The Co-activation of CH_4 and CO_2 To Syngas and Ethylene Simultaneously

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Introduction

Recently, the activation and co-activation of CH_4 and CO_2 have received much attention for environmental and industrial reasons[1-3]. Previous studies focused either on the production of syngas or ethylene. Syngas could be produced either from the partial oxidation or CO_2 reforming of CH_4 over several kinds of catalyst, and ethylene could also be fabricated from the partial oxidation of CH_4 by both O_2 and CO_2. However, in CO_2 reforming of CH_4, the deactivation of the catalyst by coke formation reserves a great challenge in the development of a practical catalyst, and in the partial oxidation of CH_4 to produce ethylene, the deep oxidation forming carbon oxides is inevitable. In order to activate the two green house gases simultaneously and make effective use of both of them, a new process, that is, activating the two gases simultaneously to produce ethylene and syngas, is proposed in present work. The overall reaction could be written as: $5CH_4+CO_2+2O_2 \rightarrow 2CO+2H_2+2C_2H_4+4H_2O$. This path has the following advantages: (1) The reforming of methane with CO_2 is an endothermic reaction, and in contrast, the partial oxidation of methane by O_2 is exothermic. While the proposed process combines the partial oxidation and CO_2 reforming of methane together, resulting in a compensation of heat required and even achieving a thermo-neutral reaction by manipulating the CH_4:CO_2:O_2 ratio[4]. (2) The products (the mixture of CO, H_2 and C_2H_4 with proper ratio) formed from the reaction mentioned above could be used to the synthesis of propanal, and the atom utilization of the later reaction is 100% and the commercial value of natural gas and carbon dioxide could then be elevated. (3) The presence of O_2 in the combination process decreases coke formation [5], though it is a serious and general problem in CO_2 reforming of methane.

Experiment

Catalysts preparation

(1)Grind catalysts. TiO_2 and CeO_2 are ground to 20-40 mesh and impregnated with aqueous solution of the corresponding metal nitrate for 24h. The pastes were dried in vacuum and calcined in air flow for 3h at 500℃ before use.

(2) Monolithic catalysts. Various supports mentioned above were ground to >80 mesh, and treated in a similar way as the preparation of conventional grind catalysts before coating. Cordierite support was cut into small column (length 25mm, diameter 12mm) and impregnated by the paste of the above sample by a special process to coat the catalytic components on the cordierite, and then the sample is dried and calcined at 500℃. A thin surface layer was formed on cordierite

The catalytic reaction

The reaction was carried out in a tubular fixed-bed quartz reactor (15mm o.d., 12.5mm i.d.) under atmospheric pressure. The mole ratio of CH_4、CO_2 and O_2 was controlled to be 1:1:1 with a GHSV of 10^4h^{-1}. The analysis of the effluents mixture was performed by a 1790 gas chromatograph with a plot-C2000 capillary column on line, and a microcomputer was used to quantify the composition.

Results and discussion

It is observed that CO、H_2 and C_2H_4 formed simultaneously on the catalysts investigated in present work. The catalytic activity and C_2H_4 selectivity on the catalysts over the temperature range of 650℃-800℃ are shown in Figure 1 and Figure 2. It is seen that both CH_4 conversion and C_2H_4 selectivity are improved with increasing reaction temperature. On the catalyst Ca-Ni/TiO_2(Ca, 21wt%; Ni, 0.15wt%), CH_4 conversion increases monotonically with increasing temperature over the temperature range tested, while C_2H_4 selectivity increases initially and reaches its maximum value at 770℃. Nevertheless, on the catalyst Ca-Ni*/TiO_2 (Ca,14wt%; Ni, 0.1wt%), the C_2H_4 selectivity increases monotonically with increasing temperature while CH_4 conversion shows its maximum value at 750℃. Higher surface area TiO_2 is also used to prepare Ca-Ni/TiO_2

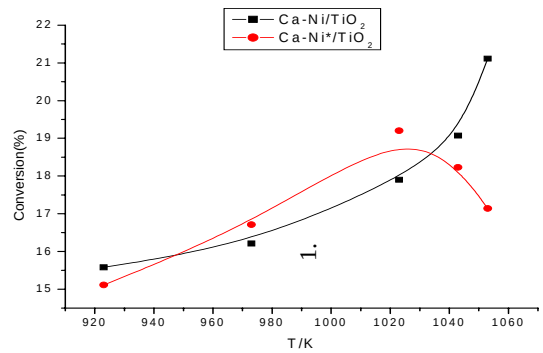

Figure 1 The variation of CH_4 conversion with increasing

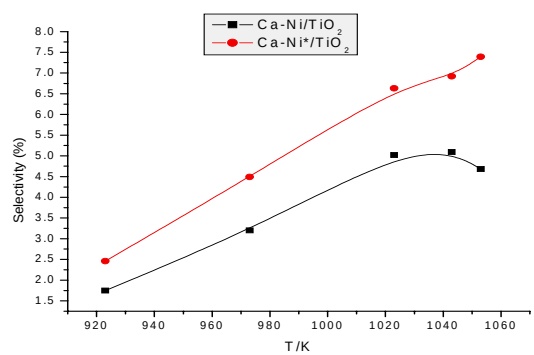

Figure 2 The variation of C_2H_4 selectivity with increasing temperature

catalyst, and it is found that CH_4 conversion and C_2H_4 selectivity are obviously improved and C_2H_4 yield could reach 3.7%. $NaWO_4$ is considered to be an effective promoter in the partial oxidation of CH_4 to ethylene[6], it is used to modified Ca-Ni/TiO_2* system in present work, the resulting catalyst exhibit higher C_2H_4 selectivity, but C_2H_6 is also detected in the efluent. Monolithic cordierite show better mechanical intensity and thermal stability than conventional grind supports, and monolithic catalysts were widely used in the purification of vehicle's exhaust gas and methane combustion, but there are few reports in partial oxidation of methane.[7] In present work, monolithic supported catalysts containing Ni/CeO_2 and Ca/TiO_2 is prepared and used to co-activate methane and CO_2. It is interesting

that the grind forms of Ni/CeO_2 and Ca/TiO_2 show no activity to the target reaction, but they become active when prepared into monolithic catalysts, CO、H_2 and C_2H_4 are obtained at the same time indicating a process intensification effect. Monolithic supported Ca-Ni/TiO_2 catalyst shows activity at about 750℃, and at 770℃, C_2H_4 selectivity reaches 4.3%, and the mole ratio of CO,H_2 and C_2H_4 is 88.5:7.15:4.3.

Conclusions

The simultaneous production of ethylene and syngas from the co-activation of CH_4 and CO_2 is realized over conventional grind Ca-Ni/TiO_2 catalyst. The composition of the catalyst affects the activity and selectivity. The optimal temperature for higher ethylene selectivity over the catalyst Ca-Ni/TiO_2(Ca, 21wt%; Ni, 0.15wt%) is about 770 ℃ .High surface area TiO_2 and $NaWO_4$ promoter is beneficial for the formation of ethylene. Monolithic supported Ni/CeO_2 and Ca/TiO_2 catalysts are also effective in the co-activation of methane and CO_2 simultaneously to ethylene and syngas. Process intensification may be important for the co-activation of methane and carbon dioxide.

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