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Partial oxidation of methane to hydrogen and carbon monoxide over a Ni/TiO_2 catalyst

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Abstract

Partial oxidation of methane to hydrogen and carbon monoxide (POM) over a Ni/TiO_2 catalyst has been investigated using a fixed-bed reactor. Ni/TiO_2 catalyst has high initial activity but undergoes deactivation during POM. Activation of methane on Ni/TiO_2 was studied by employing a pulse reaction technique in the absence of gas phase oxygen. Methane pulse reactions demonstrate that the methane oxidation mechanism changes as the nickel oxidation state changes over Ni/TiO_2. CH_4 is efficiently oxidized into CO and H_2 via a direct oxidation mechanism when Ni/TiO_2 is reduced; while CH_4 may be converted by a non-selective oxidation process over oxidized Ni/TiO_2.

Keywords: Methane; Ni/TiO_2 catalyst; Hydrogen and carbon monoxide; Partial oxidation; Nickel oxidation states; TiO_2

1. Introduction

Many studies on partial oxidation of methane (POM) have been done and various viewpoints about it have been reported. POM has been interpreted to proceed via a two-step reaction pathway [1,2]. The complete oxidation of a part of the methane to carbon dioxide and steam occurs at first, and then comes the second step of reforming of the remaining methane with carbon dioxide and steam to syngas. However, direct partial oxidation of methane to syngas has also been suggested by Hickman and Schmidt [3]. They proposed a mechanism where methane was converted into carbon species on the catalyst surface via a catalytical pyrolysis followed by oxidation of the surface carbon and hydrogen desorption. So the mechanism of POM remains controversial. Therefore, a better understanding of the reaction mechanism and of the nature of the active catalytic sites is required.

Mallens et al. [4,5] found differences using Rh versus Pt catalysts, in the selectivity toward CO and H_2 during POM. These differences were attributed to the lower activation energy for methane decomposition on Rh versus that on Pt. Mallens et al. suggested that the catalyst's ability to activate methane determines (1) the product distribution and (2) the concentration of active surface species of oxygen, carbon and hydrogen. Fathi et al. [6] studied the partial oxidation of methane to syngas over platinum catalysts and proposed that the product distribution is determined by both the concentrations and the types of surface oxygen species present at the catalyst surface. Qin et al. [7] suggested that the support might also influence the concentration of adsorbed oxygen and, as a consequence, the activation of methane and the product distribution. Li et al. [8] studied the effect of gas phase O_2, reversibly adsorbed oxygen and oxidation state of the nickel in the Ni/Al_2O_3 catalyst on CH_4 decomposition and partial oxidation using transient response techniques at 700 °C. They concluded that the surface state of the catalyst affects the reaction mechanism and plays an important role in POM conversions and selectivities. Li et al. [8] also argued

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that direct oxidation is the major POM route, and that the indirect oxidation mechanism cannot become dominant under their experimental conditions.

TiO_2 is a reducible metal oxide with several crystal structures. Titanium possesses a variety of oxidation states. Titania-supported metal catalysts have also been used for converting methane into syngas. Ruckenstein et al. [9,10] used 13.6 wt.% Ni/TiO_2 for POM and 1 wt.% Rh/TiO_2 for reforming methane with carbon dioxide to syngas. They found that the 13.6 wt.% Ni/TiO_2 catalyst was deactivated during the POM. Zhang et al. [11] studied the reforming methane with carbon dioxide to produce syngas over Rh catalysts supported on TiO_2, γ-Al_2O_3, MgO, SiO_2 and La_2O_3, and found that the participation of TiO_2 via a strong metal–support interaction contributed to catalyst deactivation. Direct partial oxidation of the methane to syngas occurs with the proper choice of the Ru/TiO_2 catalyst [12] according to transient experiments using isotope-labeled molecules. Braford and Vannice [13,14] suggested that the metal–TiO_x interaction promotes the catalyst activity.

