MnTiO₃-driven low-temperature oxidative coupling of methane over TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst

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Oxidative coupling of methane (OCM) is a promising method for the direct conversion of methane to ethene and ethane (C₂ products). Among the catalysts reported previously, Mn₂O₃-Na₂WO₄/SiO₂ showed the highest conversion and selectivity, but only at 800° to 900°C, which represents a substantial challenge for commercialization. We report a TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst by using Ti-MWW zeolite as TiO₂ dopant as well as SiO₂ support, enabling OCM with 26% conversion and 76% C₂-C₃ selectivity at 720°C because of MnTiO₃ formation. MnTiO₃ triggers the low-temperature Mn²⁺↔Mn³⁺ cycle for O₂ activation while working synergistically with Na₂WO₄ to selectively convert methane to C₂-C₃. We also prepared a practical Mn₂O₃-TiO₂-Na₂WO₄/SiO₂ catalyst in a ball mill. This catalyst can be transformed in situ into MnTiO₃-Na₂WO₄/SiO₂, yielding 22% conversion and 82% selectivity at 650°C. Our results will stimulate attempts to understand more fully the chemistry of MnTiO₃-governed low-temperature activity, which might lead to commercial exploitation of a low-temperature OCM process.

INTRODUCTION

Methane is a clean and cheap hydrocarbon resource that is abundantly available in natural gas, shale gas, and gas hydrates (1, 2). It can also be sustainably produced from renewable biomass, offering much greater availability than crude oil. In this context, the depletion of global crude oil has stimulated intense efforts on converting methane into high-value chemicals and transportable fuels, which are traditionally derived by petrochemical routes (2, 3). In particular, light olefins, the key building blocks in modern chemical industry, need an urgent shift from crude oil to methane. To date, the industrial-scale conversion of methane to olefins uses an indirect route, where methane is transformed into CO and H₂ above 700°C, followed by conversion to methanol and then to olefins (4–6). Recently, a bifunctional catalyst (ZnCrO₄ combined with mesoporous SAPO zeolite) (7) and cobalt carbide nanoprisms (8) have been reported to be capable of directly converting CO and H₂ into olefins with surprising selectivity under mild conditions. Despite these advances, the strong C–H bonds in methane make this an energy-demanding approach, and such an indirect pathway has a low atom utilization efficiency. One developing technology is the direct conversion of methane into olefins and aromatics in the absence of molecular oxygen (O₂) using suitable catalysts. Zeolite-supported Mo catalysts (Mo/zeolites) have been intensively studied (9), and recently, a single-atom iron catalyst embedded in a silica matrix (Fe@SiO₂) was reported to have promising methane conversion and light olefin selectivity (10). However, commercial prospects for these processes may be hampered by rapid catalyst deactivation (for Mo/zeolites) and ultrahigh reaction temperature (up to 1100°C for Fe@SiO₂).

In principle, methane can also be directly converted into C₂ hydrocarbons [ethene (C₂H₄) and ethane (C₂H₆)] in the presence of O₂ in the so-called oxidative coupling of methane (OCM) (11). The pioneering work by Keller and Bhasin in 1982 initiated a worldwide research effort to explore this process (12). It has been recognized that the OCM process includes both a heterogeneous catalytic step, which involves the activation of O₂ and CH₄ on the catalyst surface to generate methyl (CH₃⋅) radicals (13), and a homogeneous gas-phase step, involving the coupling of CH₃⋅ radicals to C₂H₆ followed by dehydrogenation to C₂H₄ (3, 11, 14). However, introduction of O₂ is double-edged: Although it saves energy to activate CH₄, overoxidation is unavoidable. Hundreds of catalysts have been examined since 1982, for C₂ selectivity and ability to suppress overoxidation. One early representative catalyst is lithium-doped magnesia (Li/MgO), where [Li⁺O²⁻] centers are formed to effectively generate CH₃⋅ from CH₄, but rapidly deactivates due to Li loss (15). Another typical class of catalysts is based on lanthanide oxide in both pure and promoted forms (16, 17), whose surface oxygen vacancies are responsible for generating reactive oxygen, but with relatively low C₂ selectivity. Of these catalysts, Mn₂O₃-Na₂WO₄/SiO₂, first reported by Fang et al. (18), is considered optimal in terms of its hundreds of hours of stability and high-temperature productivity (that is, 60 to 80% C₂ selectivity and 20 to 30% methane conversion at 800° to 900°C) (19). Since its discovery, this catalyst has been extensively studied with respect to preparation/modification, catalytic mechanism, and microkinetic modeling (19–23). Despite these intensive efforts, no catalysts have been successfully applied in a commercial process because of the high reaction temperature (24).

It is widely accepted that the OCM reaction is usually initiated on the solid catalyst surface by reacting CH₄ with surface oxygen species to form methyl radicals and continues in the gas phase (19). Activating O₂ into desirable species on the catalyst surface is a pivotal step that governs the CH₄ activation to CH₃⋅ and subsequent oxidative dehydrogenation of C₂H₆. Recently, Cui et al. provided a highly ordered CaO film doped with Mo²⁺ ions and suggested that the formed superoxide anions (O₂⁻) attribute to CH₄ activation (25). Schwach et al. showed that polycrystalline MgO codoped with Fe and Au can effectively activate O₂ to peroxo (O₂–) species, greatly enhancing the C₂ formation with good stability (26). Titanium-containing oxides were also used with the aim to activate O₂ into desirable active species, but the C₂ yield seemed to be improved only to a limited extent (27, 28). An important question is whether the OCM reaction temperature is dominated by the activation of O₂. If so, lowering the O₂ activation temperature by catalyst modification will be the key to improving the low-temperature activity of OCM catalysts such as Mn₂O₃-Na₂WO₄/SiO₂. To test this idea, we explored a TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst for the OCM reaction. MnTiO₃
was formed under the reaction conditions and showed a marked enhancement in activity and selectivity at low reaction temperature (that is, catalyst bed temperature): 26% CH₄ conversion with 76% C₂ plus C₃ (C₂–C₅ propene (C₃H₆) and propane (C₃H₈)) selectivity at 720°C or 22% conversion with 62% C₂–C₃ selectivity at 650°C, using a typical feed of 50% CH₄ in air at a total gas hourly space velocity (GHSV) of 8000 ml g⁻¹cat⁻¹ hour⁻¹. Moreover, this catalyst is stable for at least 500 hours on stream for the OCM process. Most notably, the in situ-formed MnTiO₃ triggers the low-temperature Mn⁴⁺→Mn³⁺ chemical cycle of O₂ activation, thereby leading to improvement in the OCM activity at low temperatures.

