

Platinum supported on alkaline and alkaline earth metal-doped alumina as catalysts for dry reforming and partial oxidation of methane

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ABSTRACT

Pt catalysts with low metal loadings (0.02, 0.1 and 0.5 wt%) supported on alkaline (Na and K) or alkaline earth (Mg) metals-doped alumina were tested in the catalytic partial oxidation and dry reforming of methane. Supports were characterized by X-ray diffraction and also by determining their BET surface area, temperature-programmed desorption of CO₂, and isopropanol dehydration; while catalysts were characterized by X-ray diffraction, temperature programmed reduction, tests of cyclohexane dehydrogenation, temperature-programmed oxidation, and transmission electronic microscopy. The presence of the dopants modified the thermal stability of the γ -Al₂O₃ phase by calcination at 1000 °C and the acidity of the support. The $\gamma \rightarrow \theta$ transition took place for K- and Na-doped catalysts, the acidity being almost suppressed. Conversely, the Mg-doped γ -Al₂O₃ was thermally stable, and the catalysts still showed some acidic sites. The catalytic performances in both partial oxidation and dry reforming processes were dependent on the support dopants, with a more notable effect observed at low-noble-metal loadings. K- and Na-doped catalysts showed poor activities in the catalytic partial oxidation reaction, whereas the presence of Mg in the alumina promoted the catalytic activity. In the dry reforming reaction an improvement was found in the catalytic activity for the sample with the highest Pt content; moreover, the K-doped catalysts were slightly more efficient.

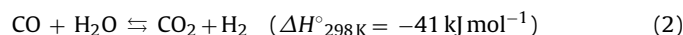
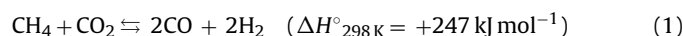
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1. Introduction

The conversion of methane into syngas (CO and H₂) or H₂ is a very important and interesting route for the utilization of natural gas [1–4]. Syngas is an important feedstock for the chemical industry and H₂ can be used as a clean energy source in both fuel cells and automobiles [5]. In addition, as the natural gas reserves are larger than petroleum reserves, the economic aspect is also very favorable [6]. However, since natural gas deposits are frequently far away from the consumption centers [6,7], a good alternative may be its in situ processing into liquid products (gas-to-liquids, GTL), by first transforming the natural gas into syngas (CO + H₂), which is then converted into liquid products [8–12]. The production of syngas is an expensive step, the most expensive one in the GTL process [10,13]. Steam reforming (SR) is the most used process to convert methane on an industrial scale [14]. However, SR has some drawbacks deriving from the significant power requirements (being a highly endothermic process), and the high H₂/CO

molar ratio (3/1) in the syngas thus produced makes it less suitable for GTL processes. For these reasons, autothermal reforming (ATR) and partial oxidation (POX) are used in GTL [8]. In the former, the heat required for the reforming is supplied by the partial internal combustion of the feed, and in order to control the H₂/CO ratio, the composition of the inlet mixture and the operation conditions are varied [15]. Non-catalytic partial oxidation requires high temperatures (1300–1400 °C) to achieve high conversion and a H₂/CO ratio of about 1.7–1.8 [2]. Alternatives to the above-mentioned processes are reforming using CO₂ (dry reforming, DR) and the catalytic partial oxidation (CPO) of methane.

In the first case (DR), the H₂/CO molar ratio close to 1 in the product is more appropriate for use in several chemical processes, such as the manufacture of higher hydrocarbons and oxygenates [16,17]. The main reactions in DR process are:



The first reaction requires high temperatures to favor the thermodynamic equilibrium. However, the main problem of the DR is

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