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 ($CO+H_2$) was carried out using strontium tantalate ($Sr_2Ta_2O_7$) supported Pd catalyst prepared by photodeposition method. The conversion of CH_4 reached 80.3% and the yield of syngas was up to 71.8% for H_2 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 $Sr_2Ta_2O_7$ 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 ($Sr_2Ta_2O_7$). The catalyst was characterized and the catalytic performance for POM reaction was evaluated and discussed.

2. Experimental

$Sr_2Ta_2O_7$ powder was prepared by solid state reaction. The starting materials $SrCO_3$ and Ta_2O_5 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 $Sr_2Ta_2O_7$ was dispersed in $PdCl_2$-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@$Sr_2Ta_2O_7$. For comparison, the same amount of Pd was also deposited on another share of $Sr_2Ta_2O_7$ with the traditional impregnation-calcination method. Briefly, $Sr_2Ta_2O_7$ was dispersed in $PdCl_2$-hydrochloric solution and then evaporated to $PdCl_2$-$Sr_2Ta_2O_7$ mixture. The mixed powder was heated to 773 K to remove the residual Cl^- with $PdCl_2$ transformed to PdO, and then treated in 1% H_2 + 99% Ar gas at 773K for reducing PdO to Pd. The catalyst was labeled as rPdO@$Sr_2Ta_2O_7$. Additionally, in order to discuss the effect of different support materials, Pd@TiO_2 was prepared by the same photo-deposition method using commercial rutile TiO_2 (MT150A).

Catalytic performance was evaluated in a fixed bed electric-heating reactor with 1%CH_4 + 0.5% O_2 + 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@$Sr_2Ta_2O_7$. At 623 K, only the total oxidation reaction occurred that 14.8% of CH_4 was converted to CO_2 and H_2O. The generation of syngas started when the temperature increased to 673 K, along with the vast majority of O_2 (88.6%) was consumed. The partial oxidation became the primary reaction at 773 K as the yields of H_2 and CO reached 30.8% and 23.0%, respectively, exceeding those of H_2O (12.9%) and CO_2 (21.2%). The lower yields of CO and H_2O in the partial or total oxidation product is probably due to the water gas shift reaction of them to form CO_2 and H_2. The conversion of CH_4 increased to 80.3% at 973 K. Simultaneously, the yield of syngas reached as high as 71.8% for H_2 and 73.8% for CO. The similar value of H_2 and CO yields indicated the volume ratio of H_2/CO was close to 2, the ideal result of POM reaction. There was no significant improvement for both the conversion of CH_4 and the yield of syngas at higher temperatures.

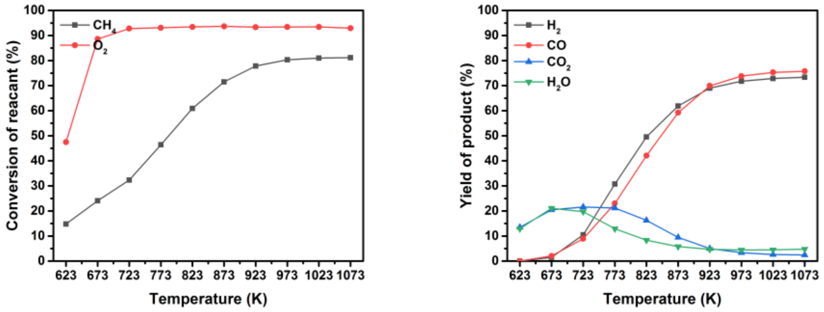

Figure 1. (a) Conversion of the reactants (CH_4 and O_2), and (b) yields of products (H_2, CO, CO_2 and H_2O) using $Pd@Sr_2Ta_2O_7$ as the catalyst form 673 K to 1073 K.

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. $rPdO@Sr_2Ta_2O_7$ can also catalyze POM reaction but both the methane conversion and the selectivity to syngas were much lower than those when using $Pd@Sr_2Ta_2O_7$. 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 $Sr_2Ta_2O_7$ to TiO_2, only trace of syngas generated, and the products were almost CO_2 and H_2O, indicating the interaction between $Sr_2Ta_2O_7$ support and Pd nanoparticles was significant to the direction of catalytic reaction.

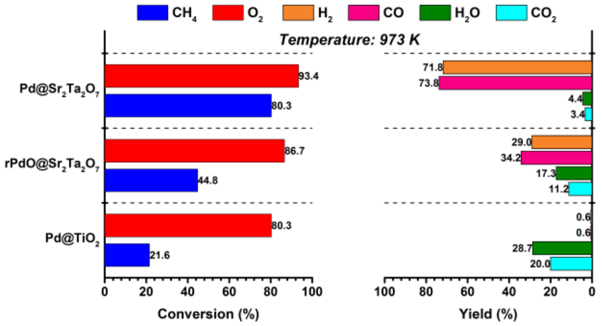

Figure 2. Comparative study by changing the Pd deposition method and the support material at 973K

4. Conclusions

A novel catalyst for POM reaction, $Pd@Sr_2Ta_2O_7$ was developed by depositing Pd nanoparticles on $Sr_2Ta_2O_7$ support via photocatalytic reaction. $Pd@Sr_2Ta_2O_7$ presented superior performance for the conversion of CH_4 to syngas than the catalyst with the same composition prepared by traditional impregnation-calcination method followed by H_2 reduction. In addition, $Sr_2Ta_2O_7$ support cannot substituted by the common photocatalytic material, TiO_2, which drives the CH_4 conversion to the total oxidation direction. The high dispersion and small size of Pd particles and the interaction between Pd and $Sr_2Ta_2O_7$ support were considered the reason of the high catalytic performance.

References

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