**RESULTS AND DISCUSSION**

**Low-temperature active and selective TiO₂-doped MnO₂–Na₂WO₄/SiO₂ catalyst**

We initially prepared a series of catalysts by supporting 2.7 weight % (wt %) Mn₂O₃ and 5.0 wt % Na₂WO₄ on various Ti-containing materials [including Ti-MWW and TS-1 zeolites with Si:Ti molar ratio of 40:1, pure anatase-TiO₂ (α-TiO₂), TiₓO₁₇, and perovskite CaTiO₃, which all delivered very poor catalytic performance for the OCM reaction (fig. S1)], and the as-prepared catalysts were referred to as MnO₂–Na₂WO₄/Ti-MWW (TS-1, α-TiO₂, TiOₓ, and CaTiO₃). For comparison, a reference catalyst MnO₂–Na₂WO₄/SiO₂ (2.7 wt % Mn₂O₃ and 5.0 wt % Na₂WO₄) was prepared strictly according to the widely applied and recommended procedures (18, 19). The detailed preparation information is given in the Supplementary Materials. All the catalysts were examined in the OCM reaction initially from 800°C (commonly used for the MnO₂–Na₂WO₄/SiO₂ catalyst), cooling down to 760°C using a feed mixture of 50% CH₄ in air at a total GHSV of 8000 ml g⁻¹cat⁻¹ hour⁻¹ to quickly screen for a catalyst that might afford acceptable low-temperature catalytic activity and selectivity. The reference catalyst MnO₂–Na₂WO₄/SiO₂ delivered a performance (Fig. 1A) similar to performances reported at 800°C (18–23, 29, 30), indicating its effectiveness in screening these catalysts. On the basis of this reference catalyst, we can separate experimental trials into two groups: Ti-MWW– and TS-1–supported catalysts with higher performance, and pure TiO₂– and CaTiO₃–supported counterparts with lower performance (fig. S1). Consequently, the Ti-MWW–, TS-1–, and SiO₂–supported catalysts were further examined with temperature further decreased from 760° to 720°C; the results are shown in Fig. 1A. The MnO₂–Na₂WO₄/Ti-MWW showed the best OCM performance, delivering 26% CH₄ conversion and 76% C₂–C₃ selectivity at 720°C; another zeolite-supported catalyst MnO₂–Na₂WO₄/Ti-MWW delivered slightly lower activity than the MnO₂–Na₂WO₄/Ti-MWW catalyst. In contrast, MnO₂–Na₂WO₄/SiO₂, which is generally considered to be the state-of-the-art catalyst, yielded much lower CH₄ conversion and C₂–C₃ selectivity of only 7.2% and 9.2%, respectively, at 720°C. Thus, the unprecedented low-temperature OCM activity observed on the Ti-MWW– and TS-1–produced catalysts is attributed to the Ti-doping effect.

**In situ MnTiO₃ formation–dependent low-temperature activity improvement**

To optimize the observed Ti-doping effect and exploit it more rationally in future work, it is imperative to explore the origin of the phenomenon, which we accomplished by structural and chemical characterizations of the MnO₂–Na₂WO₄/Ti-MWW (Si/Ti of 40:1), MnO₂–Na₂WO₄/TS-1 (Si/Ti of 40:1), and MnO₂–Na₂WO₄/SiO₂ catalysts. Notably, the abovementioned three catalysts (that is, first reacting at 800°C for 2 hours and then at 720°C for 0.5 hour; see detailed treatment history in table S1) were exclusively denoted as Cat-Ti-MWW for MnO₂–Na₂WO₄/Ti-MWW, Cat-TS-1 for MnO₂–Na₂WO₄/TS-1, and Cat-SiO₂ for MnO₂–Na₂WO₄/SiO₂. First, the elemental analyses and low-temperature N₂-sorption measurements of these three catalysts revealed almost identical content of Mn, W, and Na as well as similar specific surface areas (1.2 to 1.4 m² g⁻¹) (table S2 and fig. S2), indicating that the low-temperature activity difference should be correlated with their different phase or chemical properties rather than element content and surface area. Subsequently, the phase properties of the Cat-Ti-MWW, Cat-TS-1, and Cat-SiO₂ were probed by x-ray diffraction (XRD). The XRD patterns are shown in Fig. 1B, and the magnified 2θ part from 31° to 37° is shown in Fig. 1C. For the reference catalyst Cat-SiO₂, the phase of the main α-cristobalite as well as of Na₂WO₄ and MnO₂, which is commonly reported, was detected (18–23); the Cat-Ti-MWW and Cat-TS-1 also had α-cristobalite and Na₂WO₄ phases. There was a phase transformation from MnO₂ to a new compound, MnTiO₃, with almost full transformation for the Cat-Ti-MWW and partial for the Cat-TS-1 (Fig. 1C). This observation, combined with the higher activity/selectivity over the Cat-Ti-MWW and Cat-TS-1, indicates an improvement effect similar to that of MnTiO₃ on the CH₄ low-temperature conversion. As noted above, after undergoing OCM reaction at 800°C before running at 720°C, associated with a CH₄ conversion of 25% and a C₂–C₃ selectivity of 73% for the Ti-MWW–supported catalyst but a conversion of only 4% and a C₂–C₃ selectivity of 16% for the TS-1–supported catalyst (fig. S3). Once MnTiO₃ was formed for the TS-1–supported catalyst after reaction at 800°C, a high CH₄ conversion of 23% could be obtained with C₂–C₃ selectivity increased to 69% as the reaction temperature was decreased to 720°C. The abovementioned results demonstrate that the appearance of MnTiO₃ is responsible for the low-temperature CH₄ conversion (fig. S3).

