

Research paper

TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst for oxidative coupling of methane: Solution combustion synthesis and MnTiO₃-dependent low-temperature activity improvement

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ABSTRACT

The Mn₂O₃-Na₂WO₄/SiO₂ catalyst is the most promising one among the enormous catalysts for the oxidative coupling of methane (OCM) but only at above 800 °C. No doubt that lowering temperature of the OCM process is at the forefront of this catalysis field. A promising low-temperature active and selective TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst, consisting of 6 wt% TiO₂, 6 wt% Mn₂O₃, 10 wt% Na₂WO₄ and SiO₂ in balance, is developed by solution combustion synthesis (SCS) method. This catalyst is capable of converting 20% CH₄ with 70% selectivity to C₂-C₃ hydrocarbons even at 700 °C (catalyst bed temperature) and is stable for at least 250 h without deactivation sign, for a feed gas of 50% CH₄ in air using a gas hourly space velocity of 8000 mL g_{cat}⁻¹ h⁻¹. In contrast, the non-TiO₂-doped SCS catalyst is almost inactive at 700 °C whereas it can achieve reactivity (~24% CH₄ conversion and ~74% C₂-C₃ selectivity) comparable to the TiO₂-doped one at 800 °C. XRD and Raman results evidently reveal that the formation of MnTiO₃ during the OCM process appears to be important for the low-temperature OCM activity improvement by TiO₂-doping.

1. Introduction

With the ever-growing resource and world output of natural gas and shale gas, methane conversion into the value-added chemicals and fuels has received more and more attentions from the worldwide petrochemical and energy industries, in order to alleviate our strong dependence on depleting oil resource [1,2]. Particularly, light olefins, the key building blocks in modern chemical industry, need an urgent production shift from oil to methane. Up to now, methane has been industrially converted into olefins in an indirect route, where methane is firstly and forcibly broken into the syngas (i.e., CO and H₂) through the catalytic steam or autothermal reforming at above 700 °C, followed by large-scaled conversion to methanol and then to olefins [3–5]. Additionally, syngas could also be directly converted into olefins in the presence of solid catalysts, such as the very recently reported bifunctional ZnCrO_x-SAPO catalyst [6] and the cobalt carbide nanoprisms [7] with outstanding selectivity under mild conditions. However, the syngas route is negatively energy-costing and such indirect manner causes low atom-utilization efficiency. Therefore, the direct methane conversion into olefins is highly desirable and a large number of researches have been dedicated for a couple of decays to achieving this

goal.

The oxidative coupling of methane (OCM) is considered to be a promising route to directly convert methane into C₂-C₃ hydrocarbon products in the presence of molecular oxygen. It has been well indicated from many studies that OCM is a sequential process combining the heterogeneous-catalysis and homogeneous-coupling to achieve the methane-to-olefins transformation [8–10]. The OCM catalysts aim to generate methyl radicals (CH₃·) and avoid deep oxidation (i.e., to form CO, CO₂, and H₂O) over their surface [11,12]. Therefore, the most critical performance of OCM catalyst is able to generate selective surface oxygen radicals that act as the active sites for generating CH₃· [13–15]. Great attempts have been making to setup a catalyst recipe with such properties from the simple and complex oxides of alkaline, alkaline earth, and rare-earth elements [16–20]. Hundreds of catalysts have been examined aiming to favor C₂-C₃ selectivity and suppress overoxidation, such as the representative Li/MgO [21,22] and La-based oxides catalysts [23,24]. Li in Li/MgO catalyst acts as a structural modifier to enhance the catalyst OCM performance [21], but suffers from its loss during the long-term running [22]; the La-based catalysts suffer from the relatively lower C₂-C₃ selectivity. Among these catalysts, the Mn₂O₃-Na₂WO₄/SiO₂ is considered to be the most promising one, in

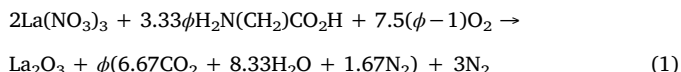
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terms of 20 ~ 30% methane conversion with 60 ~ 80% C₂-C₃ selectivity and in particular hundreds of hours stability [25]. However, this catalyst must be operated at above 800 °C and the slight reduction of temperature to below 800 °C will deteriorate sharply the catalyst activity even quench the OCM reaction [26].

