Partial oxidation of ethane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide

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The catalytic activity, thermal stability and carbon deposition of various modified NiO/γ-Al₂O₃ and unmodified NiO/γ-Al₂O₃ catalysts were investigated with a flow reactor, XRD, TG and UVRRS analysis. The activity and selectivity of the NiO/γ-Al₂O₃ catalyst showed little difference from those of the modified nickel-based catalysts. However, modification with alkali metal oxide (Li, Na, K) and rare earth metal oxide (La, Ce, Y, Sm) can improve the thermal stability of the NiO/γ-Al₂O₃ and enhance its ability to suppress carbon deposition during the partial oxidation of ethane (POE). The carbon deposition contains graphite-like species that were detected by UVRRS. The nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide have excellent catalytic activities (C₂H₆ conversion of ~100%, CO selectivity of ~94%, 7 × 10⁴ l/(kg·h), 1123 K), good thermal stability and carbon-deposition resistance.

Keywords: partial oxidation of ethane, syngas, nickel-based catalysts, modification, alkali metal oxide, rare earth metal oxide, thermal stability, carbon deposition

1. Introduction

Although natural gas is predominantly CH₄, it also contains from 5 to 30% C₂H₆, C₃H₈ and C₄H₁₀. Commonly, C₂H₆ is the most abundant secondary component in natural gas [1]. The partial oxidation of methane (POM) to syngas (CO + H₂) reaction over nickel-based catalysts has received intensive attention [2,3], and many researches have been devoted to the conversion of ethane to ethylene [4]. Ethylene has been shown to be formed from ethane by thermal dehydrogenation (C₂H₆ = C₂H₄ + H₂) and oxidative dehydrogenation (C₂H₆ + (1/2)O₂ = C₂H₄ + H₂O). Thermal dehydrogenation of ethane exhibits a high selectivity to ethylene (~80%) with a fairly high conversion (~60% per pass), and these reactions represent the main processes for commercial olefin production. The oxidative dehydrogenation of ethane over oxide catalysts such as V₂O₅/SiO₂ has also been shown to be fairly selective to ethylene at low conversions [5]. These catalysts are 100% selective to ethylene at conversions of ethane <1%. However, at a conversion of only 5% C₂H₆, the ethylene selectivity falls to only 80%. Since these processes are operated under severely fuel-rich conditions, carbon deposition and, consequently, deactivation can be the major problems, and this contributes to the poor conversions of many processes. At higher conversions, not only does selectivity decrease but also coke formation becomes an issue [6]. Provided that syngas can be produced from C₂H₆ over nickel-based catalysts with high selectivity and conversion, it can be directly obtained from mixture gases containing CH₄, C₂H₆ from natural gas, FCC (fluidized catalytic cracking) tail gas, etc. (Syngas can be produced from CH₄ over nickel-based catalysts with high selectivity and conversion [3].)

This may lead to better utilization of the light fractions from natural gas and refineries, etc. Schmidt et al. [7,8] reported that syngas can be produced from CH₄, C₂H₆ and C₃H₈ over a supported Rh catalyst with high selectivity and conversion, and the presence of C₂H₆ in natural gas will not lead to catalyst deactivation by carbon deposition. However, little work about partial oxidation of ethane (POE) to syngas over nickel-based catalysts has been reported.

Previously, we reported the partial oxidation of methane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide, and pointed out that ABNiO/γ-Al₂O₃ (A = Li, Na, K; B = La, Sm, Ce, Y) were excellent POM reaction catalysts [3,9,10]. On the basis of these results, the partial oxidation of ethane to syngas over nickel-based catalysts was investigated. One of the aims for this investigation on the POE reaction is to search for a catalyst that is not only suitable for the POE reaction, but also for the POM reaction, hence enabling mixture gases containing CH₄ and C₂H₆ from natural gas and FCC tail gas to be converted to syngas with high conversion and selectivity. In the present work, the catalytic activity, thermal stability and carbon deposition over the nickel-based catalysts were discussed in detail.