To confirm the as-observed MnTiO₃–governed low-temperature activity improvement, we synthesized a series of Ti-MWW zeolites with varying Ti:Si ratio from 1:80 to 1:40, as well as a full-Si zeolite as a reference (fig. S4A); all the Ti-MWW–supported MnO₂–Na₂WO₄ catalysts were directly tested at 720°C. With increase of the Ti:Si ratio in the zeolites, the catalysts showed a monotonously increasing CH₄ conversion and a synchronous MnTiO₃ intensity (Fig. 1, D to F). Moreover, TS-1 zeolites with varying Ti:Si ratios were also synthesized (fig. S4B), and their supported catalysts were also tested in the OCM reaction. Running all these TS-1–supported catalysts directly at 720°C did not lead to MnTiO₃ and was associated with a very low CH₄ conversion of <5% and a C₂–C₃ selectivity of <20%. However, MnTiO₃ was formed after the reaction at 800°C and could be sustained when reaction temperature was decreased to 720°C, and CH₄ conversion was also progressively increased at 720°C along with the corresponding amount of MnTiO₃ (fig. S4, C to E). These results provide solid proof for the critical role played by MnTiO₃ in enhancing catalyst performance, although the slight differences, which likely result from the structural rigidity difference between Ti-MWW and TS-1 zeolites, were not explored further. Despite the clear proof from XRD characterization, the question naturally arises as to the surface composition and structure of the Cat-Ti-MWW and Cat-TS-1 compared with the Cat-SiO₂ because the catalytic reaction is a surface-dependent process. To answer this question, we further probed the surface states of these three catalysts by the surface-sensitive techniques of x-ray photoelectron spectroscopy (XPS)
and Raman spectroscopy as good complements for XRD. The XPS results show almost identical surface content of W, Mn, and Na for these catalysts (table S3), indicating that their activity/selectivity should be controlled by other factors rather than the surface element contents. However, it should be noted that the XPS spectrum of Mn in Mn$_2$O$_3$ is identical to that in MnTiO$_3$ (fig. S5A); therefore, the Mn$_2$O$_3$-to-MnTiO$_3$ evolution cannot be distinguished by XPS. Moreover, the binding energies of W, Mn, and Na species on the Cat-Ti-MWW and Cat-TS-1 shifted very slightly compared with the Cat-SiO$_2$ surface (fig. S5, B to F), indicating that the MnTiO$_3$ formation did not markedly modify the original electronic states of these species on the catalyst surface.

Another surface-sensitive technique of Raman spectroscopy was used because it is sensitive to the local structure of oxides especially with poor crystallinity (31, 32). For the Cat-Ti-MWW, Cat-TS-1, and Cat-SiO$_2$, Mn$_2$O$_3$ and Na$_2$WO$_4$, which are generally considered to be crucial for the traditional SiO$_2$-supported catalyst in the OCM reaction (19), and MnTiO$_3$, which is paramount for low-temperature activity improvement as evidenced by the above experiments, were analyzed in particular. For the Cat-SiO$_2$ catalyst, we observed signals of Mn$_2$O$_3$ and Na$_2$WO$_4$ as well as $\alpha$-cristobalite (Fig. 1G and fig. S6) that were identical to those reported previously (33). On the Cat-Ti-MWW and Cat-TS-1, in contrast, we detected no signals of Mn$_2$O$_3$ but found strong signals

**Fig. 1.** The MnTiO$_3$-governed OCM performance of the TiO$_2$-doped Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts. (A) CH$_4$ conversion and C$_2$-C$_3$ selectivity over the Ti-MWW-, TS-1-, and SiO$_2$-supported Mn$_2$O$_3$-Na$_2$WO$_4$ catalysts. (B) XRD patterns of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW, Mn$_2$O$_3$-Na$_2$WO$_4$/TS-1, and Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts, with (C) the magnified part of 2θ from 31° to 37°. a.u., arbitrary units; $\alpha$-Crist., $\alpha$-cristobalite. (D) CH$_4$ conversion and C$_2$-C$_3$ selectivity and (E) XRD patterns as well as (F) the magnified part of 2θ from 31° to 37° of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalysts with different Si:Ti molar ratio in Ti-MWW zeolites after directly running at 720°C. (G and H) Raman spectra of the Ti-MWW-, TS-1-, and SiO$_2$-supported Mn$_2$O$_3$-Na$_2$WO$_4$ catalysts. Reaction conditions: GHSV of 8000 ml g$_{\text{cat.}}$ hour$^{-1}$ of a feed of 50% CH$_4$ in air. C$_3$ selectivity was 3 to 5%, 2 to 3%, and 0 to 2% for all catalysts at a C$_2$-C$_3$ total selectivity above 60%, between 40 and 60%, and below 40%, respectively.


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of MnTiO$_3$, and clear signals of Na$_2$WO$_4$ and $\alpha$-cristobalite (Fig. 1G and fig. S6). These Raman results also showed a clear transformation from Mn$_2$O$_3$ to MnTiO$_3$ on the Cat-Ti-MWW and Cat-TS-1, which confirmed again the critical role of MnTiO$_3$ in improving low-temperature activity. Quite different temperature-dependent surface evolution was also captured by Raman for the Ti-MWW– and TS-1–supported catalysts (Fig. 1H). When directly running at 720°C for 0.5 hour, Mn species in the Ti-MWW–supported catalyst were almost fully transformed into MnTiO$_3$ associated with a CH$_4$ conversion of 25%, whereas the TS-1–supported catalyst displayed a spectrum identical to that of TiO$_2$ with a conversion of 4%. As expected, after the TS-1–supported catalyst underwent the OCM reaction at 800°C for 2 hours in advance, dominant MnTiO$_3$ was detected, associated with a sharp increase of CH$_4$ to 23% at 720°C (fig. S3). The Raman–indicated correspondence of the high CH$_4$ conversion to the appearance of surface MnTiO$_3$ corroborated the similar improvement effect of MnTiO$_3$ on the low-temperature CH$_4$ conversion once again.