In order to enhance the low-temperature performance of the Mn₂O₃-Na₂WO₄/SiO₂ catalyst, enormous work has been carried out on catalyst preparation and additive modification. The Mn₂O₃-Na₂WO₄/SiO₂ catalyst is usually prepared by the traditional methods such as incipient wetness impregnation, mixture slurry, and sol-gel methods [27]. Recently, solution combustion synthesis (SCS) strategy becomes more and more attractive to prepare homogeneous, high-purity, and complex nanostructured metal-oxides catalysts [28]. Compared to the traditional methods, SCS is a one-step method by self-propagating high-temperature synthesis with the raw materials mixed in liquid phase [29–31]. For example, the typical reaction between metal nitrate and glycine for the preparation of nanostructured La₂O₃ catalyst is shown by Eq. (1), where ϕ represents the fuel/oxidizer ratio: ϕ of 1 indicates the stoichiometric ratio that no more molecular oxygen is required; ϕ below 1 implies that molecular oxygen is generated; while ϕ above 1 means that molecular oxygen is needed [32]. Notably, modulating synthesis parameters such as fuel/oxidizer ratio and the property of fuels can tune the structure and texture of the as-synthesized catalyst [33,34]. Recently, the SCS method has been reported to be successfully applied to synthesize several promising OCM catalysts such as Sr-Al complex oxides, La₂O₃, La-Sr-Al complex oxides, and Mn₂O₃-Na₂WO₄/SiO₂ [35], with improved C₂-C₃ yield. In particular, the SCS-prepared Mn₂O₃-Na₂WO₄/SiO₂ catalyst successfully reduces the reaction temperature from above 800 °C for the regularly-prepared counterparts to 750 °C along with high C₂-C₃ yield of ca. 25% (for a feed gas of CH₄:O₂:N₂ = 2:1:0.63). In addition, Ce and La can also be easily introduced into the Mn₂O₃-Na₂WO₄/SiO₂ catalyst by SCS method [35,36], which generates more reactive oxygen to further enhance the catalyst performance.



Besides opening up new preparation method, additive modification is another aspect to promote the catalyst low-temperature performance [37–39]. As mentioned above, activating oxygen molecules into desirable reactive oxygen species on the catalyst surface is a critical step that induces the methane activation to produce CH₃· and then C₂-C₃ products. Freund et al. [37] reported a highly ordered CaO film modified with Mo²⁺, and supposed that the generated superoxide anions (O₂^{·−}) attributes to methane activation. Trunschke et al. [38] provided the Fe and Cu co-doped polycrystalline MgO, which can effectively activate oxygen to produce peroxy (O₂^{2−}) species for promoting the ethane or ethylene formation. Therefore, a question jumping out is whether the OCM reaction temperature is dominated by the O₂ activation temperature. If so, making efforts to lower the O₂ activation temperature by additive modification seems to be another key to improving the low-temperature activity for the Mn₂O₃-Na₂WO₄/SiO₂ catalyst.

In this paper, we present a strategy to introduce TiO₂ into the Mn₂O₃-Na₂WO₄/SiO₂ catalyst by SCS method to prepare TiO₂-doped counterpart, with the aim to enhance the low-temperature catalytic activity and selectivity for the OCM process. The catalyst preparation parameters (including Ti-precursors, fuel/oxidizer ratio, calcination temperature, and active component loadings) and OCM reaction conditions (including CH₄/O₂ molar ratio, gas hourly space velocity (GHSV), and reaction temperature) were systematically investigated. Excitingly, the reaction temperature (the real catalyst bed temperature in present work) could be reduced from > 800 °C for the regular literature Mn₂O₃-Na₂WO₄/SiO₂ catalyst to 700 °C after TiO₂-doping through the SCS method, achieving 20% CH₄ conversion with 70% selectivity to C₂-C₃. Probing of catalyst phase and surface, using XRD and Raman, reveal that the in-situ formation of MnTiO₃ is paramount

for the enhancement of catalyst low-temperature activity for the OCM process.

