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Article

Oxidative coupling of methane: 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 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 TiO_2 , MgO , Ga_2O_3 , and ZrO_2 . Among the synthesized catalysts, the 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 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 TiO_2 modification results in significant improvement in the low-temperature activity/selectivity, whereas the MgO modification has almost no impact and the Ga_2O_3 and ZrO_2 modifications have a negative effect. The X-ray diffraction (XRD) and Raman results reveal that the formation of a MnTiO_3 phase and a 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 (CO and 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 CO or 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 C₂–C₃ hydrocarbons), as well as to CO and CO₂ 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 C₂–C₃ 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 C₂–C₃ 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 (CH₃·) and avoid the deep oxidation of methane to form CO, CO₂, and H₂O on their surface [15,16]. Therefore, selective surface oxygen species with appropriate oxygen mobility, acting as active sites for generating CH₃· 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⁺O²⁻] centers are produced to efficiently generate CH₃· from CH₄, 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 C₂ and C₃ products. Among the enormous catalysts, multicomponent systems typically show better performance compared to pure metal oxide-based ones [29,30]. In particular, Mn₂O₃–Na₂WO₄/SiO₂, first discovered in 1992 by Fang et al. [31,32], is one of the most effective and stable catalysts, delivering 20%–37% CH₄ conversion and 65%–80% C₂–C₃ 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 (O₂), using special catalysts, has been developed. Bao and coworkers [40] reported a single-atomic iron catalyst embedded in a silica matrix (Fe@SiO₂) 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 V₂O₅/SnO₂ 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 V₂O₅ 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 NiCo₂O₄ 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 TiO₂-modified Mn₂O₃–Na₂WO₄/SiO₂ catalyst has been previously reported by our group, and the MnTiO₃-driven low-temperature [Mn³⁺↔Mn²⁺] chemical cycle for O₂ activation was found to be responsible for the improvement of the low-temperature OCM performance of the TiO₂-modified catalyst [49,50]. Inspired by this interesting finding, we considered whether some other metal oxides such as MgO, Ga₂O₃, and ZrO₂, which can react with MnO_x to form mixed oxides similar to MnTiO₃ when used as additives, could also show the ability to improve the low-temperature OCM performance of Mn₂O₃–Na₂WO₄/SiO₂. Test results show that the TiO₂-modified Mn₂O₃–Na₂WO₄/SiO₂ catalyst still delivers the best low-temperature OCM performance, with ~23% CH₄ conversion and ~73% C₂–C₃ selectivity at 700 °C, owing to the formation of MnTiO₃ during the OCM reaction, which is consistent with previous results [49,50]. The introduction of MgO has no effect on the Mn₂O₃–Na₂WO₄/SiO₂ catalyst, because the newly generated Mg₂MnO₄ may play the same role as Mn₂O₃, achieving the [MnWO₄↔Mg₂MnO₄] chemical cycle instead of the high-temperature [MnWO₄↔Mn₂O₃] one. However, the Ga₂O₃- and ZrO₂-modified catalysts have a negative effect on the OCM performance, because the introduction of Ga₂O₃ and ZrO₂ facilitates the reduction of Mn₂O₃ and the subsequent reaction with Na₂WO₄ to form the relatively inactive MnWO₄, while completely suppressing the transformation of SiO₂ 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 SiO₂ gel and anatase TiO₂

powder were purchased from Aladdin Industrial Co., Shanghai, China. All chemicals were used as received.

2.2. Catalyst preparation

MO_x -modified Mn_2O_3 - $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts with Mn loading of 4 wt% (with $\text{Mn}(\text{NO}_3)_2$ aqueous solution as precursor) and Na_2WO_4 loading of 10 wt% (with $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as precursor), at a Mn:M molar ratio of 1 (M = Ti, Mg, Ga, or Zr), were prepared by the incipient wetness impregnation (IWI) method [32]. The MO_x additives (except TiO_2 , for which the powder was used directly) were placed into the catalysts using their nitrates as precursors. For example, a mixture of amorphous SiO_2 gel (2.0 g) and TiO_2 powder (0.18 g) was sequentially impregnated with appropriate concentrations of aqueous solutions of 0.38 g $\text{Mn}(\text{NO}_3)_2$ and 0.28 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ at room temperature, followed by constant stirring for 5 h at room temperature, and then by further vigorous stirring for 1 h at 180 °C. The obtained slurry was dried at 100 °C overnight, and then calcined in air at 800 °C for 2 h. The catalyst sample was crushed into a fine powder and sieved to a 40–60 mesh size for use in OCM tests.

