



Partial oxidation of methane to syngas on bulk NiAl₂O₄ catalyst. Comparison with alumina supported nickel, platinum and rhodium catalysts

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ABSTRACT

In this work the catalytic performance of NiAl₂O₄ catalyst in the partial oxidation of methane (CH₄(1)/O₂(0.5)/N₂(8.5) and 4800 mL CH₄ g⁻¹ h⁻¹) was investigated. This bulk catalyst resulted more active (70% conversion at 625 °C) than alumina supported nickel catalysts prepared by conventional impregnation (11%Ni/Al₂O₃-30% conversion at 625 °C and 14%Ni/Al₂O₃-65% conversion at 625 °C) and a commercial platinum catalyst (1%Pt/Al₂O₃-30% conversion at 625 °C). Further, the behaviour of NiAl₂O₄ was comparable to that of a commercial rhodium catalyst (1%Rh/Al₂O₃-75% conversion at 625 °C). Fresh and spent catalysts were characterised by N₂-physisorption, H₂-TPR, UV-vis-DRS, WDXRF, XRD, TGA-MS, TEM and Raman spectroscopy. After catalyst reduction CH₄ conversion over bulk NiAl₂O₄ was associated with the formation of large amounts of metallic nickel crystallites with a relatively small size. Although significant coking was noticed, conversion and selectivity to H₂/CO were not significantly affected after prolonged time on stream.

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1. Introduction

There has been substantial interest in recent years in alternative routes for conversion of natural gas (methane) to synthesis gas, a mixture of CO and H₂, which can be used to produce chemical products with high added values, such as hydrocarbons and oxygenated compounds, or as energy carrier [1–3]. Compared with other sources, natural gas may be one of the cheapest options for hydrogen generation. Today hydrogen is mainly produced via steam reforming of methane, a process highly endothermic and very expensive due to the high heat demand. A promising reaction route, which has recently received great attention, is the catalytic oxidation of methane (POM). This strategy offers many advantages with respect to the conventional steam reforming. It is a weakly exothermic reaction requiring lower energy input and capital costs, it is mechanically simpler without need of any externally fired heaters, and it can operate at low contact times, allowing the use of small reactors. In addition, it provides a syngas with a suitable H₂/CO ratio (equal to 2) for use in production of methanol and synthetic fuels, and the water gas shift reaction produces significant amounts of carbon dioxide in the product gas [4–6].

For effective production of H₂, the role of the reforming catalyst becomes more significant. A number of catalysts have proven to be

active in POM, mainly platinum group metals on various supports, such as Rh, Ru, Pd, Pt and Ir [7–10]. Rh has been reported to be the most active and stable catalyst towards deactivation. However, because of the high cost of noble metal-based catalysts, it is clear that, from the industrial standpoint, the development of cheaper and alternative metal-based catalysts would be desirable. In particular, alumina supported Ni catalysts have been widely investigated because of their lower cost and relatively high activity in the partial oxidation of methane [4,11,12]. The major drawbacks with these catalysts are usually their tendency to form coke deposits and nickel sintering upon reaction during extended time on stream.

When operating at short residence time, a highly active behaviour may require reaction temperatures exceeding 750 °C. This in turn requires a thermal stabilisation of the Ni/Al₂O₃ catalyst at very high temperatures. During preparation Ni²⁺ could disperse on the surface of Al₂O₃ or diffuse into the bulk structure of Al₂O₃ to different extents to form nickel aluminate. As a consequence, the resulting catalyst usually is comprised of a mixture of two nickel phases, namely nickel oxide and nickel aluminate. It is thus of interest to evaluate the impact of this complex interaction between nickel and the alumina support on the catalytic performance. In this sense, some previous studies have focused on evaluating the catalytic behaviour of bulk nickel aluminate spinel in CH₄ reforming reactions [13–15]. It was found that, whilst calcined aluminates did not show appreciable conversion, the reduced forms were remarkably active.

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