The role of metal–support interaction on catalytic methane activation

Vesna Havran Mueller, Milorad P. Duduković, Cynthia S. Lo *

Department of Energy, Environmental and Chemical Engineering, Washington University in Saint Louis, One Brookings Drive, St. Louis, MO 63130, USA

A B S T R A C T

In this work, we study CH_4 chemisorption over Pt-containing catalysts at low temperature (200–450 °C) in a fixed bed reactor. We report the systematic investigation of the effect of temperature, support (ceria vs. silica), and Pt content, on the amount of chemisorbed CH_4 and the structure and reactivity of adsorbed CH_x species, as formed during 1 min exposure of the catalyst to the CH_4 flow. The total CH_4 chemisorbed and the state of carbonaceous film were determined by Temperature Programmed Desorption (TPD) and Temperature Programmed Surface Reaction (TPSR), as performed immediately upon catalyst exposure to the CH_4 flow. The hydrogenation of carbon ad-species produced only methane. It was found that the strong metal–support interaction, present in ceria samples, plays an important role in CH_4 conversion, and lends further evidence to the hypothesis that the metal–support interface causes a large spillover of adsorbed C and H species from Pt onto ceria – thus clearing the Pt active sites for further CH_4 dehydrogenation. Not only did the ceria based samples activate up to 5 times more CH_4 than the silica based samples, but the nature of the adsorbed CH_x species and how they bond to the Pt surface varied on different supports. Thus, both the catalyst structure and operating conditions were found to play key roles in controlling the amounts of chemisorbed CH_4 and the structure and the reactivity of the adsorbed carbonaceous film, so they should be carefully considered when rationally designing catalysts for methane activation and conversion.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Although catalytic activation of methane on supported transition metals has been extensively investigated, there is still no breakthrough technology since most reactions involving methane are thermodynamically and/or kinetically unfavorable. Besides the large amount of energy needed for reaction, a suitable catalyst that would both decrease the energy of activation [1] and achieve a suitable product distribution has yet to be developed. Controlling the degree of CH_4 dehydrogenation, without the unselective breaking of all four C–H bonds that results in complete oxidation, is a challenging task [2,3]; as such, this will require judicious design of catalysts and proper understanding of reaction pathways on catalytic surfaces.

CH_4 has been shown to chemisorb on various transition metals at moderate temperatures and decompose to carbonaceous adspecies (i.e., CH_x species, where $x = 0$, 1, 2 or 3) and hydrogen (H_2) at higher temperatures [4,5]. This dissociation depends on the structure and composition of both the metal nanoparticles and their support, along with the operating conditions (e.g., exposure time, temperature, and pressure). It has been reported that above 130 °C, the dehydrogenation of CH_x species becomes fast and that elemental carbon ($x = 0$) is more stable, forms strong bonds with the metal surface [4]. Depending on the temperature, three forms of deposited carbon can exist on the metal surface: (1) C_α-reactive, mobile or chemisorbed carbon, (2) C_β-surface amorphous carbon, and (3) C_γ-inactive, strongly bonded graphitic carbon [4,6]. Determining the conditions that result in the formation of more reactive CH_x and carbon species, and avoiding formation of graphitic unreactive carbon which causes catalyst deactivation, is of great importance in selective methane oxidation reactions (e.g. CH_3 species are assumed to promote production of acetic acid [7]) For example, in a two-step flow reaction of methane with carbon dioxide, the state of the adsorbed carbonaceous film, upon exposure of the catalyst on support to the methane flow, can strongly affect the product distribution [7–9]. Ding et al. [9] also established based on the maximum H_2 evolution rates subsequent to CH_4 chemisorption, that the optimum duration of exposure to the methane flow is around 1 min, during which the surface reaction (i.e., methane dissociation to surface carbonaceous species) is completed so that the co-reactant (e.g., CO_2) may be introduced. Thus, catalysts that can both chemisorb CH_4 and yield more hydrogen-rich carbonaceous species seem to be most promising for exhibiting improved selectivity towards certain oxygenates.

