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Fractal Features of CeO_2/ZnO Nanocatalysts and its Preparation

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Abstract:CeO_2/ZnO nanocatalysts was synthesized by a nonalkoxide solCgel process at different temperatures,to obtain solid materials ($40°C$). The CeO_2/ZnO nanocatalysts had much higher activity than the common catalystsThere was no regular relationship between the average size of CeO_2/ZnO nanocatalysts and their catalytic performancehoweverThe conversion of methane increased with the increase of the fractal dimension of CeO_2/ZnO nanocatalysts.

Keywords: fractal dimension; CeO_2/ZnO nanocatalysts; oxidative coupling

1 Introduction

Materials based on CeO_2 have been extensively used as glass polishing materials [1], oxygen ion conductor in solid oxide fuel cells [2], gas sensors [3], and catalytic supports or promoter for automotive exhaust gas conversion reaction [4].The surface features are usually described by the Euclidean parameters such as size, specific surface area, pore diameter and pore-size distribution, which are estimated under the presupposition that materials are smooth and have regular shapes. However, the surface usually is not regular and has many defects, which results in distinct warp when using the Euclidean parameters to describe their surface features [5, 6].

Fractal theory has special predominance in description of the sophisticated solid surface. Many results have proved that the fractal dimension of catalysts have some connections to their catalytic performanceand can be served as a supplementary parameter to token the surface characteristics of catalysts.

2 Experimental

Solid system CeO_2/ZnO was synthesized from an ethanolic suspension of $Zn(CH_3COO)_22H_2O(0.4mol/L)$ and cerium nitrate, heated under re?ux with successive additions of lactic acid until total dissolution of $Zn(CH_3COO)_22H_2O$ and formation of a stable and transparent sol. The Zn/Ce molar ratio in solution was $9:1$.

The sample could be submitted to drying at $40°C$ temperature. The powders were calcined at $600°C$ for $2h$ until complete elimination of the organic material. The catalytic activities for oxidation of organic materials were determined by oxidative coupling of methane.

3 Results and discussion

3.1 Fractal features of CeO_2/ZnO nanocatalysts

The fractal dimension of catalysts was calculated by the box-dimension methodThe surface image was collected by the electronic microscope firstthen the photograph was converted into digital picture of $512x512x8$ bits through scanner and transducerand compressed to the picture of $64x64$The gray level of pictures was regarded as the third dimensionand in

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this way the cubic box of $64x64x64$ was foundedThe quantity of gray level contained by each boxB_{ij}; was statistically calculatedThe fractal dimension of catalysts$D_f$could be obtained from the following equation

$$D_f = \frac{\lg \sum_{i=0}^{63} \sum_{i=0}^{63} B_{ij}}{\lg 63}. \tag{1}$$

3.2 Catalytic performance of CeO_2/ZnO nanocatalysts

The SEM images in Fig. 1 revealed the general morphological aspect of the powder particles. The synthesis of the solCgel system led to the formation of particles clusters of spheroidal shape. The average particle size was estimated between 50 and $100nm$ for the synthesized samples. Therefore, according to crystallite size, each spheroidal-shaped particle from the CeO_2/ZnO system must be formed by nanocrystallites in the range from 40 to $80nm$.

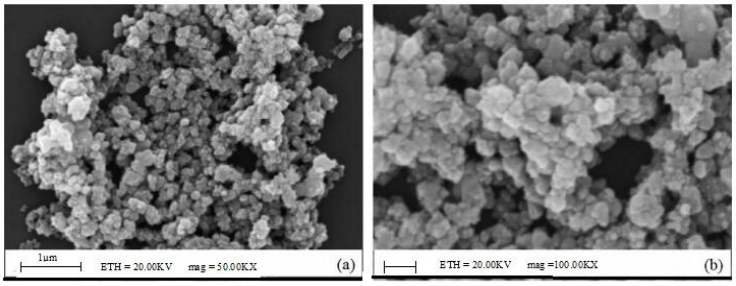

Figure 1: SEM images of CeO_2/ZnO

3.2.1 Effect of the reaction temperature

The conversion of methane by the CeO_2/ZnO nancotalysts was apparently higher than that common catalysts(see Fig. 2). In the former case, the oxidative coupling reaction could take place at $650°C$,which was about $100°C$ lower than the startup temperature when using common catalysts.