**Synergetic catalysis of MnTiO$_3$ with Na$_2$WO$_4$**

Our probes of phase and surface structures consistently showed the critical role of MnTiO$_3$ in enhancing the low-temperature OCM performance of the TiO$_2$-doped Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst; even more notably, CH$_4$ conversion and C$_2$–C$_3$ selectivity were progressively enhanced with increasing amount of MnTiO$_3$ (Fig. 1, D to F, and fig. S4), suggesting that MnTiO$_3$ contains the active sites for the OCM reaction. To verify this point, we prepared and examined an MnTiO$_3$/SiO$_2$ catalyst in the OCM reaction. At 800°C, this catalyst offered slightly lower CH$_4$ conversion (22% versus 26%) and much lower C$_2$–C$_3$ selectivity (47% versus 75%) than the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst, but similar at 760°C (17% versus 14%; 34% versus 38%) and much higher at 720°C (15% versus 7.2%; 27% versus 9.2%) (fig. S7). Nevertheless, both the activity and the selectivity of the MnTiO$_3$/SiO$_2$ catalyst was much lower than the results of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW with MnTiO$_3$-Na$_2$WO$_4$ combination (26 to 28% conversion and 76 to 79% C$_2$–C$_3$ selectivity at 720° to 800°C; Fig. 1A). Moreover, two other catalysts, Mn$_2$O$_3$/SiO$_2$ and Na$_2$WO$_4$/SiO$_2$, were prepared and tested, delivering much lower CH$_4$ conversion (8 to 14% for Mn$_2$O$_3$/SiO$_2$ and 5 to 10% for Na$_2$WO$_4$/SiO$_2$) and C$_2$–C$_3$ selectivity (14 to 18% for Mn$_2$O$_3$/SiO$_2$ and 28 to 33% for Na$_2$WO$_4$/SiO$_2$) at 720° to 800°C (fig. S7). It is thus rational to infer that the coexistence of Na$_2$WO$_4$ and MnTiO$_3$ is paramount for the low-temperature OCM reaction activity. Subsequently, the question arises whether the MnTiO$_3$-Na$_2$WO$_4$ combination affects their physical structure [such as solely improving dispersion to enhance CH$_4$ conversion (34)] or the intrinsic catalytic performance. Therefore, a kinetic study was carried out over the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ and Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalysts, and the apparent activation energies ($E_a$) were calculated with the results as shown in fig. S8. Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW provided a much lower $E_a$ (80 to 110 kJ/mol) than Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ (180 to 210 kJ/mol) (see the Supplementary Materials for the calculation details), indicating that there are different active sites in the two catalysts and that the MnTiO$_3$-Na$_2$WO$_4$ combination markedly promotes the catalyst intrinsic performance.

**MnTiO$_3$-triggered Mn$^{2+}$↔Mn$^{3+}$ chemical cycle—The nature of low-temperature OCM catalysis**

As mentioned above, it has been recognized that the OCM process obeys the mechanism of heterogeneous-homogeneous radical reactions (3, 11, 14), and the heterogeneous surface activation of O$_2$ and CH$_4$ is the pivotal prerequisite for the OCM process. Therefore, we inferred that the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst can activate O$_2$ and CH$_4$ more effectively than the other catalysts. To confirm this conjecture, we designed and conducted a three-step experiment over the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW and Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts: reducing in CH$_4$ stream for 0.5 hour and then switching to an O$_2$ stream, followed by switching to CH$_4$ at the desired temperature for some time (see detailed treatment history in table S1). The evolution of phase structures and surface states of these as-resulting catalysts was characterized by XRD and Raman techniques, with results as shown in Fig. 2. After reducing in CH$_4$ at 800°C, Mn species for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst existed in the form of the MnTiO$_3$ phase; then, full oxidation of MnTiO$_3$ to form Mn$_2$O$_3$ took only 1 min in the O$_2$ stream, and the subsequent reversal of Mn$_2$O$_3$ into Ti-MWW catalyst at 800°C (Fig. 2A). Differently, the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst after reducing in the CH$_4$ stream at 800°C displayed clear MnWO$_4$ diffractions. Thereafter, full oxidation of MnWO$_4$ to form Mn$_2$O$_3$ took 3 min in the O$_2$ stream, whereas the reversal of Mn$_2$O$_3$ into MnWO$_4$ took 15 min in the CH$_4$ stream at 800°C (Fig. 2A). At 760°C, the evolution of the Mn$_2$O$_3$↔Mn$_3^+$ cycle slowed down slightly for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst, but that of the MnWO$_4$↔Mn$_2$O$_3$ cycle slowed down greatly for the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst (Fig. 2B). The oxidation of MnTiO$_3$ to form Mn$_2$O$_3$ took 2 min, and the reversal of Mn$_2$O$_3$ to MnTiO$_3$ took 15 min. However, the transition of MnWO$_4$ to Mn$_2$O$_3$ took a much longer time of 15 min, and that from Mn$_2$O$_3$ into MnWO$_4$ also took a much longer time of 45 min. At 720°C, the Mn$_2$O$_3$↔Mn$_3^+$ cycle could easily take place despite a longer time: Mn$_2$O$_3$ to Mn$_3^+$ took 4 min and Mn$_3^+$ to Mn$_2$O$_3$ took 30 min (Fig. 2C). Most notably, MnWO$_4$ to Mn$_2$O$_3$ took 30 min, but Mn$_2$O$_3$ could not be fully reversed into MnWO$_4$ even after 1.5 hours in a CH$_4$ stream at 720°C (Fig. 2C). Obviously, the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst delivered a much easier Mn$^{2+}$↔Mn$^{3+}$ cycle especially at 720°C (Fig. 2, D to F) because of the participation of MnTiO$_3$. Combining the OCM results of these two catalysts, we conclude that the more facile Mn$^{2+}$↔Mn$^{3+}$ cycle of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst matches neatly with its much higher performance at 720°C. In addition, the Raman results of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW and Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts (Fig. 2, G to I) corroborated that the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst offered a much easier Mn$^{2+}$↔Mn$^{3+}$ cycle, implying a much higher activity to activate O$_2$ (via one half-cycle of Mn$^{2+}$↔Mn$^{3+}$) and to seize the reducing species (for the other half-cycle of Mn$^{3+}$↔Mn$^{2+}$) than the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst at low temperature.