* Corresponding author. Tel.: +1 314 935 8055.
  E-mail address: clo@wustl.edu (C.S. Lo).

Belgued et al. [4,10] designed a two-step experiment that provides insight into the structure of adsorbed carbonaceous species on a Pt/silica catalyst after exposure to methane flow; their experiment consists of Temperature Programmed Desorption (TPD) followed by Temperature Programmed Surface Reaction (TPSR). During TPD/TPSR, the adsorbed carbonaceous species are reacted off the catalyst surface and exit the reactor, either through methane back-formation or as heavier hydrocarbons. Since the shapes of TPD and TPSR profiles are very sensitive to the conditions of the exposure, they constitute a fingerprint of the carbon ad-species at the end of the adsorption step [4]. For all catalysts studied (i.e., EUROPT-1, [4,10]), Ru/SiO$_2$ [11] Rh-CeO$_2$/SiO$_2$ [12]) several factors, including increases in temperature and duration of exposure to the CH$_4$ flow and CH$_4$ partial pressure, were reported to result in measurable increases in the total amount of chemisorbed CH$_4$. Their TPD and TPSR profiles indicated, in the case of Pt, that no more reactive C1 species remained after TPD; only some greatly H-deficient carbonaceous fragments stayed on the Pt surface. The H-deficiency of these ad-species increased with the temperature and exposure time to CH$_4$ flow during the original chemisorption experiment. The researchers also noticed that, for all investigated metals, the evolution of H$_2$ at temperatures above 100–150 °C occurred within the first minute of exposure to CH$_4$ flow; similar to findings in the studies by Ding et al. [9].

In a study of methane activation over Pt/SiO$_2$, Pt/Al$_2$O$_3$ and Pt/ZrO$_2$, Martins et al. [5] found that when Pt/silica and Pt/alumina were mixed with MoO$_3$, the hydrogenation of C ad-species was enhanced. The presence of MoO$_3$ improved the mobility of CH$_x$ ad-species, which favors C–C bond formation. Also, as reported earlier, Mo suppressed the formation of nonreactive adsorbed graphitic layers during the dissociative adsorption of CH$_4$ [5]. When a noble metal is supported on reducible metal oxides, such as CeO$_2$, TiO$_2$, Nb$_2$O$_5$ and La$_2$O$_3$, the metal–support interaction can strongly affect the nature of the active sites [13]. In their study of H$_2$ production from natural gas, Odier et al. [14] attributed the huge difference in the activity of Pt/silica and Pt/ceria to the large spillover of H$_2$ and carbonyls to the ceria support, which liberates the Pt sites for further methane activation This is in accordance with the DFT analysis of CH$_4$ adsorption over Pt nanoclusters on silica and ceria performed by Cheng et al. [15] who proposed that increased electron density at both the low-coordinated Pt sites and oxygen vacancies at the metal–support interface – present in Pt–ceria, but absent in Pt–silica, – contribute to the enhanced catalytic activity.

There are no systematic investigations of the effect of ceria on the structure and distribution of adsorbed carbonaceous species after methane chemisorption under various operating conditions. Studying the effect of the catalyst structure (e.g., support, Pt loading), and the operating conditions (e.g., temperature) on both the amount of chemisorbed CH$_4$ and the structure and reactivity of the adsorbed carbonaceous film is of importance in advancing our knowledge about methane activation and rational catalyst design for its activation.