2. Experimental

NiO/γ-Al₂O₃, NiO/SiO₂ and NiO/MgO catalysts were prepared by impregnating γ-Al₂O₃, SiO₂ and MgO, respectively, with an appropriate amount of Ni(NO₃)₂ for
24 h then drying at 393 K, and calcining in air at 823–1073 K for 4 h. Preparation of the ABCO/γ-Al₂O₃ (A = Li, Na, K; B = La, Sm, Ce, Y; C = Fe, Co, Ni) catalysts was described previously [3].

Heat treatment of the samples was carried out at 1123, 1373, 1423, 1523 and 1573 K, respectively, under a flow of air. Temperature was slowly brought to the final value with a variable current automatic controller, then set at the predetermined reading for the desired temperature. At this temperature, the catalysts were activated for 5 h. After that, the samples were slowly cooled to room temperature under a flow of air. The sample calcined at 1373 K for 5 h was labelled as “catalyst”-1373, e.g., NiO/γ-Al₂O₃-1373, etc.

Catalysts were tested in an atmospheric pressure fixed-bed flow microreactor. Reaction performance was tested using a microreactor with an internal diameter of 4 mm, and 50 mg of catalyst with an average particle size of 0.37–0.25 mm was employed, giving a catalyst bed length of 7 mm (no dilution). An EU-2 type thermocouple fixed with the quartz reactor was placed at the exit of the catalyst bed to control the electric furnace temperature, which was taken as the reaction temperature. The catalyst was reduced at 1123 K with H₂ (20 ml/min) for 1 h in situ before it was used for the POE reaction. Products of the reaction were analyzed by gas chromatography using a TCD detector. The conversion of ethane and the selectivity were calculated on the basis of carbon numbers of the ethane reacted. The amount of H₂ was corrected by the external standard method.

TG tests were recorded and treated by a Perkin–Elmer 3600 workstation at a programmed temperature velocity of 10 K/min in air, with a flow rate 25 ml/min. XRD characterization was performed with a Rigaku D/Max-RB X-ray diffractometer using a copper target at 40 kV × 100 mA and scanning speed of 8°/min.

UV resonance Raman spectra (UVRRS) characterization was performed in air at room temperature, using an UV resonance Raman spectroscope. The ultraviolet laser beam for exciting UV Raman spectra was generated by frequency doubling of the 488 nm output of an Ar⁺ ion laser to 244 nm using a BBO crystal. The Raman scattering from the sample surface was collected by an AlMgF2-coated ellipsoidal reflector using back-scattering geometry, and then focused into a 0.32 nm single grating spectrograph through a notch filter.

3. Results and discussion

The effect of reaction temperature on the activity of the LiLaNiO/γ-Al₂O₃ catalyst is shown in figure 1. Ethane and oxygen were almost converted completely (not shown). When the reaction temperature was subsequently increased from 973 to 1123 K, the CO selectivity increased gradually, while the CH₄ selectivity decreased. Under the constant space velocity by keeping the flow rate of C₂H₆ (10 ml/min) and the total flow rate (50 ml/min) of O₂ and He constant, the respective flow rates of O₂ and He were changed to obtain different C₂H₆/O₂ ratios. The effect of the C₂H₆/O₂ ratio on the activity of the LiLaNiO/γ-Al₂O₃ was investigated (figure 2). As the C₂H₆/O₂ ratio changed from 0.56 to 0.94, the CO selectivity increased from 80 to 94%, and the CH₄ selectivity changed slightly. However, with the C₂H₆/O₂ ratio increasing from 0.94 to 1.54 the CO selectivity decreased slowly, while the CH₄ selectivity increased drastically. There exists an optimum value at C₂H₆/O₂ ratio of 0.94, where the CO selectivity is 94%. Under 1123 K and an O₂/C₂H₆/He ratio of 1.06/1/4, the influence of space velocity on the activity of the LiLaNiO/γ-Al₂O₃ was also studied (figure 3). The results indicated that the influence of space velocity was not appreciable, e.g., the LiLaNiO/γ-