Conflicting reports on the structure of the active sites of the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst are found in literature, and three typical descriptions have been widely proposed (19). The unitary site of Na–O–Mn was suggested because of the similarity between the catalytic performance of Mn$_2$O$_3$-Na$_2$WO$_4$/MgO and Na$_2$Mn$_2$WO$_6$/MgO. In contrast, a redox mechanism involving a W$^{6+}$/W$^{4+}$ couple with W–O–Si bonds was suggested, and the gas-phase O$_2$ was proposed to be involved in electron transfer. In particular, a two-metal site model was proposed, where O$_2$ is activated on an Mn$^{3+}$ site to take charge of catalyst activity and CH$_4$ is activated on the neighboring W$^{6+}$ site to increase catalyst selectivity, with oxygen spillover from Mn$_2$O$_3$ to the Na$_2$WO$_4$ to accomplish the reactive cycle. Our results indicate that the Mn$^{2+}$↔Mn$^{3+}$ cycle is confined to Mn$_2$O$_3$ and MnWO$_4$ (Fig. 2, A to C); therefore, we prefer the Mn–W combined site model for the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst in our present OCM reaction. Moreover, the evolution rate of the Mn$^{3+}$↔Mn$^{2+}$ cycle in Mn$_2$O$_3$-MnWO$_4$ was much lower than in MnTiO$_3$-Na$_2$WO$_4$, especially at low temperatures (Fig. 2); therefore, we hypothesized that MnTiO$_3$ plays a dominant role in enhancing low-temperature activity and Na$_2$WO$_4$ is key to
improving C2-C3 selectivity. To further confirm this conclusion, we prepared four catalysts, including MnWO4-Mn2O3, MnTiO3-Mn2O3, MnWO4-Mn2O3-Na2WO4, and MnTiO3-Mn2O3-Na2WO4, by grinding. As expected, the catalysts containing MnTiO3 delivered a much higher CH4 conversion at 720° to 760°C than the counterparts with absence of MnTiO3, and the catalysts with Na2WO4 delivered a much higher C2-C3 selectivity at 720° to 800°C (fig. S9). For example, the MnTiO3-Mn2O3 catalyst delivered a CH4 conversion of 16%, whereas Mn2O3-MnWO4 delivered only 4% at 720°C, but selectivities were very low for both catalysts (42% for MnWO4-Mn2O3 and 29% for MnTiO3-Mn2O3). As we added Na2WO4 into MnTiO3-Mn2O3, C2-C3 selectivity was sharply increased from 29 to 73%, whereas CH4 conversion was slightly increased from 16 to 22%. These experimental results clearly demonstrate that MnTiO3 was mainly responsible for low-temperature O2 and CH4 activation and Na2WO4 for increased selectivity, indicating that their combination (Na2WO4-MnTiO3) resulted in a much higher conversion rate and selectivity. This observation could be tentatively attributed to the synergetic interactions between Mn species (Mn2O3 or MnTiO3) and Na2WO4 [see temperature-programmed reduction (TPR) results in fig. S10 and the corresponding discussion in the Supplementary Materials], in which the detailed spectroscopic/microscopic investigations are particularly desirable.