2.3. Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV (Japan) diffractometer with $\text{Cu } K_\alpha$ radiation, operated at 35 kV and 25 mA, and inductively coupled plasma-atomic emission spectrometry (ICP-AES, ICP Thermo IRIS Intrepid II XSP, USA). The specific surface area (SSA) of the samples was determined from N_2 adsorption isotherms at –196 °C using the standard Brunauer-Emmett-Teller (BET) method on a Quantachrome Autosorb-3B instrument (USA). Raman measurements were carried out using a Ren-

ishaw inVia spectrometer with a 532 nm semiconductor laser as excitation source; the samples were scanned from 800 to 2000 cm^{-1} . The spectrometer was equipped with a charge coupled device (CCD) camera, enabling microanalysis on a sample point.

2.4. Catalyst tests

The OCM reaction was performed in a fixed-bed quartz tube reactor (600 mm length and 16 mm inner diameter) under atmospheric pressure. The catalyst (0.8 g) was packed in the reactor and the catalyst bed thickness was approximately 10 mm in each OCM reaction. The methane (99.99%) and highly pure air (99.99%) reactants were co-fed into the reactor by two calibrated mass flow controllers. In the present work, the reaction temperature is the catalyst bed temperature, which was monitored by a thermocouple placed in the middle of the catalyst bed. To examine the temperature dependence of the catalyst performance, each catalyst sample underwent the OCM reaction at 800 °C for 2 h and was then tested at selected low-temperature points of 780, 760, 740, 720, and 700 °C. All reaction data were collected after running for at least 0.5 h (ensuring that steady-state conditions were reached) at each temperature. The dry effluent gas was analyzed with an online gas chromatograph (7900A, Techcomp Co., Ltd., China) equipped with a thermal conductivity detector (TCD), using a 30 m DM-Plot Q capillary column (for the separation of CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8) and a 60 m DM-Plot Msieve 5A column (for the separation of N_2 , O_2 , CO , and CH_4) in parallel.

3. Results and discussion

3.1. Morphology and phase composition of the MO_x -modified

Fig. 1. SEM images (A–D, F) and XRD patterns (E) of the MO_x -modified and unmodified Mn_2O_3 - $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. MO_x : (A) TiO_2 , (B) none, (C) MgO , (D) Ga_2O_3 , and (F) ZrO_2 .

Mn₂O₃-Na₂WO₄/SiO₂ catalysts

The as-prepared TiO₂-, MgO-, Ga₂O₃-, and ZrO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalysts, as well as the unmodified one, were characterized by SEM and XRD methods, and the results are shown in Fig. 1. The SEM images show that after calcining at 800 °C all catalysts have similar smooth surfaces, which is a typical characteristic of high-temperature calcination. Notably, the TiO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalyst exhibits a smaller particle size compared to the others (Fig. 1(A–D, F)). The XRD results in Fig. 1(E) show that the phase composition of the catalysts depends on the modification. The α -cristobalite, Na₂WO₄, and Mn₂O₃ phases are clearly observed for the TiO₂-modified catalyst, and a similar composition is found for the unmodified Mn₂O₃-Na₂WO₄/SiO₂ catalyst. In comparison with the latter (Fig. 1(E), patterns (a) and (b)), the Mn²⁺ (from the Mn(NO₃)₂ precursor) is fully oxidized to Mn³⁺ and no MnWO₄ phase is detected in the TiO₂-modified catalyst. In the case of the MgO-modified catalyst, besides α -cristobalite, Na₂WO₄, and Mn₂O₃, a new Mg₂MnO₄ compound (combining MgO and MnO₂) is formed after 800 °C calcination (Fig. 1(E), pattern (c)). On the other hand, MnWO₄ is the dominant phase and no α -cristobalite, Na₂WO₄, or Mn₂O₃ phases are observed in the Ga₂O₃- and ZrO₂-modified catalysts (Fig. 1(E), patterns (d) and (e)). A possible explanation is that the Ga₂O₃ or ZrO₂ additive facilitates the formation of MnWO₄ but hinders the transformation from amorphous SiO₂ to α -cristobalite.