It has been well known that metal–support interactions can affect both catalytic activity and stability [15,16]. TiO_2-supported Group VIII metal catalysts suppress carbon formation during the reforming of methane to syngas, presumably due to the decoration of metal surfaces with TiO_x species. The TiO_x presence destroys the large ensembles of metal atoms that serve as active sites for carbon deposition [17,18]. Interfacial metal–support sites may promote catalyst activity [19]. Reactions on Pt/TiO_x catalysts have supported this hypothesis [20]. Titania-supported nickel catalysts are more active in carbon monoxide hydrogenation than silica- or alumina-supported catalysts [21]. Suppression of hydrogen and carbon monoxide adsorption on TiO_2-supported metals has been observed and attributed to the strong interaction between metal and titania by Moon and co-workers [22].

The present work concerns the performance of Ni/TiO_2 catalysts for POM and methane activation mechanism over the catalyst. A key question remaining in POM is that whether the oxygen initiating the reaction is directly from the metal oxide (NiO) lattice or from the support TiO_2. This question was pursued by conventional pulse experiments and catalytic activity tests. The influence of temperature and time on stream on the catalytic performance was also investigated. Special attention was given to the correlation between the nickel oxidation states and the methane activation mechanism over the Ni/TiO_2 catalyst.

2. Experimental

2.1. Catalyst preparation

The supported nickel catalyst Ni/TiO_2 was prepared by impregnating TiO_2 (John Matthey Chemicals Limited, 70 m^2/g 60–80 mesh) with an aqueous solution of 0.1 M $Ni(NO_3)_2 \cdot 6H_2O$. This was followed by drying overnight at 110 °C and calcination in air at 700 °C for 6 h. The nickel loading was 8 wt.%.

2.2. Reactivity test of catalyst

Catalytic performance tests were carried out in a fixed tubular quartz micro-reactor (200 mm length, 6 mm i.d.). A 500 mg catalyst sample was used for all runs. The reactor system was purged first with nitrogen for 0.5 h, and then the catalyst was reduced at 700 °C under pure hydrogen (10 mL/min) for 1 h. The reactant (CH_4/O_2 (2/1)) was then introduced to the reactor. Analyses of reactant/product mixtures were achieved by a gas chromatograph (model 103G) with a TC detector. A carbon sieve TDX-01 (packed column, 2 m length, 4 mm i.d.) column was used in order to separate hydrogen, carbon monoxide, carbon dioxide, oxygen and methane. The amount of carbon deposited on the catalyst was determined by TG analysis.

2.3. Temperature-programmed reductions (TPR) and pulse reactions

TPR and pulse reaction experiments were carried out in a fixed-bed tubular quartz micro-reactor with an inner diameter of 3 mm and a length of 18 cm. Hundred milligrams catalyst sample was used in each run. An on-line Balzer quadrupole mass spectrometer (QMS 200) continuously monitored the reactor effluent, which might contain hydrogen ($m/z = 2$), He ($m/z = 4$), methane ($m/z = 15$ or 16), water ($m/z = 18$), carbon monoxide or nitrogen ($m/z = 28$), oxygen ($m/z = 32$) and carbon dioxide ($m/z = 44$). High purity helium was used as carrier gas.

For the TPR experiment the fresh catalyst was first pretreated in air at 700 °C for 1 h and then cooled to room temperature under a helium flow. Then, the helium flow was replaced by a flow of 3% (V) hydrogen in nitrogen (30 mL/min). After the concentration of effluent was stabilized, the temperature was ramped at a rate of 15 °C/min to 1000 °C. For the used catalyst, a helium flow was introduced for 20 min, and the catalyst was cooled to room temperature. Then the flow was switched to a 3% H_2/N_2 mixture. Temperature was then increased at a rate of 15 °C/min to 1000 °C.

The pulse reaction experiments were performed at 700 °C. A gas pulse containing 1 mL CH_4/Ar (1/20) was injected through a six-port valve into a helium carrier gas flow, which continuously flowed through the reactor during the experiments. An unreduced Ni/TiO_2 catalyst sample was kept under a helium flow at 700 °C for 30 min before methane was pulsed. While a reduced catalyst sample was treated under pure hydrogen (10 mL/min) at 700 °C for 30 min before the pulse reaction.

2.4. X-ray diffraction (XRD) and nickel dispersions of Ni/TiO_2

XRD patterns were obtained with a Philips PW 1840 powder diffractometer. Co Kα radiation was employed, covering