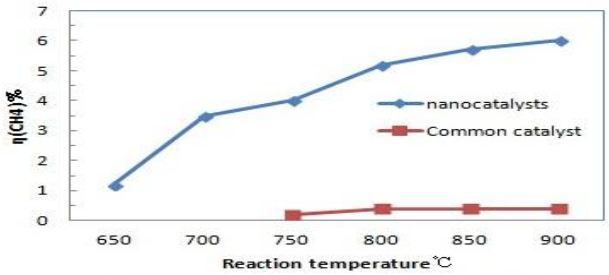

Figure 2: Variation of the conversion of methane with the reaction temperature

3.2.2 Effect of the average size of nanocatalysts

CeO_2/ZnO nanocatalysts with smaller size did not show higher activity as the consequence of their size (see Fig. 3)This result may be reasoned as follows while the average size was estimated under the hypothesis that the nanocatalysts had

spherical morphology and smooth surfacethe nanocatalysts were not strictly spherical and had many defects on their surface actuallyThe surface defectssuch as crushdistortionentanglement and collapseplayed a critical role in the activity of catalystsThe average size of nanocatalysts could not describe such defect in satisfactory detailstherefore it was difficult to find a distinct relationship between the average size of nanocatalysts and the conversion of methaneAs the variation of the catalyst particle was narrowit was necessary to carry out more experiments to testify the above deduction

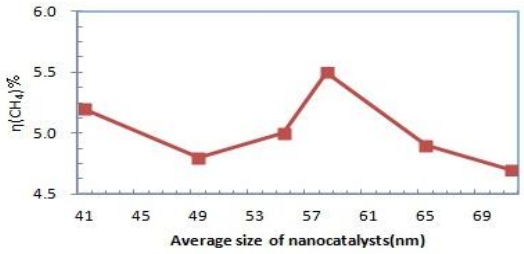

Figure 3: Variation of the catalytic performance at 800 with the average size of nanocatalysts

3.2.3 Effect of fractal dimension of CeO_2/ZnO nanocatalyst

Fig. 4 showed the variation of the conversion of methane with the fractal dimension of nanocatalystsAs shown in this Figurethe conversion of methane increased with the rise of the fractal dimension of the nanocata1vsts. The reason can be considered to be that the catalytic performance of heterogeneous catalysts was mainly dependent on their geometric and electronic featuresThe fractal dimension was the measurement of the geometric features of the catalyst surface [7]Bigger fractal dimension indicated that there were more defect structures on the catalyst surfacewhich resulted in the higher activity of the catalysts and the higher conversion of methane

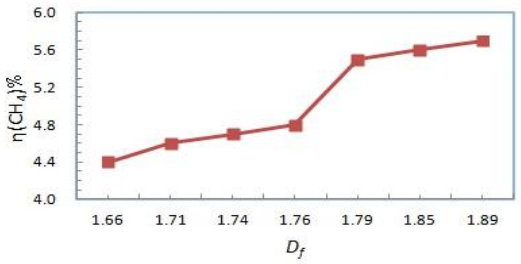

Figure 4: Variation of the catalytic performance with the fractal dimension of nanocatalysts

3.2.4 Operative life of CeO_2/ZnO nanocatalysts

The conversion of the methane decreased slowly with the running time incipiently and kept almost constant after $25h$ (see Fig. 5)The crystal structure of CeO_2/ZnO nanocatalysts became more regular and carbon deposition on them increased with the running timewhich reduced the active sites on the surface of nanocatalysts and weakened their catalytic performanceAfter $25h$the crystal structure and the carbon deposition of CeO_2/ZnO nanocatalysts became relatively stablewhich led to the slow decrease of their activity

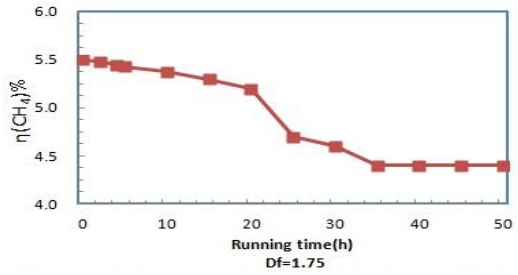

Figure 5: Variation of conversion of methane and fractal dimension with the running time

4 Conclusions

CeO_2/ZnO nanocatalysts was synthesized by a nonalkoxide solCgel process at different temperatures,to obtain solid materials($40°C$).The catalytic performance of CeO_2/ZnO nanocatalysts on the oxidative coupling of methane with carbon dioxide was higher than the common catalystsThere was no direct relationship between the conversion of methane and the average size of the CeO_2/ZnO nanocatalystswhile the conversion of methane increased with the increase of the fractal dimension of the nanocatalysts.

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