramic honeycomb monolith with a catalytic coating. For automotive supports, cordierite is usually produced from a mixture containing clay (usually kaolinite). The use of clay in the extrusion batch inherently provides the plasticity necessary for the extrusion process [5].

The cerium oxide has the ability to exchange oxygen reversibly via redox processes involving the Ce^{4+}/Ce^{3+} couple and acts as an attendant oxygen vacancies, catalytically active sites [6]. At relatively low temperatures, active oxygen can be created from CeO_2 surface, forming oxygen vacancies in lattice. Because CeO_2 possesses the unique oxygen storage capacity it has been adopted as an additive to the catalysts to adjust the oxygen concentration [7] as well as to lower the temperature at which soot combustion occurs [8].

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The cordierite and 10 wt% of CeO$_2$ was recommended as a suitable catalytic convertor for the purification effect to the exhaust gases [9]. As CeO$_2$ does not react with cordierite up to 1200 °C, it can therefore be used as a catalyst to lower the diesel particulate ignition temperature [10]. Only a small amount of the CeO$_2$ dissolves into cordierite and the CeO$_2$ particles could be finely and uniformly distributed on the surface of the interconnected pores of the cordierite ceramics.

The structural properties of clay minerals significantly affect the properties of cordierite ceramics. In recent years, cordierite/steatite/CeO$_2$ ceramics prepared from raw talc, kaolin and CeO$_2$ nanoparticles precipitated on vermiculite from the Paraiba region of Brazil was for the first time successfully tested for the photocatalytic N$_2$O decomposition without presence of reducing agent [5]. The aim of this work is to verify the effects of the photocatalytic decomposition of CO$_2$ over the cordierite ceramic containing amount of ceria from 4 to 9 wt.% using the methods of the X-ray powder diffraction, N$_2$ physisorption, transmission electron microscopy and the test of the photocatalytic reduction of CO$_2$.

2. EXPERIMENTAL PART

2.1. Material and samples

The cordierite mixtures were prepared from talc (T) (supplied by Koltex Color, Ltd., Czech Republic, particle size fraction < 25 µm), kaolin (K) from Czech Republic (paper kaolin KKN, particle size fraction < 2µm of 72.6% from LB Minerals, Ltd., Czech Republic) and vermiculite (Ver) from the Santa Luzia mine in the Paraiba region of Brazil, South Africa (supplied by Grena Ltd, Czech Republic). Vermiculite was milled and prepared to the size fraction < 40 µm from sieve.

2.2. Preparation of Ver/CeO$_2$

Vermiculite in 5 wt% aqueous dispersion (pH = 9.6) was stirred for 15 min and then 100 ml of the dispersion was added dropwise to the solution of 80 ml of aqueous cerium nitrate Ce(NO$_3$)$_3$·6H$_2$O (0.4 M) and 13 ml of NH$_4$OH (1.4 M) (pH = 1.2) and stirred for 3 h at 50 °C. The solid product (Ver/CeO$_2$) was separated by centrifugation and washed several times with distilled water and then dried overnight at 80 °C.

2.3. Preparation of cordierite/steatite/CeO$_2$ samples

Cordierite/steatite/ceramic samples were sintered from the five preceramic clay mineral mixtures in their oxide ratio close to the composition of cordierite Mg$_2$Al$_2$O$_3$·5SiO$_2$ (Table 1). Each sample (3 g) was sintered in crucible in the furnace at the heating rate of 5 °C/min up to 1000 °C and 2 °C/min up to a sintering temperature 1300 °C, staying at that temperature for 1 h and the cooling speed rate of 1.5 °C/min.

| Sample | Talc (w %) | Kaolin (w %) | Vermiculite/CeO$_2$ (w %) | (i.e. CeO$_2$ in mixture) (w %) |
|-------|------------|-------------|--------------------------|--------------------------------|
| 1.    | 20         | 50          | 30                       | 9.0                            |
| 2.    | 25         | 49          | 26                       | 7.8                            |
| 3.    | 30         | 48          | 22                       | 6.6                            |
| 4.    | 35         | 47          | 17                       | 5.1                            |
| 5.    | 40         | 47          | 13                       | 3.9                            |
2.4. Photocatalytic CO\textsubscript{2} reduction experiment

