[Communication]

Study on Carbon Deposition of CH₄, C₂H₆ and C₂H₄ Cracking over Ni-based Catalysts *

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Abstract Influence of the additions of different type semiconductor oxides to Ni-based catalyst on the characteristics of carbon deposition of CH₄, C₂H₆ and C₂H₄ cracking was studied by using pulse microreaction technique. It was discovered that, the addition of *n*-type semiconductor CeO₂ to Ni catalyst would decrease carbon deposition activity of CH₄ and C₂H₆ cracking, whereas the addition of *p*-type semiconductor Co₃O₄ would increase carbon deposition activity of CH₄ and C₂H₆ cracking. On the other hand, the effect of semiconductor oxide additives on the characteristics of carbon deposition of C₂H₄ cracking is opposite to that of CH₄ and C₂H₆ due to the different activated mechanism. XPS results reveal that there is a metal-semiconductor interaction (MScI) between active metal Ni and semiconductor oxide, which is the most important factor leads to the above phenomenon.

Keywords: Methane, Ethane, Ethylene, Nickel catalyst, Metal-semiconductor interaction

The breaking of C – H bond is a key factor in order to convert hydrocarbon molecules. In the past, metal^[1] or oxide^[2] catalysts were used to activate hydrocarbon molecules. Ni-based catalyst is an excellent catalyst for activating CH₄^[3] and C₂H₆^[4] molecules. In addition, it is liable to decompose C₂H₄ over Ni-based catalyst^[5]. In this paper, the effect of adding semiconductor (*n*-type or *p*-type) oxides to Ni-based catalyst on the carbon deposition in the reaction of CH₄, C₂H₆ and C₂H₄ cracking has been studied by using pulse microreaction technique. A new explanation for the carbon deposition is put forward in the view of the interaction between active metal Ni and semiconductor oxide.

The Ni/γ-Al₂O₃ catalyst was prepared by a conventional impregnation method using commercial γ-Al₂O₃ and Ni(NO₃)₂ · 6H₂O aqueous solution. The Ni/γ-Al₂O₃ catalyst was modified by semiconductor oxide CeO₂ (*n*-type) or Co₃O₄ (*p*-type) by co-impre-

gnation method using γ-Al₂O₃ and mixture aqueous solution of appropriate nitrate salts. After impregnation, the samples were dried in air at 110 °C and then calcined at 400 °C for 2 h. The Ni/γ-Al₂O₃ catalyst and modified catalysts were named as Ni, Ni-Ce and Ni-Co, respectively.

Pulse-Chromatographic apparatus was employed to study the carbon deposition of CH₄, C₂H₆ and C₂H₄ cracking over Ni, Ni-Ce and Ni-Co catalysts. Pulse reactions were carried out in a quartz reactor (inside diameter 4 mm) with 40 mg of the catalyst. The catalyst was first reduced in H₂ at 700 °C for 30 min, then the reactor was flushed with Ar for 40 min, and then pulse reaction of CH₄, C₂H₆ or C₂H₄ was performed at the required temperature. The content of carbon deposited on the catalyst was examined by thermo-gravimetric analysis (TGA). The Ni 2p_{3/2} electron binding energy of catalyst was determined by means of XPS.

Table 1 shows the comparison of carbon deposi-

Table 1 Comparison of carbon deposition activity of CH₄, C₂H₆ and C₂H₄ over different catalysts

Catalysts	Ni	Ni – Ce	Ni – Co
pulse of CH ₄ (700 °C)			
CH ₄ (1)	87.1*	87.0	89.5
CH ₄ (2)	86.2	85.0	89.0
CH ₄ (3)	83.3	81.7	87.6
pulse of C ₂ H ₆ (550 °C)			
C ₂ H ₆ (1)	89.0	85.9	90.9
C ₂ H ₆ (2)	81.7	77.3	85.2
C ₂ H ₆ (3)	72.8	69.8	80.7
pulse of C ₂ H ₄ (400 °C)			
C ₂ H ₄ (1)	92.5	94.9	91.0
C ₂ H ₄ (2)	81.2	82.3	81.0

* Conversion of CH₄, C₂H₆ or C₂H₄ cracking (% , mass fraction)

tion activity of CH₄, C₂H₆ and C₂H₄ over Ni, Ni-Ce and Ni-Co catalysts. The carbon deposition activity is represented by the change of the conversion of CH₄, C₂H₆ and C₂H₄ in their cracking reaction. For example, the less conversion of CH₄ cracking decreases with the increase of pulse numbers, the higher carbon deposition activity of catalyst, i. e. it is easy to form carbon over this catalyst. It is shown from Table 1 that the addition of CeO₂ to Ni catalyst could decrease carbon deposition activity of CH₄ and C₂H₆ cracking, while the addition of Co₃O₄ to Ni catalyst would increase the carbon deposition, i. e. a tendency of carbon deposition for CH₄ or C₂H₆ cracking was observed: Ni – Co > Ni > Ni – Ce. It is interesting to notice that the pattern of above adding effect on the carbon deposition for C₂H₄ cracking is just the opposite. It could be concluded that the *n*-type semiconductor CeO₂ promotes carbon deposition, while the *p*-type semiconductor Co₃O₄ inhibits

Table 2 The content of carbon deposited on the catalysts (% , mass fraction)*

Catalysts	Ni	Ni – Ce	Ni – Co
CH ₄	2.12	2.00	3.51
C ₂ H ₆	1.54	1.40	2.79
C ₂ H ₄	4.03	5.42	3.84

* Carbon content on the catalyst after 60 pulse of CH₄, C₂H₆ or C₂H₄

it during the C₂H₄ cracking reaction. Meanwhile, the above results were verified by TGA measuring (Table 2). It seems that there exists an interaction between active component Ni and semiconductor oxide, which could affect the process of carbon deposition of CH₄, C₂H₆ or C₂H₄ cracking.

