Molecular Catalysis 435 (2017) 13–23

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Editor's choice paper

Selective oxygen species for the oxidative coupling of methane

Ilho Kim[a,1], Gihoon Lee[a,1], Hyon Bin Na[a], Jeong-Myeong Ha[b], Ji Chul Jung[a,*]

[a] Department of Chemical Engineering, Myongji University, Yongin 17058, Republic of Korea
[b] Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

ARTICLE INFO

Article history:
Received 30 December 2016
Received in revised form 8 March 2017
Accepted 9 March 2017

Keywords:
Selective oxygen species
Methane conversion
Oxidative coupling
Perovskite catalyst
Electrophilic lattice oxygen

ABSTRACT

Herein, we attempt to identify selective oxygen species for the oxidative coupling of methane using lanthanum-based perovskite catalysts ($LaXO_3$, X = Al, Fe, or Ni), which are well-known not only as stoichiometric materials with simple and definite structures but also as materials with outstanding catalytic activities in various methane conversion reactions. The catalytic activities of $LaXO_3$ in the presence or absence of oxygen clearly demonstrated that surface lattice oxygen species are responsible for the selective conversion of methane. More importantly, electrophilic ($LaAlO_3$), moderate ($LaFeO_3$), and nucleophilic ($LaNiO_3$) lattice oxygen species selectively catalyze the oxidative coupling of methane to C_2 hydrocarbons, the direct partial oxidation of methane to carbon monoxide, and the methane combustion to carbon dioxide, respectively. In addition, adsorbed oxygen species originating from gas-phase oxygen play roles both in converting methane to CO_x and in filling surface lattice oxygen vacancies, which are caused by the reaction of lattice oxygen and methane. Finally, we concluded that electrophilic lattice oxygen species and the facile filling of surface lattice oxygen vacancies by gas-phase oxygen are key factors for the systematic design of efficient catalysts for the oxidative coupling of methane.

1. Introduction

The conversion of methane into value added chemicals has been a consistently important issue in the area of catalysis research. Recently, advances in technology used for the production of shale gas, which mainly consists of methane gas, have triggered more intensive studies on catalytic methane conversion [1–5]. Methane has significant potential for conversion into various valuable chemicals and fuels [6–10]. However, its chemical stability limits its application as a starting material in catalytic reactions. Moreover, selectivity is a difficult problem to solve for methane conversion.

To overcome these problems, many researchers have dedicated significant effort to strategies involving indirect methane conversion via synthesis gas (CO and H_2), which is very versatile and can be easily obtained from methane steam reforming [11–14]. Nonetheless, direct methane conversion to value added chemicals such as methanol, ethylene, and aromatics are considered the best way to efficiently use methane gas because of their simple one-step catalytic production of target products [15–17]. In particular, the oxidative coupling of methane (OCM) to C_2 hydrocarbons has attracted much research attention over the past three decades because ethylene is the most widely used petrochemical globally.

In the OCM catalytic reaction, methane (CH_4) and oxygen (O_2) react over a catalyst exothermically to form C_2 hydrocarbons (ethylene (C_2H_4) and ethane (C_2H_6)), water (H_2O), and heat, according to the following reaction [18].

$$CH_4 + \frac{1}{2}O_2 \rightarrow \frac{1}{2}C_2H_4 + H_2O,\ \Delta H_{800^\circ C} = -139\ \text{kJ/mol}\ CH_4$$

$$CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O,\ \Delta H_{800^\circ C} = -87\ \text{kJ/mol}\ CH_4$$

Although thousands of studies have been undertaken to develop an efficient and selective catalyst for this reaction, there remains a great deal of ambiguity on the identity and nature of the catalytically active sites [19–23]. $Na_2WO_4/Mn/SiO_2$, which is regarded as the best catalyst for the OCM at present, is also not yet fully understood [24]. The complex composition and structure of $Na_2WO_4/Mn/SiO_2$ mean that many studies on this catalyst system have focused on increasing its catalytic activity by varying its composition and the use of various additives. In our opinion, more fundamental research is necessary to clarify the catalytically active sites for the OCM, and accordingly, to design a systematic and efficient catalyst for an economically viable OCM process.

Despite the considerable controversy surrounding the catalytically active sites for the OCM, the majority of researchers agree

---

[*] Corresponding author.
E-mail addresses: jcjung@mju.ac.kr, jcjung98@gmail.com (J.C. Jung).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.mcat.2017.03.012

that surface oxygen species in the metal oxide are closely related to methane conversion [25–27]. They also believe that the OCM consists of two processes: a heterogeneous reaction and a homogeneous reaction. In the heterogeneous reaction, surface oxygen species in the catalyst play a key role in generating a methyl radical by abstracting hydrogen from methane. Once the methyl radicals form, they can be dimerized to C_2 hydrocarbons in the homogenous gas-phase reaction at temperatures above 700 °C [28–31]. Nonetheless, there has been much debate surrounding the identity of the surface oxygen species responsible for hydrogen abstraction from methane, with candidates including chemisorbed oxygen ($O_2{}^{-1}$), dissociative adsorbed oxygen (O^{-1}), adsorbed oxygen ions (O^{2-}), and lattice oxygen (O^{2-}). Also, the nature of the oxygen cycle comprising gas-phase oxygen, oxygen vacancies, and the various above-mentioned surface oxygen species is still unclear [32–37].