The photocatalytic reduction of CO\textsubscript{2} proceeded in home-made batch stainless-steel photoreactor (volume 348 ml) with a quartz window on the top of reactor. As a light source, the UV 8 W Hg lamp (peak intensity at 254 nm wavelength) was used and was located over the quartz window of reactor. 100 mL of 0.2 M sodium hydroxide along with 0.1 g of a photocatalyst (concentration 1 g/L) were used as reaction suspension. Before performing the reaction, the suspension was saturated with CO\textsubscript{2} for 30 min in the dark under constant pressure (140 kPa) and then tightly sealed. Vigorous agitation ensuring ideal mixing of the suspension was achieved by a magnetic stirrer. The gaseous samples were discontinuously taken before the reaction (time 0 h) and after switching on the UV lamp during the experiment in defined time intervals 0 - 8 h and immediately analyzed on a gas chromatograph (GC-BID).

3. RESULTS AND DISCUSSION

X-ray diffraction patterns (Figure 1) were measured to identify crystalline phases. Hexagonal form of cordierite (PDF card no. 01-082-1884), enstatite (PDF card no. 01-076-6772) and ceria, CeO\textsubscript{2} (PDF card no. 01-078-2601) were identified in all six ceramic samples.

![XRD patterns of ceramic samples 1-5. Peaks are marked: E- enstatite, CeO\textsubscript{2}-ceria; Cordierite peaks are unmarked.](image)

Selected structural properties of prepared ceramic photocatalysts nanoparticles crystallite size of CeO\textsubscript{2} (according to TEM), specific surface area \(S_{\text{BET}}\) and \(V_{\text{NET}}\) (net pore volume) are in Table 2.

| Sample | Size of the CeO\textsubscript{2} nanoparticles \(\text{nm}\) | \(S_{\text{BET}}\) \(\text{m}^2/\text{g}\) | \(V_{\text{NET}}\) \(\text{mm}^3/\text{g}\) |
|--------|--------------------------------------------------|-----------------|-----------------|
| 1.     | 9.98                                            | 0.620           | 1.043           |
| 2.     | 9.37                                            | 0.769           | 0.967           |
| 3.     | 8.59                                            | 1.009           | 1.512           |
| 4.     | 9.87                                            | 0.644           | 1.811           |
| 5.     | 7.78                                            | 0.621           | 1.313           |
TEM image (Figure 2C) revealed the nanocrystallites of CeO$_2$ in clusters of the similar size between 8 and 10 nm (Figure 2, Table 2). The EDS analysis confirmed the elements corresponding to the surface of vermiculite layers and CeO$_2$ crystals.

![Figure 2](image)

**Figure 2** Time dependence of yields of (A) hydrogen, (B) carbon monoxide and (C) methane over ceramic samples. (D) TEM image of CeO$_2$ nanoparticles in ceramic sample No. 1.

The main products of the photocatalytic reduction of CO$_2$ are hydrogen, carbon monoxide and methane (Figures 2 A, B, C) confirmed by GC/BID. The highest photocatalytic activity of samples 4 and 5 containing 5.1 and 3.9 wt. % CeO$_2$ is in agreement with high photocatalytic activity for decomposition of N$_2$O over 3 wt.% CeO$_2$ in cordierite ceramic [5].

4. **CONCLUSION**

A new set of ceramics cordierite/CeO$_2$ photocatalysts was prepared from the mixtures containing kaolin and variable amount of talc and vermiculite/CeO$_2$ nanoparticles. Photocatalytic activity was examined for the photocatalytic reduction of CO$_2$. Main products of the photocatalytic reduction of CO$_2$ were hydrogen, carbon
monoxide and methane. The detected hydrogen is produced from photocatalytic water splitting which is necessary for the photocatalytic reduction of CO$_2$. All prepared samples showed higher photocatalytic activity than the commercial TiO$_2$ P25.

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