Fig. 2. The temperature-dependent evolution of phase structures and surface states for the Ti-MWW– and SiO2-supported Mn2O3-Na2WO4 catalysts in O2 or CH4 at 720° to 800°C. (A to C) XRD patterns. The Mn3+ fractions evolving at (D) 800°, (E) 760°, and (F) 720°C. (G to I) Raman spectra. The Ti-MWW–supported catalyst reduced in CH4 at 800°C for 0.5 hour exhibits dominant MnTiO3 signal. After subsequent oxidation in O2 stream for 1 min at 800°C, 2 min at 760°C, and 4 min at 720°C, the MnTiO3 signal disappears, whereas the TiO2 appears, and is reformed in CH4 stream for 9 min at 800°C, 15 min at 760°C, and 30 min at 720°C. The SiO2-supported catalyst reduced in CH4 at 800°C for 0.5 hour exhibits a dominant MnWO4 signal. After subsequent oxidation in O2 stream for 3 min at 800°C, 15 min at 760°C, and 30 min at 720°C, the MnWO4 signal disappears, whereas the Mn2O3 appears, and can be reformed in CH4 stream for 15 min at 800°C, 35 min at 760°C, and 60 min at 720°C. The detailed calculations of the Mn3+ fractions are given in the Supplementary Materials.
On the basis of the evolution behavior from Mn$^{2+}$ to Mn$^{3+}$ (associated with MnTiO$_3$ or MnWO$_4$ in Mn$_2$O$_3$ for O$_2$ activation) of the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW and Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts in the O$_2$ stream at 720°C to 800°C (Fig. 2, D to F), the transition rate from Mn$^{2+}$ to Mn$^{3+}$ was calculated and shown in Fig. 3A (see the Supplementary Materials for the calculation details). At 800°C, the transition rate from Mn$^{2+}$ to Mn$^{3+}$ was 98%/min for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst and 53%/min for the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst, associated with similar CH$_4$ conversion (26 to 28%) and C$_2$-C$_3$ selectivity (76 to 79%). At 760°C, the rate from Mn$^{2+}$ to Mn$^{3+}$ for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW was 37%/min with a CH$_4$ conversion of 27% and a C$_2$-C$_3$ selectivity of 78%, whereas the rate for Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ was decreased to only 7%/min with a low CH$_4$ conversion of 14% and a poor C$_2$-C$_3$ selectivity of 38%. At 720°C, most notably, the rate from Mn$^{2+}$ to Mn$^{3+}$ for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW was still retained at 13%/min with a high CH$_4$ conversion of 26% and a high C$_2$-C$_3$ selectivity of 76%, but a very slow rate of only 4%/min was obtained for the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ with only 7.2% CH$_4$ conversion and 9.2% C$_2$-C$_3$ selectivity. These results show that [Mn$_2$O$_3$-Na$_2$WO$_4$]-based catalytic performance was strongly dependent on the Mn$^{2+}$–to–Mn$^{3+}$ rate independent of temperature, and a transition rate of 10%/min seemed critical to increased OCM conversion/selectivity. As previously shown for the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst, O$_2$ is activated on the Mn$^{2+}$ site and CH$_4$ on the W$_{6+}$ site, and the active oxygen species play a key role in activating CH$_4$ after spillover to the W$_{6+}$ site (19). Accordingly, it is safe to say that the Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst has an adequate O$_2$ activation rate only through the Mn$_2$O$_3$–to–MnWO$_4$ chemical cycle at 800°C and therefore delivers acceptably high OCM performance only at 800°C (Fig. 3, A and B). For the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst, in contrast, because of the MnTiO$_3$-triggered low-temperature Mn$^{2+}$–to–Mn$^{3+}$ chemical cycle, a high O$_2$ activation rate could be obtained at lower temperature (for example, 720°C); as a result, this catalyst yielded better low-temperature OCM performance (Fig. 3, A and B).

**A practical MnTiO$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst**

Inspired by the obtained insight into the MnTiO$_3$-enhanced low-temperature catalysis for the OCM process, we successfully prepared a catalyst by a solvent-free method, simply grinding commercial Mn$_2$O$_3$, TiO$_2$, Na$_2$WO$_4$, and SiO$_2$ gel in a high-speed ball mill. By varying the loadings of Mn$_2$O$_3$, TiO$_2$, and Na$_2$WO$_4$, and SiO$_2$ gel in a high-speed ball mill. By varying the loadings of Mn$_2$O$_3$, TiO$_2$, and Na$_2$WO$_4$, and SiO$_2$ gel making up the balance (fig. S11). For example, the 6.2Mn$_2$O$_3$-6.3TiO$_2$-10Na$_2$WO$_4$/SiO$_2$ catalyst (6.2 wt % Mn$_2$O$_3$, 6.3 wt % TiO$_2$, and 10 wt % Na$_2$WO$_4$) was first activated in the reaction stream at 800°C for 2 hours and delivered an interesting CH$_4$ conversion of 24% with 73% C$_2$-C$_3$ selectivity at 720°C (comparable to the conversion/selectivity for the Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW catalyst at 720°C in Fig. 1A) and a more interesting 22% CH$_4$ conversion with 62% C$_2$-C$_3$ selectivity even at 650°C (Fig. 4A). After the reaction from 800°C to 650°C, TiO$_2$ and Mn$_2$O$_3$ were in situ–transformed into MnTiO$_3$ (Fig. 4, B and C) with the corresponding loading of 11.8 wt %. The catalytically initiated reaction over this 11.8MnTiO$_3$-10Na$_2$WO$_4$/SiO$_2$ catalyst (that is, derived from 6.2Mn$_2$O$_3$-6.3TiO$_2$-10Na$_2$WO$_4$/SiO$_2$ after undergoing OCM reaction at 800°C to 650°C) compared very favorably with other reported OCM catalysts, as summarized in table S4. Among them, an ordered mesoporous SBA-15–supported Mn$_2$O$_3$-Na$_2$WO$_4$ catalyst (34) has been recently reported to yield better results than the reference catalyst Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ at 750°C: CH$_4$ conversion, 14% versus 7%; C$_2$-C$_3$ selectivity, 63% versus 50%. By comparison, our 11.8MnTiO$_3$-10Na$_2$WO$_4$/SiO$_2$ catalyst delivered a much better low-temperature performance than these reported catalysts for the OCM process (table S4). Besides the enhanced low-temperature activity and selectivity, such 11.8MnTiO$_3$-10Na$_2$WO$_4$/SiO$_2$ catalyst provided promising chemical/mechanical stability during the OCM reaction. With a total GHSV of 8000 ml g$_{cat.}^{-1}$ hour$^{-1}$, a scale-up experiment using 10 ml of particulate catalyst (20 to 40 meshes) was carried out for the stability test, and no deactivation was observed during a 500-hour run at 720°C with a feed gas of 50% methane in air (Fig. 4D). CH$_4$ conversion remained at 22 to 25% throughout the entire 500-hour testing, whereas C$_2$-C$_3$ selectivity was retained at 68 to 73% with an ethylene/ethane ratio of ~1.9. Similar behavior was also seen at 800°C, with well-retained CH$_4$ conversion to 24% at 28% and C$_2$-C$_3$ selectivity at 73 to 77% for a 400-hour run (fig. S12). Moreover, our 6.2Mn$_2$O$_3$-6.3TiO$_2$-10Na$_2$WO$_4$/SiO$_2$ catalyst showed a marked low-temperature reaction ignition property that is an important consideration for the practical OCM process. The OCM reaction could be directly started over this catalyst at a low reaction temperature (that is, catalyst bed temperature) of 650°C, offering a high conversion of 17% but a low C$_2$-C$_3$ selectivity of only 47%. As the reaction temperature was increased from 650°C to 720°C, a high C$_2$-C$_3$ selectivity of 73% could be obtained with an improved conversion of 25% (fig. S13A) because of the facilitation of in situ formation of MnTiO$_3$ at that high temperature point. The MnTiO$_3$ phase was detected on the sample after direct reaction at 720°C for only 1 hour and remained almost unchanged with prolonged time on stream. In contrast, only a small amount of