To name a few, Y. Osada et al. investigated Y_2O_3-CaO catalysts for the OCM. In this paper, they claimed that superoxide species ($O_2{}^{-1}$) could play an important role in selectively converting methane [32]. According to the study of T. Yang et al., which is about the role of surface oxygen species, superoxide species ($O_2{}^{-1}$) could be also used as selective active sites for methane activation [33]. On the other hand, some publications by R. Spinicci et al. and W. Jeon et al. revealed that lattice oxygen species are more selective for formation of C_2 hydrocarbons in the OCM [34,35]. Also, V. Fleischer et al. recently reported that strongly adsorbed oxygen or lattice oxygen species are responsible for methane activation in the OCM because of its much lower energy level compared to adsorbed molecular oxygen [36].

In this study, we investigated the selective oxygen species for the OCM by evaluating the catalytic properties and performances of three kinds of perovskite catalysts over a wide range of reaction temperatures from 500 to 800 °C in the presence or absence of gaseous oxygen. We selected lanthanum-based perovskite catalysts ($LaXO_3$, X = Al, Fe, or Ni) as model catalysts to investigate the selective oxygen species because they are well-known as stoichiometric materials with simple and definite structures and exhibit outstanding catalytic activities in various methane conversion reactions. Furthermore, their versatility in methane conversion allowed our study to consider several other important catalytic methane conversion reactions, such as methane partial oxidation, methane combustion, and methane reforming reactions. Finally, we thoroughly addressed the identity and function of selective oxygen species for converting methane into C_2 hydrocarbons, carbon monoxide, and carbon dioxide, with the aim of facilitating the systematic design of high-performance catalysts for the OCM.

2. Experimental

2.1. Catalyst preparation

Three kinds of lanthanum-based perovskite catalysts ($LaXO_3$, X = Al, Fe, or Ni) were prepared by a citrate sol-gel method. All chemicals were used directly after purchase without further purification. In a typical synthesis of a $LaXO_3$ catalyst, 2.7 g of lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$, Sigma-Aldrich) and 4.8 g of citric acid ($C_6H_8O_7$, Sigma-Aldrich) were dissolved in 75.0 mL of deionized water. A stoichiometric amount of the X metal precursor was separately dissolved in 25.0 mL of deionized water (2.3 g of aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, Sigma-Aldrich), 2.5 g of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, Sigma-Aldrich), or 1.8 g of nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich) were employed for the preparation of $LaAlO_3$, $LaFeO_3$, or $LaNiO_3$, respectively). The X precursor solution was then added dropwise into the solution containing the lanthanum nitrate and citric acid under vigorous stirring. After stirring the resulting solution at room temperature for 1 h, it was evaporated to obtain a gel. The gel was then dried overnight at 200 °C. After grinding the dried gel, it was finally calcined at 950 °C for 5 h in air.

2.2. Catalyst characterization

The crystalline structures of the prepared catalysts were confirmed by powder X-ray diffraction (XRD) measurement using an X'pert-Pro PAN analytical diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). XRD patterns were recorded within a 2θ range of 5–90°. XRD patterns of the prepared catalysts at 750 °C in air were also obtained using a Rigaku D/max-2200 diffractometer equipped with a high-temperature attachment in order to confirm their thermal stability at the reaction temperature of the OCM.

Specific surface areas were determined using the Brunauer-Emmett-Teller (BET) method using a BELSORP-miniII (BEL Japan). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was also conducted using an ICPS-8100 (Shimadzu) to confirm the chemical composition of the catalysts. X-ray photoelectron spectroscopy (XPS) was performed using a Sigma probe (Thermo VG scientific) equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.71$ eV, 15 kV, 100 W) to measure the O 1s binding energies of the catalysts, which were calibrated based on the C 1s peak at 284.5 eV.

Temperature programmed desorption of oxygen (O_2-TPD) was carried out using a conventional TPD instrument (BELCAT B, BEL Japan) in order to investigate the properties of the oxygen species in the catalysts. Each catalyst (ca. 0.1 g) was charged into a quartz reactor of the TPD apparatus, and then it was pretreated at 800 °C for 2 h in a stream of 5% oxygen in helium (30 mL/min). After cooling the catalyst sample to 100 °C, it was purged with a stream of helium (30 mL/min) for 1 h. The O_2-TPD profile was recorded from 100 to 900 °C at a heating rate of 5 °C/min. The desorbed oxygen was detected using a thermal conductivity detector (TCD).

2.3. Catalytic reaction

The oxidative coupling of methane was performed using a continuous flow quartz reactor with an internal diameter of 6 mm. The catalyst was loaded by closing the upper and lower ends of the catalyst with quartz wool. Also, the empty space of the reactor was filled with zirconia–silica ceramic beads. The reactor was heated to 500 °C under nitrogen flow, and the feed was then changed to the reactant feed (CH_4:O_2:N_2 = 4:1:1, *v*/*v*/*v*). The total flow rate of the reactant feed was fixed at 20 mL/min with a gas hourly space velocity (GHSV) of 10,000 h^{-1}. The catalytic reaction was performed in the temperature range of 500 to 800 °C with 50 °C intervals (i.e., 500, 550, 600, 650, 700, 750, and 800 °C). When the reactor reached the desired temperature, it was isothermally maintained at that temperature for 40 min. Afterwards, the catalytic activity was finally confirmed by using a cold trap to remove water vapor produced during the reaction and an on-line gas chromatography system (YL-6500, Younglin) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) to analyze the dry products. A carboxen-1000 column was used to separate the reaction products. Methane and C_2 hydrocarbons were detected by the FID, whereas CO and CO_2 were detected by the TCD. The yield of C_2 hydrocarbons was obtained by multiplying methane conversion and C_2 selectivity.

$$Methane\ conversion\ (\%) = \frac{moles\ of\ CH_4\ consumed}{moles\ of\ CH_4\ in\ the\ feed} \times 100$$

$$C_2\ Selectivity\ (\%) = \frac{2\ \times\ moles\ of\ C_2\ hydrocarbons}{moles\ of\ CH_4\ consumed} \times 100$$