Catalytic partial oxidation and steam reforming of methane on La$_2$O$_3$–Al$_2$O$_3$ supported Pt catalysts as observed by X-ray absorption spectroscopy

K.O. Rocha$^a$, J.B.O. Santos$^a$, D. Meira$^a$, P.S. Pizani$^b$, C.M.P. Marques$^c$, D. Zanchet$^d$, J.M.C. Bueno$^{a,*}$

$^a$ Departamento de Engenharia Química, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, SP, Brazil
$^b$ Departamento de Física, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, SP, Brazil
$^c$ Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos, SP, Brazil
$^d$ Instituto de Química, Universidade Estadual de Campinas (UNICAMP), C.P. 6154, 13083-970 Campinas, SP, Brazil

A R T I C L E   I N F O

Article history:
Received 3 February 2012
Received in revised form 5 April 2012
Accepted 13 April 2012
Available online 20 April 2012

Keywords:
Pt catalysts
La$_2$O$_3$–Al$_2$O$_3$ oxides
Partial oxidation of methane
Steam reforming of methane
Pt-supported catalysts
In situ XAFS

A B S T R A C T

Structural transformations of Pt supported on Al$_2$O$_3$ or La$_2$O$_3$–Al$_2$O$_3$ were studied by X-ray absorption near edge structure (XANES) at the Pt L$_3$ edge during heating and cooling under partial oxidation of methane (POM) conditions, and by extended X-ray absorption fine structure (EXAFS) under steam reforming of methane (SRM) conditions. Ignition of the POM reaction occurred simultaneously with the reduction of PtO$_2$ to metallic Pt, indicating that the ignition occurs on metallic Pt. When the temperature of the POM reaction was decreased, carbon accumulated on the metallic Pt surface, and the activation of CH$_4$ was suppressed at about 370 °C. Nevertheless, the oxidation of carbon remaining on the metallic Pt surface continued until a temperature of around 270 °C was reached, when oxidation of Pt occurred and the oxidation reactions were extinguished. The EXAFS data obtained during SRM and under H$_2$ suggest that complex alterations in the structure of Pt particles occur with changes of temperature and reactant composition. The SRM activity of Pt catalysts depends on both the access of CH$_4$ to active Pt sites, and the changes in the structure of Pt particles under reaction conditions. For both reactions, Pt supported on La$_2$O$_3$–Al$_2$O$_3$ was more stable than Pt supported on Al$_2$O$_3$, indicating a higher stability of Al$_2$O$_3$ modified with La$_2$O$_3$.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Natural gas, which consists mainly of methane (CH$_4$), is used as a feedstock for the production of syngas or hydrogen by steam reforming of CH$_4$ (SRM), and the syngas produced can be converted into higher hydrocarbons by the Fischer–Tropsch process [1]. However, SRM is highly endothermic, and the H$_2$/CO ratio is higher than the ideal value of 2. A promising alternative method for syngas production is partial oxidation of CH$_4$ (POM), because the process is only mildly exothermic, and the syngas formed has an ideal H$_2$/CO ratio.

POM occurs on several supported metal catalysts [2–8], and the reaction pathway has been the subject of many studies [3–6,9]. These have shown that the reaction mechanism can be described by either indirect [3,6,9] or direct routes [4,5]. The direct route involves the initial formation of CO and H$_2$, whereas the indirect route occurs through total oxidation of CH$_4$ and steam and CO$_2$ reforming of CH$_4$.

A technical difficulty in producing H$_2$ or syngas from CH$_4$ is deactivation of the catalyst by carbon adsorbed on the surface. Catalytic deactivation has been observed during POM on Pt/Al$_2$O$_3$ and Pt/ZrO$_2$ catalysts [10,11]. Carbon is formed on the surface by methane decomposition (CH$_4$ → C$^+$ + 2H$_2$) and CO disproportionation (2CO → C$^+$ + CO$_2$), where C$^+$ is the carbon adsorbed on the surface. Promotion of the catalyst with other oxides has been used in order to minimize the degree of deactivation [10,12]. Works have recently demonstrated that the activity and stability of supported noble metals used for POM are strongly dependent on the support [2,13,14]. For example, Pt/Al$_2$O$_3$ promoted with CeO$_2$, La$_2$O$_3$, and Sm$_2$O$_3$ was active and stable for in excess of 24 h at 800 °C [14]. For Pt/Co–Al$_2$O$_3$ catalysts, the stability was attributed to the oxygen storage capacity and oxygen vacancies near the Pt particles, while LaPt$_3$O$_5$-like sites on Pt/Al$_2$O$_3$–La$_2$O$_3$ catalysts increased the ability to gasify carbon [2].

The characterization of catalyst structure and its relationship with activity studied using in situ spectroscopic techniques has had a strong impact on the development of catalysts for many reactions [15–16]. For instance, POM on supported metal catalysts has been studied by in situ X-ray absorption spectroscopy (XAS) [17–22], and Raman spectroscopy [23]. The ignition process for POM on Pt/Al$_2$O$_3$ catalysts has been investigated at atmospheric pressure using in situ