2. Experimental

2.1. Catalyst preparation

Supported Pt catalysts were prepared by an incipient wetness method. The ceria support was synthesized by precipitation from Ce(NO$_3$)$_3$ × 6H$_2$O (Sigma–Aldrich) aqueous solution, while adding NH$_3$ × H$_2$O solution under vigorous stirring at 60 °C until the pH of the mixture was greater than 9. The precipitate was then aged in the mother liquid for 4 h and washed with deionized (DI) water three times. The solid obtained by centrifugation was dried at 100 °C overnight and calcined at 450 °C for 4 h in air. Davicat SI 1301 (Grace

Davison) was used as the silica support. Corresponding amounts of Pt(NH$_3$)$_4$(NO$_3$)$_2$ salt (Sigma–Aldrich) were dissolved in DI water for the preparation of the 0.3 and 1.7 wt% ceria samples, and for the 1.7 wt% silica sample. Upon wetting with precursor solution, the samples were dried overnight at 100 °C.

2.2. Catalyst characterizations

The actual loading of Pt on the catalyst samples was determined using elemental chemical analysis on a Siemens SRS-300 X-ray fluorescence (XRF) spectrometer with a rhodium tube at 55 kV. The specific surface area was determined by the BET method, using N$_2$ adsorption measurements at liquid nitrogen temperature. Before analysis, the samples were degassed for 24 h at 100 °C in vacuum. H$_2$ chemisorption at 40 °C in a Quantachrome Autosorb 1-C apparatus was used for determining Pt dispersion, by assuming a 2:1 ratio of Pt:H$_2$, and estimating Pt size.

Temperature programmed reduction (TPR) experiments were performed over pre-oxidized catalysts, which consisted of around 200 mg of 1.7% Pt/ceria and 100 mg of 1.7% Pt/silica. Samples were first degassed under helium flow at 200 °C for 1 h. Reduction was performed under a flow of a 5% H$_2$/Ar mixture (50 ml/min), using a heating rate of 10 °C/min. Both dispersion and TPR measurements were performed by Quantachrome Instruments.

2.3. Apparatus

The catalyst samples (0.2 g) were sandwiched between quartz wool in a U-shape stainless steel packed bed reactor, of 4 mm inner diameter and 44 cm total length. The gas flows were controlled by two Brooks flowmeters. All gases (N$_2$, H$_2$ and CH$_4$) used were ultra-high purity (Airgas USA, LLC). The gasses were preheated by flowing first through the stainless steel coiled tube (0.25 cm diameter), which was placed in the furnace together with the reactor and later connected to it. The temperature of the catalyst bed was controlled by the Quantachrome apparatus. A K-type thermocouple was placed in the reactor with its tip touching the catalyst bed. Gasses exiting the reactor were sent to a gas chromatograph (SRI 8610C) equipped with a stainless steel Molesieve column (0.91 m length, 0.32 cm thickness, 13x 80/100 molecular sieve) and two detectors, TCD and FID, connected in series.

2.4. Procedures

2.4.1. Pretreatment of the catalyst

Each sample was first exposed to N$_2$ flow (50 ml/min) up to 100 °C at the heating rate of 6 °C/min, and then to H$_2$ flow (50 ml/min) up to 450 °C at the same heating rate. The sample was then kept at 450 °C for 15 h under the same H$_2$ flow. The adsorbed H$_2$ was removed by a N$_2$ purge, and the reduced sample was then cooled to the reaction temperature, also under N$_2$ flow. The sample was then exposed to CH$_4$ flow. Between the experimental runs, the sample was always heated up at the same rate to 100 °C under N$_2$ flow (50 ml/min), and then H$_2$ flow (50 ml/min) up to 450 °C, where it was kept for 30 min. This length of time was sufficient to ensure there were no carbonaceous species on the surface before the new exposure to methane. The sample was always purged with N$_2$, to remove the adsorbed H$_2$ before the reaction step and exposure to CH$_4$ [4].

2.4.2. Determination of the amount of chemisorbed CH$_4$

The amount of chemisorbed CH$_4$ was obtained by following a slightly modified protocol from that described in Belgued et al. [4]. The catalyst was first exposed to a CH$_4$ flow of 200 ml/min for 1 min, as this has been reported to be the optimal duration to