3.2. OCM performance of the catalysts

Fig. 2 shows the temperature dependence of the CH₄ conversion and C₂-C₃ selectivity for the OCM reaction using the

TiO₂-, MgO-, Ga₂O₃-, ZrO₂-modified, and unmodified Mn₂O₃-Na₂WO₄/SiO₂ catalysts, tested using a CH₄:O₂:N₂ (5:1:4 molar ratio) feed gas at a gas hourly space velocity (GHSV) of 8000 mL·g_{cat}⁻¹·h⁻¹. Interestingly, only the TiO₂-modified catalyst maintains its activity/selectivity when the reaction temperature (catalyst bed temperature) is decreased from 800 to 700 °C, achieving 23% CH₄ conversion and 73% C₂-C₃ selectivity at 700 °C. In contrast, the unmodified Mn₂O₃-Na₂WO₄/SiO₂ catalyst shows an almost complete loss of activity/selectivity when the temperature decreases to 700 °C, delivering a low CH₄ conversion of only 2.6% and a C₂-C₃ selectivity of 7.5%. The MgO-modified catalyst has almost no impact on the catalyst performance, showing activity and selectivity values comparable to those of the unmodified catalyst in the whole reaction temperature range studied. The Ga₂O₃ and ZrO₂ modifications cause an obvious deterioration of the catalyst activity/selectivity. For instance, both modified catalysts achieve a CH₄ conversion < 12% with a C₂-C₃ selectivity < 45% even at 800 °C (Fig. 2). The above results clearly show that the TiO₂ modification is essential for the improvement of the low-temperature activity/selectivity of the Mn₂O₃-Na₂WO₄/SiO₂ catalyst in the OCM reaction.

3.3. Insight into the effect of MO_x modification

XRD and Raman measurements were employed to monitor the evolution of the phase and surface composition of the catalysts after undergoing the OCM reaction at 800 °C for 2 h and then at 700 °C for another 0.5 h; the results are shown in Fig. 3. The α -cristobalite, Na₂WO₄, and Mn₂O₃ phases are clearly detected for the TiO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalyst; it is interesting to note that a new clear MnTiO₃ phase ($2\theta = 32.5^\circ$

Fig. 2. Temperature dependence of CH₄ conversion and C₂-C₃ selectivity for the OCM reaction using the MO_x-modified and unmodified Mn₂O₃-Na₂WO₄/SiO₂ catalysts. MO_x: (A) TiO₂, (B) none, (C) MgO, (D) Ga₂O₃, and (E) ZrO₂. Reaction conditions: 0.8 g catalyst, 0.1 MPa, GHSV = 8000 mL·g⁻¹·h⁻¹, CH₄:O₂:N₂ = 5:1:4.

Fig. 3. XRD patterns (A) and Raman spectra (B) of the $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts with and without MO_x modification (MO_x : (a) TiO_2 , (b) none, (c) MgO , (d) Ga_2O_3 , and (e) ZrO_2). (C) Raman spectra of pure Mn_2O_3 , MnWO_4 , MnTiO_3 , Mg_2MnO_4 , and Na_2WO_4 as references.

