Photodeposited palladium catalyst on strontium tantalate for partial oxidation of methane to syngas

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Abstract: Partial oxidation of methane (POM) to syngas (CO+H2) was carried out using strontium tantalate (Sr2Ta2O7) supported Pd catalyst prepared by photodeposition method. The conversion of CH4 reached 80.3% and the yield of syngas was up to 71.8% for H2 and 73.8% for CO. Comparative study indicated the superior catalytic performance is probably attributed to the high dispersed and nano-sized Pd particles and the interaction between Pd and Sr2Ta2O7 support.

Keywords: Partial oxidation of methane, Photodeposition, Palladium, Strontium tantalite

1. Introduction

With the production of shale gas beginning to climb and the mining technology of combustible ice developed rapidly, methane has been considered as the uppermost fuel resource in the 21st century. A spontaneous exothermic reaction, partial oxidation of methane (POM) to carbon monoxide and hydrogen, namely syngas, is an economical and promising route to produce value-added energy source and chemical raw materials.1 Photodeposition is a convenient method to prepare nano-sized noble catalyst with high dispersion, which may allow its activity and selectivity defeating the traditional catalyst.2 In this paper we fabricated a catalyst by depositing Pd nanoparticles on strontium tantalate (Sr2Ta2O7). The catalyst was characterized and the catalytic performance for POM reaction was evaluated and discussed.

2. Experimental

Sr2Ta2O7 powder was prepared by solid state reaction. The starting materials SrCO3 and Ta2O5 were mixed in ball mill with the molar ratio 2 : 1, followed by annealing in an electric furnace at 1573 K for 24 h. For the photo-deposition of Pd, 500 mg of Sr2Ta2O7 was dispersed in PdCl2-methanol-hydrochloric solution (m[Pd] = 5 mg), and irradiated by UV light in a closed glass cell with a quartz cover under Ar atmosphere for 1 h. The dispersed powder was finally filtered and dried in an oven. The obtained catalyst was labeled as Pd@Sr2Ta2O7. For comparison, the same amount of Pd was also deposited on another share of Sr2Ta2O7 with the traditional impregnation-calcination method. Briefly, Sr2Ta2O7 was dispersed in PdCl2-hydrochloric solution and then evaporated to PdCl2-Sr2Ta2O7 mixture. The mixed powder was heated to 773 K to remove the residual Cl- with PdCl2 transformed to PdO, and then treated in 1% H2 + 99% Ar gas at 773K for reducing PdO to Pd. The catalyst was labeled as rPdO@Sr2Ta2O7. Additionally, in order to discuss the effect of different support materials, Pd@TiO2 was prepared by the same photo-deposition method using commercial rutile TiO2 (MT150A).

Catalytic performance was evaluated in a fixed bed electric-heating reactor with 1%CH4 + 0.5% O2 + 98.5% Ar mixed gas purged continuously at the flow of 10 sccm. The temperature ramped from 623 K to 1073 K and the soaking time was 30 min for each 50 K step. The gas composition and instant concentration was analyzed by a micro gas chromatography on-line examination system equipped with thermal conductivity detectors (TCD).

3. Results and discussion

Fig. 1 shows the temperature dependence of the catalytic performance of Pd@Sr2Ta2O7. At 623 K, only the total oxidation reaction occurred that 14.8% of CH4 was converted to CO2 and H2O. The generation of syngas started when the temperature increased to 673 K, along with the vast majority of O2 (88.6%) was
consumed. The partial oxidation became the primary reaction at 773 K as the yields of H₂ and CO reached 30.8% and 23.0%, respectively, exceeding those of H₂O (12.9%) and CO₂ (21.2%). The lower yields of CO and H₂O in the partial or total oxidation product is probably due to the water gas shift reaction of them to form CO₂ and H₂. The conversion of CH₄ increased to 80.3% at 973 K. Simultaneously, the yield of syngas reached as high as 71.8% for H₂ and 73.8% for CO. The similar value of H₂ and CO yields indicated the volume ratio of H₂/CO was close to 2, the ideal result of POM reaction. There was no significant improvement for both the conversion of CH₄ and the yield of syngas at higher temperatures.

The result of comparative study of different catalysts by changing the Pd deposition method and the catalyst support at the same temperature 973K was shown in Fig. 2. rPdO@Sr₂Ta₂O₇ can also catalyze POM reaction but both the methane conversion and the selectivity to syngas were much lower than those when using Pd@Sr₂Ta₂O₇. This demonstrated the high dispersed and nano-sized Pd particles deposited by photocatalytic reaction contributed to the outstanding catalytic performance. However, if changing the support from Sr₂Ta₂O₇ to TiO₂, only trace of syngas generated, and the products were almost CO₂ and H₂O, indicating the interaction between Sr₂Ta₂O₇ support and Pd nanoparticles was significant to the direction of catalytic reaction.

4. Conclusions

A novel catalyst for POM reaction, Pd@Sr₂Ta₂O₇ was developed by depositing Pd nanoparticles on Sr₂Ta₂O₇ support via photocatalytic reaction. Pd@Sr₂Ta₂O₇ presented superior performance for the conversion of CH₄ to syngas than the catalyst with the same composition prepared by traditional impregnation-calcination method followed by H₂ reduction. In addition, Sr₂Ta₂O₇ support cannot substituted by the common photocatalytic material, TiO₂, which drives the CH₄ conversion to the total oxidation direction. The high dispersion and small size of Pd particles and the interaction between Pd and Sr₂Ta₂O₇ support were considered the reason of the high catalytic performance.

References

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