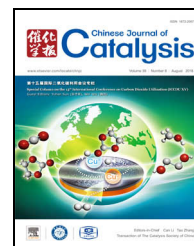


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## Article

# Oxidative coupling of methane: $\text{MO}_x$ -modified ( $\text{M} = \text{Ti}, \text{Mg}, \text{Ga}, \text{Zr}$ ) $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts and effect of $\text{MO}_x$ modification



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## ABSTRACT

$\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$  is considered as the most promising catalyst for the oxidative coupling of methane (OCM) process; however, it only has a better catalytic performance over 800 °C. To improve its low-temperature performance, an attempt has been made to modify the  $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst using  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{ZrO}_2$ . Among the synthesized catalysts, the  $\text{TiO}_2$ -modified  $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst shows markedly improved low-temperature OCM performance, achieving a high  $\text{CH}_4$  conversion of ~23% and a good  $\text{C}_2\text{-C}_3$  selectivity of ~73% at 700 °C (the catalyst bed temperature), along with promising stability for at least 300 h without signs of deactivation. In comparison with the unmodified  $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$  catalyst, the  $\text{TiO}_2$  modification results in significant improvement in the low-temperature activity/selectivity, whereas the  $\text{MgO}$  modification has almost no impact and the  $\text{Ga}_2\text{O}_3$  and  $\text{ZrO}_2$  modifications have a negative effect. The X-ray diffraction (XRD) and Raman results reveal that the formation of a  $\text{MnTiO}_3$  phase and a  $\text{MnTiO}_3$ -dominated catalyst surface is crucial for the improvement of the low-temperature activity/selectivity in the OCM process.

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## 1. Introduction

Methane is the major component of natural gas and is attracting increasing attention, owing to its lower cost and greater availability compared with crude oil [1]. However, it has four strong and localized C–H bonds (with a bond energy of 413 kJ/mol), and the absence of low-energy empty orbitals as well as the high-energy filled orbitals makes methane molecule difficult to readily participate in chemical reactions. Therefore, approaches to efficiently convert methane to high-value chemicals have been receiving increasing interest from petrochemical and energy industries worldwide. At present, methane is

industrially transformed into bulk chemicals via an indirect route. In this approach, methane is first converted to syngas ( $\text{CO}$  and  $\text{H}_2$ ) at an elevated temperature (> 700 °C) [2,3], and the syngas is then transformed into a wide spectrum of hydrocarbons or alcohols using a catalyst [4,5]. However, such indirect route is energy-intensive and expensive, and it would be preferable to convert methane to chemicals via a direct route. Unfortunately, the direct oxidative conversion of methane to chemicals such as methanol is thermodynamically feasible, but kinetically difficult [6,7]. Moreover, methanol and some other products, which are more reactive than methane, are prone to be deeply oxidized by oxygen to  $\text{CO}$  or  $\text{CO}_2$  during the reaction.

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Therefore, great efforts have been devoted to the direct conversion of methane to the desired chemicals, in order to make the direct route economically competitive with the indirect route.

Oxidative coupling of methane (OCM) is one of the direct routes for converting methane to ethane, ethylene, propane, and propene (namely, to C<sub>2</sub>–C<sub>3</sub> hydrocarbons), as well as to CO and CO<sub>2</sub> formed as undesired by-products; however, this process represents a great challenge, because methane is very stable and difficult to activate. Hundreds of OCM catalysts, after the initial one developed by Keller et al. [8], have been synthesized in order to suppress the total oxidation of methane and increase the C<sub>2</sub>–C<sub>3</sub> yield. Catalyst properties such as basicity [9], specific surface area [10], and reaction conditions [11] have been systematically investigated in detail and found to play important roles in achieving the optimal C<sub>2</sub>–C<sub>3</sub> yield. Many studies have indicated that the OCM is a complicated process, involving heterogeneous catalysis and homogeneous coupling reactions to transform methane into olefins [12–14]. The OCM catalysts aim to generate more methyl radicals (CH<sub>3</sub>·) and avoid the deep oxidation of methane to form CO, CO<sub>2</sub>, and H<sub>2</sub>O on their surface [15,16]. Therefore, selective surface oxygen species with appropriate oxygen mobility, acting as active sites for generating CH<sub>3</sub>· species, are the most critical features of the OCM catalysts [17–19]. Several traditional catalyst systems show high OCM activity, such as simple, complex, or mixed oxides of alkaline, alkaline-earth, and rare-earth oxides [20–25]. Lithium-modified magnesia (Li/MgO), where [Li<sup>+</sup>O<sup>2-</sup>] centers are produced to efficiently generate CH<sub>3</sub>· from CH<sub>4</sub>, is an early example of a typical OCM catalyst; however, this material is rapidly deactivated owing to the loss of Li [26]. Lanthanide oxides in both pure and modified forms [27,28], whose surface oxygen vacancies are responsible for generating reactive oxygen, are another type of representative OCM catalysts; however, they show relatively lower selectivity toward C<sub>2</sub> and C<sub>3</sub> products. Among the enormous catalysts, multicomponent systems typically show better performance compared to pure metal oxide-based ones [29,30]. In particular, Mn<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>, first discovered in 1992 by Fang et al. [31,32], is one of the most effective and stable catalysts, delivering 20%–37% CH<sub>4</sub> conversion and 65%–80% C<sub>2</sub>–C<sub>3</sub> selectivity in a single-run reaction at 800–900 °C [31–35]. Following that discovery, the preparation or modification, catalytic mechanism, and microkinetic modeling of OCM catalysts have been extensively studied [36–39]. Recently, a method for the direct conversion of methane to light olefins and aromatics in the absence of molecular oxygen (O<sub>2</sub>), using special catalysts, has been developed. Bao and coworkers [40] reported a single-atomic iron catalyst embedded in a silica matrix (Fe@SiO<sub>2</sub>) with promising methane conversion and light olefins selectivity. However, the corresponding reaction temperature for the non-oxidative methane conversion process is as high as 1100 °C; therefore, the commercial prospects for this process may be hampered by the ultrahigh reaction temperature involved. Despite these advances, the non-selective oxidation [41], and especially the high reaction temperature and loss of active component at such temperature [42], are still the key obstacles to