and 35.2°) is formed during the reaction, while at the same time the signal of the MnWO_4 phase becomes rather weak compared to the unmodified catalyst (Fig. 3(A), patterns (a) and (b)). Moreover, as can be seen from the Raman spectra in Fig. 3(B) and (C), the surface of the TiO_2 -modified catalyst becomes dominated by MnTiO_3 , with clearly detectable TiO_2 and Na_2WO_4 phases, at variance with the MnWO_4 -dominated surface observed for the unmodified catalyst (Fig. 3(B), spectra (a) and (b)). As was previously reported [49,50], in comparison with MnTiO_3 , MnWO_4 is much less effective in the activation of O_2 through the $[\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+}]$ chemical cycle, to form Mn_2O_3 at low temperature (such as 700°C). Combining the above findings with the improved low-temperature activity/selectivity of the TiO_2 -modified catalyst (Fig. 2), we speculate that the formation of MnTiO_3 , coexisting with the α -cristobalite, Na_2WO_4 , and Mn_2O_3 phases, promotes the low-temperature OCM on the TiO_2 -modified catalyst. In the case of the MgO -modified catalyst, the formation of the Mg_2MnO_4 phase takes place in competition with that of MnWO_4 , in association with the disappearance of the Mn_2O_3 phase (Fig. 3(A), patterns (b) and (c)). As a result, weakened MnWO_4 Raman peaks are detected, together with strengthened Na_2WO_4 signals, relative to the peaks of the unmodified catalyst (Fig. 3(B), patterns (b) and (c)). Notably, some unknown Raman peaks are clearly detected for the MgO -modified catalyst at 1010, 810, 700, and 310 cm^{-1} , which do not match those of pure Mg_2MnO_4 and cannot be attributed to either MgO or MnO_2 . The unknown Raman peaks are thought to be related to the Mg_2MnO_4 surface species. A possible explanation is that the Raman signals of Mg_2MnO_4 in the MgO -modified catalyst were strongly affected by other compositions.

It is thus proposed that, unlike the MnTiO_3 phase, Mg_2MnO_4 cannot synergistically interact with α -cristobalite and Na_2WO_4 to promote the low-temperature activity/selectivity of the catalyst. Considering the absence of negative effects of the MgO modification on the catalyst performance (relative to that of the unmodified catalyst), Mg_2MnO_4 is believed to play the same role as Mn_2O_3 , even though the manganese valence state is +4 in the former and +3 in the latter. This can reasonably explain why the MgO modification has almost no impact on the catalytic performance, compared to the unmodified catalyst. A Mg/Ti -modified, SiO_2 -supported $\text{Na}_2\text{WO}_4/\text{Mn}$ catalyst has been reported in a very recent study [52], in which Mg and Ti were

introduced into the lattice structure of α -cristobalite to form $\text{Mg}_{0.05}\text{Ti}_{0.05}\text{Si}_{0.90}\text{O}_n$ during the OCM reaction, and larger amounts of Mn and W species were exposed on the surface to promote the OCM performance. Obviously, Mg and Ti did not enter the lattice of SiO_2 in the case of the MgO - and TiO_2 -modified catalysts investigated in the present work, but combined with Mn to form Mg_2MnO_4 and MnTiO_3 , respectively.

Notably, only MnWO_4 phases are clearly observed besides α -cristobalite in the Ga_2O_3 - and ZrO_2 -modified $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts, whereas the Na_2WO_4 and Mn_2O_3 phases are not detected (Fig. 3(A), patterns (d) and (e)). The role of Na_2WO_4 in improving the selectivity and promoting the transformation from amorphous SiO_2 to α -cristobalite in the OCM reaction has been widely established [49–51]. Therefore, we tentatively speculate that the both Ga_2O_3 and ZrO_2 modifications promote the combination of Mn_2O_3 and Na_2WO_4 to form the MnWO_4 phase during the reaction, while at the same time suppressing the transformation of amorphous SiO_2 to α -cristobalite, owing to the absence of the Na_2WO_4 phase. Moreover, the two catalysts exhibit almost the same surfaces, consisting of a dominant MnWO_4 fraction with a detectable amount of Na_2WO_4 , which are quite similar to the surface of the unmodified catalyst (Fig. 3(B), spectra (d) and (e)). Based on the above results, it can be inferred that the absence of α -cristobalite may be the main cause of the very poor activity and selectivity observed for the Ga_2O_3 - and ZrO_2 -modified catalysts, even compared to the unmodified catalyst (Fig. 2(A)).

In addition, Table 1 summarizes the elemental analyses of the MO_x -modified $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts and their low-temperature N_2 sorption measurements. The

Table 1

SSA and real contents of Mn , W , Na , M ($\text{M} = \text{Ti}$, Mg , Ga , and Zr) of the catalysts.