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**Fig. 3. The Mn$^{2+}$–to–Mn$^{3+}$ transition rate and proposed catalytic recycle for OCM process. (A) Temperature-dependent transition rate of Mn$^{2+}$ to Mn$^{3+}$ correlated to CH$_4$ conversion. (B) The Mn$_2$O$_3$-Na$_2$WO$_4$/Ti-MWW and Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalysts and the proposed catalytic cycles of Mn$_2$O$_3$-Na$_2$WO$_4$ and MnTiO$_3$-Na$_2$WO$_4$ combinations. Detailed calculations of the transition rate are given in the Supplementary Materials.**
MnTiO₃ was formed after a direct reaction at 650°C for 1 hour; however, its content increased with prolonged time on stream, after 8 hours becoming comparable in results to those of a direct reaction at 720°C for 1 hour (fig. S13B). Not surprisingly, at 650°C, CH₄ conversion and C₂-C₃ selectivity gradually increased from 17 and 47% at the beginning to 21 and 60% after 8 hours on the reaction stream in association with clear MnTiO₃ phase formation while remaining almost stable along with further prolonged time on stream to 12 hours (fig. S13B). Moreover, because of the similarity of MnTiO₃ phase intensity between samples after direct reaction at 720°C for 1 hour and those after direct reaction at 650°C for 8 hours or longer (fig. S13B), the former catalyst sample, not surprisingly, delivered results comparable to those of the latter one, as the reaction temperature was reduced from 720°C to 650°C (fig. S13).

CONCLUSIONS

Our results established a TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst system, which provides an enhanced low-temperature activity and selectivity in combination with promising stability for the OCM process. MnTiO₃ is in situ–generated in the reaction stream and triggers the low-temperature MnTiO₃ ↔ Mn₂O₃ chemical cycle for O₂ activation, thereby leading to a marked improvement of the low-temperature activity/selectivity. Guided by these findings, we discovered an MnTiO₃/SiO₂, Mn₂O₃/SiO₂, and Na₂WO₄/SiO₂ catalysts prepared by the ball milling method using Mn₂O₃, TiO₂, Na₂WO₄, and SiO₂ gel as starting materials, of which the reaction temperature can be further lowered to 650°C with acceptable CH₄ conversion (~22%) and C₂-C₃ selectivity (~62%). We suggest that the reaction temperature might be decreased further if the Mn⁴⁺ ↔ Mn³⁺ chemical cycle could be accelerated at much lower temperatures for the [Mn₂O₃-Na₂WO₄]–based catalysts. To accomplish this goal, discovery of new Mn⁴⁺ ↔ Mn³⁺ chemical cycles and a deep understanding of the chemistry of the MnTiO₃ (or analog)–governed low-temperature OCM activity/selectivity at the atomic level are particularly desirable. In addition, yield or selectivity of C₂-C₃ products will need to be further improved, perhaps in an appropriate reactor concept such as a membrane and/or structured reactor.

MATERIALS AND METHODS

Catalyst preparation

The Mn₂O₃-Na₂WO₄/support catalysts with Mn₂O₃ loading of 2.7 wt % [Mn(NO₃)₂ aqueous solution as precursor] and Na₂WO₄ loading of 5 wt % (Na₂WO₄·2H₂O as precursor) for the OCM reaction were obtained by the incipient wetness impregnation (IWI) method (18, 19). The supports, including Ti-MWW and TS-1 zeolites (Si:Ti molar ratio of 40:1 to 80:1), amorphous SiO₂ gel (~73 m, 99.8%), pure α-TiO₂ (~44 m, 99.8%), and CaTiO₃ (~44 m, 99%+), were impregnated with an aqueous solution of Mn(NO₃)₂ [analytical reagent grade (AR), Sinopharm Chemical Reagent Co.] and Na₂WO₄·2H₂O (AR, Sinopharm Chemical Reagent Co.) containing appropriate concentrations at room temperature, followed by constant stirring for 5 hours at room temperature and for 1 hour at 180°C. The resulting slurry was dried at 100°C overnight and then calcined in air at 550°C for 2 hours. The Ti-MWW and TS-1 zeolites (Si:Ti molar ratio of 40:1 to 80:1) were synthesized according to the reported methods (35, 36). The amorphous SiO₂ gel and α-TiO₂ were purchased from Aladdin Industrial Corporation. The Ti₂O₃ and CaTiO₃ were purchased from Alfa Aesar Co. Ltd.

The MnTiO₃/SiO₂, Mn₂O₃/SiO₂, and Na₂WO₄/SiO₂ catalysts were also prepared by the IWI method. The Mn, Na, and W contents of these three catalysts were consistent with the abovementioned loadings. Taking the MnTiO₃/SiO₂ catalyst as an example, the amorphous...
SiO2 gel was mixed with α-TiO2 (Si:Ti molar ratio of 40:1) and impregnated with an aqueous solution of Mn(NO3)2 (AR, Sinopharm Chemical Reagent Co.). The solution system was stirred for 5 hours at room temperature and for 1 hour at 180°C. The obtained slurry was dried at 100°C overnight and then calcined in air at 550°C for 2 hours.

The MnWO4-Mn2O3 (5:4 weight ratio), MnTiO3-Mn2O3 (1:1 weight ratio), MnWO4-Mn2O3-Na2WO4 (5:4:1 weight ratio), and MnTiO3-Mn2O3-Na2WO4 (5:5:1 weight ratio) catalysts were prepared by grinding in a high-energy planetary ball mill (37). These four catalysts were milled for 2 hours to obtain a homogeneous mixture. The mass ratio of the balls to particles was 10:1, and the rotation speed was 320 rpm.