2. Experimental

2.1. Materials

All chemicals in this work were purchased from Sinopharm Chemical Reagent Co., Ltd, China: sodium tungstate dihydrate (AR), 50 wt% manganese(II) nitrate aqueous solution (AR), tetraethyl orthosilicate (AR), tetrabutyl titanate (CP), titanium isopropoxide (CP), titanium *n*-propoxide (CP), and 65 wt% nitric acid aqueous solution (AR). They were all used as received.

2.2. Catalyst preparation

Regular Mn₂O₃-Na₂WO₄/SiO₂ catalyst and the TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst were prepared by the reported SCS method [35,36]. Mn(NO₃)₂ aqueous solution and Na₂WO₄ were employed as precursors for Mn-, Na- and W-containing components. Tetraethyl orthosilicate and titanate (titanium isopropoxide, titanium *n*-propoxide or tetrabutyl titanate) were the precursors for SiO₂ and TiO₂ compounds while serving as fuels in the SCS process. For the SCS method, HNO₃ was used as oxidizer. The ϕ (i.e., fuel/oxidizer ratio) was tuned in the range from 1 to 3 by adding appropriate amount of 65 wt% HNO₃ aqueous solution. In brief, the Mn, Na, and W precursors were mixed together with the tetraethyl orthosilicate and titanate in deionized water in a ceramic bowl, and appropriate amount of HNO₃ according to the ϕ value was added subsequently. The mixture was then continuously stirred at 80 °C until it was transformed into the sticky gel. Subsequently, the ceramic bowl with such gel was transferred into a muffle furnace. When heating the gel to 300 °C, self-ignition combustion took place to form brown solid product. A stainless steel screen with 140 mesh opening was used for covering the ceramic bowl to prevent the formed powders from escaping. All as-synthesized catalysts were calcined at 500–900 °C in air for 4 h, crashed and sieved to collect 100–120 mesh fine particles for use in OCM reaction testing. The catalyst was denoted as a-TiO₂-b-Mn₂O₃-c-Na₂WO₄/SiO₂- ϕ -x (a, TiO₂ loading; b, Mn₂O₃ loading; c, Na₂WO₄ loading; ϕ , fuel/oxidizer ratio; x, calcination temperature).

2.3. Catalyst characterization

Catalysts were characterized by X-ray diffraction (XRD, Rigaku Ultima IV diffractometer with Cu K α radiation (35 kV and 25 mA); Japan), scanning electron microscopy (SEM, Hitachi S-4800; Japan) equipped with an energy dispersive X-Ray fluorescence spectrometer (EDX, Oxford; UK) and inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP Thermo IRIS Intrepid II XSP; USA). Specific surface area (SSA) was determined from N₂ adsorption isotherm at −196 °C using standard Brunauer-Emmett-Teller (BET) theory on a Quanta chrome Autosorb-3 B instrument (USA). Raman measurements were carried out using a Raman spectrometer (Renishaw inVia) with a 532 nm semiconductor laser as excitation and the samples were scanned from 800 to 2000 cm^{−1}. It is equipped with a charge coupled device (CCD) camera enabling microanalysis on a sample point.

2.4. Reactivity tests

OCM reaction was performed in a fixed-bed quartz tube reactor (400 mm length and 16 mm inner diameter straight cylindrical tube) under atmospheric pressure. The catalyst of 1.0 g was loaded in the reactor and the catalyst bed thickness was approximately 10 mm in each OCM reaction testing. The reactants, methane (99.99%), oxygen (99.999%), and nitrogen (99.99%) as dilution, were co-fed into the reactor by three calibrated mass flow controllers. GHSV was varied in

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