overcome in order to realize the industrial applications of these systems.

Previous studies of the total and selective oxidation of methane suggest that the low-temperature conversion of methane can be achieved [43,44]. For example, methane can be selectively oxidized to methanol over the FeZSM-5 catalyst at a low temperature of 200–300 °C [45], and its catalytic combustion can take place over oxide catalysts at 400–600 °C [46]. Recently, Hibino and coworkers [47] investigated the direct oxidation of methane to methanol using a fuel cell-type reactor with V<sub>2</sub>O<sub>5</sub>/SnO<sub>2</sub> as anode, and a high methanol production with 88.4% selectivity was obtained at 100 °C. It was revealed that methanol was produced by the reaction of methane with active oxygen species generated over the V<sub>2</sub>O<sub>5</sub> catalyst. These results indicate that, despite the strong C–H bonds of methane, its selective oxidation temperature can be effectively reduced if molecular oxygen is properly activated. More recently, Tao and coworkers [48] reported an interesting NiCo<sub>2</sub>O<sub>4</sub> catalyst capable of completely oxidizing methane in the temperature range of 350–550 °C. The interesting aspect of this work is that the mixed oxide compound can activate oxygen more readily than the single oxide. In fact, a TiO<sub>2</sub>-modified Mn<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst has been previously reported by our group, and the MnTiO<sub>3</sub>-driven low-temperature [Mn<sup>3+</sup>↔Mn<sup>2+</sup>] chemical cycle for O<sub>2</sub> activation was found to be responsible for the improvement of the low-temperature OCM performance of the TiO<sub>2</sub>-modified catalyst [49,50]. Inspired by this interesting finding, we considered whether some other metal oxides such as MgO, Ga<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>, which can react with MnO<sub>x</sub> to form mixed oxides similar to MnTiO<sub>3</sub> when used as additives, could also show the ability to improve the low-temperature OCM performance of Mn<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>. Test results show that the TiO<sub>2</sub>-modified Mn<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst still delivers the best low-temperature OCM performance, with ~23% CH<sub>4</sub> conversion and ~73% C<sub>2</sub>–C<sub>3</sub> selectivity at 700 °C, owing to the formation of MnTiO<sub>3</sub> during the OCM reaction, which is consistent with previous results [49,50]. The introduction of MgO has no effect on the Mn<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst, because the newly generated Mg<sub>2</sub>MnO<sub>4</sub> may play the same role as Mn<sub>2</sub>O<sub>3</sub>, achieving the [MnWO<sub>4</sub>↔Mg<sub>2</sub>MnO<sub>4</sub>] chemical cycle instead of the high-temperature [MnWO<sub>4</sub>↔Mn<sub>2</sub>O<sub>3</sub>] one. However, the Ga<sub>2</sub>O<sub>3</sub>- and ZrO<sub>2</sub>-modified catalysts have a negative effect on the OCM performance, because the introduction of Ga<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> facilitates the reduction of Mn<sub>2</sub>O<sub>3</sub> and the subsequent reaction with Na<sub>2</sub>WO<sub>4</sub> to form the relatively inactive MnWO<sub>4</sub>, while completely suppressing the transformation of SiO<sub>2</sub> into α-cristobalite.

## 2. Experimental

### 2.1. Materials

All chemicals (analytical reagent, AR) employed in this work (sodium tungstate dihydrate, 50 wt% manganese(II) nitrate aqueous solution, zirconium nitrate, magnesium nitrate, and gallium nitrate) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Amorphous SiO<sub>2</sub> gel and anatase TiO<sub>2</sub>

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