Table 3 shows the results of XPS analysis of the catalysts:

Table 3 The Ni2 *p*_{3/2} electron binding energy of the catalysts by XPS

Catalysts	Ni	Ni – Ce	Ni – Co
<i>E_B</i> /eV	851.9	851.6	852.1

Table 3 indicates that, the Ni2 *p*_{3/2} electron binding energy (*E_B*) of Ni – Ce is lower (about 0.3 eV) than that of Ni catalyst. It means that the addition of *n*-type semiconductor CeO₂ to Ni catalyst can increase the electron density of surface Ni atom. The above result can be explained as follows: CeO₂ is a typical *n*-type semiconductor, H₂ can be activated and deassociated on Ni⁰ site: H₂→2H, the latter could further react with CeO₂, and create a certain quantity of electron rich oxygen vacancies □_{o2}: CeO₂ + H→CeO_{2-δ} + δ□_{o2}. It is easy for the oxygen vacancies to release free electrons and to migrate from the CeO₂ through Ni/CeO₂ interface to Ni⁰ site, which results in a *d*-electron density increment of Ni atom. Generally, CH₄ or C₂H₆ have to be first adsorbed on the surface and release σ-electron prior to the breaking of C – H bond. The σ-electron can be accepted only by Ni atom with unfilled *d*-orbital. The electron rich character of Ni atom as a result of adding *n*-type semiconductor CeO₂ reasonably repulses the CH₄ or C₂H₆ molecule approaching and inhibits the adsorption of CH₄ or C₂H₆ molecule, thus decreases the carbon deposition. However, Co₃O₄ is a typical *p*-type semiconductor, the Ni2 *p*_{3/2} electron binding energy of Ni – Co catalyst is higher (about 0.2 eV) than that of Ni catalyst. The interaction between metal Ni and *p*-type semiconductor Co₃O₄ make the *d*-electron density of Ni atom decrease, and this will enhance the adsorption of CH₄ or C₂H₆ and lead to more carbon deposi-

tion. The above results indicate that the pattern of the effect of adding various type semiconductor oxide to Ni catalyst on carbon deposition is different. For C₂H₄ cracking reaction, the *d*-electrons of Ni atom must be migrated to empty antibond π -orbital of C₂H₄ during the adsorption. Such a migration of *d*-electron from Ni atom to empty antibond π -orbital can be strengthened due to the addition of *n*-type semiconductor CeO₂ to Ni catalyst. As a result, the probability of carbon deposition of C₂H₄ cracking can be increased. On the contrary, the addition of *p*-type semiconductor Co₃O₄ would inhibit the carbon deposition of C₂H₄ cracking over Ni catalyst.

In conclusion, the carbon deposition behavior of C₁ – C₂ hydrocarbon molecules over Ni catalyst could be controlled by the existence of the different met-

al-semiconductor interaction between active metal Ni and semiconductor oxide. The pattern of carbon deposition for alkane (CH₄ and C₂H₆) or olefin (C₂H₄) seems to be opposite because of the different activation mechanism.

References

- 1 Tornaiainen P M, Chu X, Schmidt L D. *J. Catal.*, **1994**, **146**: 1
- 2 Yu C Y, Li W Z, Feng W J, Qi A H, Chen Y X. *Stud. Surf. Sci. Catal.*, **1993**, **75B**: 1119
- 3 Choudhary V R, Rajput A M, Prabhakar B. *J. Catal.*, **1993**, **139**: 326
- 4 Ducarme V, Martin G A. *Catal. Lett.*, **1994**, **23**: 97
- 5 Xu H Y, Fan Y M, Ye Q, Shang Y C, Shi K Y, Xu G L. *Natural Gas Chemical Industry*, **1995**, **20**(2): 1 [徐恒泳, 范业梅, 叶青, 商永臣, 史克英, 徐国林. 天然气化工 (*Tianranqi Huagong*), **1995**, **20**(2): 1]

Ni 基催化剂上 CH₄、C₂H₆ 和 C₂H₄ 的裂解积炭性能*

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摘要 采用脉冲微反技术研究了添加半导体氧化物对 Ni 基催化剂上 CH₄、C₂H₆ 和 C₂H₄ 的裂解积炭反应特性的影响。结果表明, *n* 型半导体 CeO₂ 的添加降低了 CH₄ 和 C₂H₆ 的积炭活性, 而 *p* 型半导体 Co₃O₄ 的添加则加速 CH₄ 和 C₂H₆ 的裂解积炭; 而对于与 CH₄ 和 C₂H₆ 活化机制不同的 C₂H₄ 分子的活化, 上述影响机制正好相反, *n* 型半导体 CeO₂ 的添加促进 C₂H₄ 的裂解积炭反应, 而 *p* 型半导体 Co₃O₄ 的添加则抑制 C₂H₄ 的裂解积炭反应。XPS 分析表明, 活性金属 Ni 与半导体氧化物之间存在的金属 - 半导体相互作用是这种影响机制的主要因素。

关键词: 甲烷, 乙烷, 乙烯, 镍催化剂, 金属 - 半导体相互作用