Influence of support on resistance to carbon-deposition of catalyst for CH$_4$, CO$_2$ with O$_2$ to synthesis gas

FU Liyong (付利勇), XIE Weiguo (谢卫国), LÜ Shaogje (吕绍洁) & QIU Fali (邱发礼)

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China
Correspondence should be addressed to Fu Liyong (email: iocxuchenghua@263.net)

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Abstract In the reaction of catalytic oxidation of CH$_4$, CO$_2$ with O$_2$ to synthesis gas, carbon-deposition is an important factor for deactivation. By adding different oxides to Ni/Al$_2$O$_3$ catalyst, its resistance to carbon-deposition was improved. The experimental results indicate that the order of resistance to carbon-deposition is as follows: Ni/CaO-Al$_2$O$_3$>Ni/MgO-Al$_2$O$_3$>Ni/TiO$_2$-Al$_2$O$_3$>Ni/CeO$_2$-Al$_2$O$_3$>Ni/La$_2$O$_3$-Al$_2$O$_3$>Ni/Y$_2$O$_3$-Al$_2$O$_3$>Ni/Fe$_2$O$_3$-Al$_2$O$_3$>Ni/Al$_2$O$_3$. The catalysts were characterized by CO$_2$-TPD, O$_2$-TPD and XPS methods. Here the relation between the order of resistance to carbon-deposition and performance of catalyst is discussed.

Keywords: methane, carbon dioxide, oxygen, synthesis gas, resistance to carbon-deposition.

A large number of studies revealed that metal Ni based catalysts had high activity, selectivity and excellent stability for catalytic oxidation of CH$_4$, CO$_2$ and O$_2$, but the carbon-deposition on catalyst was an important problem in realizing this process in industry production. Therefore, a primary subject is to improve the ability of resistance to carbon-deposition in this reaction.

It is well known that the choice of a suitable support is important for an optimal catalyst. Support can not only endow the catalyst with certain feature, strength and heatproof ability, but also can disperse active component and improve the catalyst' s resistance to carbon-deposition.

In this work, the catalytic behavior of Ni based catalysts loaded on different composite oxides was investigated, and the amount of carbon-deposition on catalysts was measured by method of temperature programmed oxidation (TPO). In the meantime, the catalysts were characterized with a series of methods including CO$_2$-TPD, O$_2$-TPD and XPS. In addition, the effect of supports on resistance to carbon-deposition was studied.

1 Experimental

1.1 Catalyst preparation

The supports were prepared by calcining the mixture of appropriate -Al$_2$O$_3$ with 20mol% Fe$_2$O$_3$, TiO$_2$, CeO$_2$, MgO, Y$_2$O$_3$, La$_2$O$_3$ and CaO, respectively, at 1250°C in air for 4 h, and then crushed into 28—48 mesh size. The Ni based catalyst was prepared by impregnating the supports with an aqueous solution of Ni(NO$_3$)$_2$ • 6H$_2$O, followed by drying and subsequent calcination at
450°C for 2h in air.

1.2 Evaluation of catalytic activity

The reaction was carried out in a fixed-bed continuous flow micro-reactor made from a 5 mm I. D. quartz glass tube under atmospheric pressure. The amount of catalyst was 0.1g. The feed typically consisted of CH₄/CO₂/O₂=1/0.4/0.5 molar ratio, and CH₄ GHSV was 50 000 h⁻¹. The product gases were analyzed by an on-line 102-GC using a TCD detector and TDX-01 carbon molecular sieve column with H₂ as a carrier gas. Before reaction, the catalyst was reduced in H₂ flow at 600°C for 1 h.

1.3 TPO

The amount of carbon-deposition on catalyst was measured by burning from room temperature to 800°C with a linear rate of 17 °C/min in O₂ flow (15 mL/min) in a quartz reactor (I. D. 4 mm). Before reaction, the catalyst was pretreated by O₂ flow at room temperature for 20 min.

1.4 TPD

The sample was degassed in Ar(15ml/min) flow at 600°C for 1 h, and quenched to room temperature, then CO₂(O₂) was admitted to the sample until the adsorption saturated, then TPD was raised from room temperature to 900°C at a rate of 15°C/min.

1.5 XPS

XPS measurements were taken on an NP-1 instrument with MgK source at 40KV × 8mA, calibrated internally by C(1s) at 284.6 eV.

1.6 Ni crystal particle size measurement

Ni crystal particle size was measured by CO pulse chromatography[1].

2 Results and discussion

2.1 The relation between carbon-deposition of catalysts with different supports and activity of catalysts

The activity evaluation of catalysts with different supports is carried out under the condition of CH₄/CO₂/O₂=1/0.4/0.5 molar ratio, and CH₄ space velocity of 50 000 h⁻¹. After the reaction, the amount of carbon-deposition on catalyst is measured by TPO. The results are listed in fig. 1 and table 1.

It is found from fig. 1 that the initial