Catalyst	SSA ($\text{m}^2\cdot\text{g}^{-1}$)	Content ^a (wt%)			
		Mn	W	Na	M
TiO_2 -modified	1.5	4.2	5.4	1.5	3.9
$\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$	1.4	4.0	5.0	1.5	0.0
MgO -modified	1.5	3.9	5.3	1.4	2.0
Ga_2O_3 -modified	8.7	4.1	5.1	1.5	5.2
ZrO_2 -modified	9.2	4.1	5.2	1.5	6.8

^a All contents were determined by ICP-AES measurements.

Fig. 4. (A) CH₄ conversion and C₂-C₃ selectivity in the OCM reaction vs. time on stream at 700 °C using the TiO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalyst. XRD pattern (B) and Raman spectrum (C) of the TiO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalyst. Reaction conditions: 0.8 g catalyst, 0.1 MPa, GHSV = 8000 mL·g⁻¹·h⁻¹, CH₄:O₂:N₂ = 5:1:4.

MO_x-modified catalysts show almost identical contents of Mn, W, and Na (~4.0, ~5.0, and ~1.5 wt%, respectively) and comparable SSAs (1.2–1.4 m²·g⁻¹), confirming that the difference in their activity/selectivity discussed above is due to their phase or surface features, rather than their elemental content and surface area.

3.4. Stability

Besides the improved activity and selectivity at relatively low temperature, the stability is another aspect of practical importance for the OCM catalysts. Fig. 4(A) shows the CH₄ conversion and C₂-C₃ selectivity of the TiO₂-modified Mn₂O₃-Na₂WO₄/SiO₂ catalyst in the OCM reaction, plotted against the time on stream at 700 °C, for a GHSV of 8000 mL·g_{cat}⁻¹·h⁻¹ and a CH₄:O₂:N₂ (5:1:4 molar ratio) feed gas. The TiO₂-modified catalyst is stable for at least 300 h, with a CH₄ conversion of ~23% and a C₂-C₃ selectivity of ~73%. Fig. 4(B) and (C) shows the XRD pattern and Raman spectrum of the catalyst after 300 h of testing, revealing almost unchanged phase and surface compositions with respect to those of the catalyst subjected to the reaction at 800 °C for 2 h and then at 700 °C for another 0.5 h (Fig. 3(A), pattern (a) and Fig. 3(B), spectrum (a)). This is the reason for the excellent activity/selectivity retention of the catalyst throughout the entire 300 h test.

4. Conclusions

A series of MO_x (M = Ti, Mg, Ga, Zr)-modified Mn₂O₃-Na₂WO₄/SiO₂ catalysts for the OCM reaction have been prepared by the impregnation method. Compared with the unmodified Mn₂O₃-Na₂WO₄/SiO₂ catalyst, the TiO₂-modified one shows a significant improvement of the low-temperature activity/selectivity, whereas the MgO modification has almost no impact and the Ga₂O₃ and ZrO₂ modifications have a negative effect. The TiO₂-modified catalyst achieves high CH₄ conversion and C₂-C₃ selectivity (~23% and 73%, respectively) at 700 °C using a simulated feed gas of 50 vol% CH₄ in air, and is stable for at least 300 h. The formation of the MnTiO₃ phase and of the MnTiO₃-dominated catalyst surface is the main cause of the remarkable improvement in the low-temperature activity/selectivity of the catalyst for the OCM reaction. The newly generated Mg₂MnO₄ could play the same role as Mn₂O₃ in achieving the [MnWO₄ ↔ Mg₂MnO₄] chemical cycle instead of the high-temperature [MnWO₄ ↔ Mg₂MnO₄] one in the MgO-modified catalyst; this explains why the latter exhibits an OCM performance comparable to that of the unmodified catalyst. The Ga₂O₃ and ZrO₂ modifications facilitate the reduction of Mn₂O₃ and its subsequent combination with Na₂WO₄ to form the relatively inactive MnWO₄, while completely suppressing the transformation of SiO₂ into α-cristobalite, which is the main

cause of their degraded OCM performance. Although the introduction of Mg, Ga, and Zr in the $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts did not improve their low-temperature OCM performance, we have clearly identified the underlying reasons for this result; in this sense, our exploration will be useful for the development of OCM catalysts.