The practical catalyst Mn2O3-TiO2-Na2WO4/SiO2 was also prepared by grinding (38) in a high-energy planetary ball mill for 2 hours with the same mass ratio of balls to particles and rotation speed as for the other catalysts. By varying the contents of Mn2O3, TiO2, and Na2WO4, the mixed system led to a highly effective OCM catalyst in the range of 8 to 15 wt% loading for Na2WO4 and 6 to 28 wt% loading for Mn2O3 plus TiO2 (with proper Mn/ Ti ratio to form MnTiO3), with amorphous SiO2 gel making up the balance.

Characterization

The catalysts were characterized by scanning electron microscopy (SEM; Hitachi S-4800) equipped with an energy-dispersive x-ray fluorescence spectrometer (EDX; Oxford), inductively coupled plasma atomic emission spectrometry (ICP Thermo IRIS Intrepid II XSP), and XPS [ESCALAB 250Xi spectrometer, Al Kα, adventitious C 1s line (284.8 eV) as the reference]. The specific surface area was determined using standard Brunauer-Emmett-Teller theory on the N2 adsorption isotherm measured at −196°C on a Quantachrome Autosorb-3B instrument. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. TPR with hydrogen (H2-TPR) was performed on a Quantachrome ChemBET 3000 chemisorption apparatus with a thermal conductivity detector (TCD). In each H2-TPR experiment, the sample (100 mg) purged by He at 300°C for 1 hour in advance was heated from 20° to 1000°C in a gas mixture of 5% H2 in N2 (30 ml min−1) at a rate of 10°C min−1. XRD was performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation (35 kV and 25 mA). The Raman measurements were carried out using a Raman spectrometer (Renishaw inVia) with a 532-nm semiconductor laser as excitation, equipped with a charge-coupled device camera enabling microanalysis on a sample point. The scanning range was set from 80 to 2000 cm−1.

Reactivity tests

The OCM reaction was performed in a fixed bed quartz tube reactor, 400 mm of straight cylindrical tubing with an internal diameter of 16 mm, under atmospheric pressure. The catalyst bed was placed between quartz wool plugs in the reactor. For the Ti-MWW–supported catalyst, 0.25 g of catalyst was loaded in the reactor with the catalyst bed thickness of approximately 10 mm; however, the density of every other catalyst is much higher than that of the Ti-MWW–supported catalyst, and to get the identical catalyst bed thickness of about 10 mm, every other catalyst of 1.5 g was loaded in the reactor. The reactants, CH4 (99.99%) and O2 (99.999%) with dilution of N2 (99.99%), were coked into the reactor using calibrated mass flow controllers. The CH4:N2 molar ratio of 5:1 imitated the contents of a coal bed gas (50 volume% CH4 in air) with a GHSV of 8000 ml g−1 hour−1. The reaction temperature (that is, catalyst bed temperature) was monitored by a thermocouple placed in the middle of the catalyst bed and was 720°, 740°, 760°, 780°, and 800°C. The effluent gas was analyzed with an online gas chromatograph equipped with a TCD using a 60-m DM-Plot Msieve 5A column (for the separation of N2, O2, CO, and CH4) and a 30-m DM-Plot Q capillary column (for the separation of CO2, CH4, C2H4, C3H6, C2H2, and C3H8) in parallel. The CH4 conversion (CCH4) and selectivity (SC2−3) were calculated using the standard normalization method on the basis of carbon atom balance and defined as follows (Eqs. 1 and 2).

\[\text{Conversion (\%)} = \frac{\sum \text{(converted reactants)}}{\sum \text{(remaining reactants)}} \times 100 \hspace{1cm} (1)\]

\[\text{Selectivity (\%)} = \frac{\text{moles of carbon atom in product N}}{\sum \text{moles of carbon atom in reaction products}} \times 100 \hspace{1cm} (2)\]

No formation of carbon deposit was observed. The desired products of the OCM reaction were C2H4, C3H6, C2H2, and C3H8. Their selectivity was described as the C2−C3 selectivity. Reaction data at each reaction condition were collected after running for at least 0.5 hour.

**Supplementary Materials**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/6/e1603180/DC1

**Supplementary Text**

fig. S1. CH4 conversion and C2−C3 selectivity for the pure supports and the supported Mn2O3-Na2WO4 catalysts.

fig. S2. SEM and EDX mapping images.

fig. S3. XRD patterns and testing results of the 2.7Mn2O3-5.0Na2WO4/Ti-MWW and 2.7Mn2O3-5.0Na2WO4/TS-1 catalysts under different reaction conditions.

fig. S4. XRD patterns and testing results for various samples with different Si/Ti molar ratio (or Ti content).

fig. S5. XPS spectra of various samples.

fig. S6. Raman spectra of various samples.

fig. S7. Testing results of the catalysts with different active components.

fig. S8. E3 calculations.

fig. S9. Testing results of the catalysts with different active components prepared by the grinding method.


fig. S12. Stability testing of the 6.2Mn2O3-6.3TiO2-10Na2WO4/SiO2 catalyst under different reaction conditions.

fig. S13. Testing results and XRD patterns for the 6.2Mn2O3-6.3TiO2-10Na2WO4/SiO2 catalyst under different reaction conditions.

table S1. Detailed treatment history of some catalysts for XRD and Raman measurements.

table S2. Specific surface areas and real contents of Mn, W, Na, and Ti of all used catalysts.

table S3. Surface contents of W, Mn, Na, Ti, Si, O, and C measured by XPS for the used catalysts.

table S4. CH4 conversion and C2−C3 selectivity over representative catalysts.

References (38–49)


MnTiO$_3$-driven low-temperature oxidative coupling of methane over TiO$_2$-doped Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst

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Sci Adv 3 (6), e1603180.
DOI: 10.1126/sciadv.1603180

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