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Graphical Abstract

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Oxidative coupling of methane: 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 MO_x modification

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A $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst is modified using TiO_2 , MgO , Ga_2O_3 , and ZrO_2 ; among the synthesized catalysts, the TiO_2 -modified one shows markedly improved low-temperature OCM performance due to the formation of the MnTiO_3 phase and of the MnTiO_3 -dominated catalyst surface.

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甲烷氧化偶联： $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ 催化剂的金属氧化物 $\text{MO}_x(\text{M}=\text{Ti, Mg, Ga, Zr})$ 改性及掺杂效应研究

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摘要: 甲烷(页岩气、天然气、可燃冰和煤层气的主要成分)是地球上储量巨大的优质能源和高品味的碳氢资源,我国也拥有储量居全球前列的页岩气、可燃冰和煤层气。虽然甲烷经由合成气可以间接转化为乙烯等产品,但工艺流程长以及合成气造气高温、高能耗和高物耗也是不争的事实,这在一定程度上降低了间接合成路线的竞争优势。特别是,甲烷的间接转化需要将本应部分保留于产品的 C—H 键全部打断生成合成气,然后再在催化剂作用下重组得到烃类产品,故而并不完美。因此,甲烷的直接转化一直是科学家孜孜以求的理想路径,甲烷氧化偶联制乙烯(OCM 反应)也再一次引起关注。

目前, $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ 是最富有应用前景的催化剂,但其适宜反应温度仍高达 800 °C 以上,极大地制约了其工业化应用。为提高其低温催化性能,本文采用金属氧化物 $\text{MO}_x(\text{TiO}_2, \text{MgO}, \text{Ga}_2\text{O}_3 \text{ 或 } \text{ZrO}_2)$ 对 $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ 催化剂进行了掺杂改性,利用扫描电子显微镜、 N_2 吸附-脱附等温曲线、X 射线衍射、拉曼光谱、电感耦合等离子体原子发射光谱等手段对改性后的催化剂进行了系统表征。结果表明, TiO_2 掺杂的 $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ 催化剂在 700 °C(催化剂床层温度)下, CH_4 转化率可达 23%,同时 $\text{C}_2\text{-C}_3$ 烃类选择性约为 73%,且能够稳定运行 300 h 无失活迹象; MnTiO_3 的形成对提高 OCM 反应的低温活性和选择性至关重要,本质在于低温 (≤ 700 °C) 化学循环“ $\text{MnTiO}_3 \leftrightarrow \text{Mn}_2\text{O}_3$ ”的形成替代了未改性催化剂的高温 (> 800 °C) 化学循环“ $\text{MnWO}_4 \leftrightarrow \text{Mn}_2\text{O}_3$ ”。对于 MgO 改性的 $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2$ 催化剂,其催化性能与未改性催化剂相当,反应过程中 Mn_2O_3 与 MgO 生成了新物相 Mg_2MnO_4 ; 虽然也形成了新的 $\text{MnWO}_4 \leftrightarrow \text{Mg}_2\text{MnO}_4$ 氧化还原循环,但是该循环与 $\text{MnWO}_4 \leftrightarrow \text{Mn}_2\text{O}_3$ 循环类似,需在高温下才可高效进行。对于 Ga_2O_3 或 ZrO_2 改性的催化剂,其催化性能低于未改性催化剂,原因在于反应过程中 Ga_2O_3 或 ZrO_2 的引入促进了 MnWO_4 物相的生成并对其有稳定作用,反应后的催化剂无论是体相还是表面都只能检测到 MnWO_4 ,推测认为 α -方石英、 Na_2WO_4 和 Mn_2O_3 的缺失是导致 Ga_2O_3 或 ZrO_2 改性催化剂性能下降的主要原因。

关键词: 甲烷氧化偶联; 低碳烯烃; 乙烯; 氧化物修饰; MnTiO_3

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