

## A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

### **Accepted Article**

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201913309 Angew. Chem. 10.1002/ange.201913309

Link to VoR: http://dx.doi.org/10.1002/anie.201913309 http://dx.doi.org/10.1002/ange.201913309

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# Single chromium atoms supported on titanium dioxide nanoparticles for synergic catalytic methane conversion under mild condition

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**Abstract:** Direct conversion of methane to value-added chemicals with high selectivity under mild conditions remains a great challenge in catalysis. Herein, we report a new kind of single chromium atoms supported on titanium dioxide nanoparticles as an efficient heterogeneous catalyst for direct methane oxidation to C1 oxygenated products with  $H_2O_2$  as oxidant under mild condition. The highest yield for C1 oxygenated products can be reached as 57.9 mol/mol<sub>c</sub>, with selectivity of around 93% at 50°C for 20 h, which is significantly higher than those of most reported catalysts. The superior catalytic performance can be attributed to the synergistic effect between single Cr atoms and TiO<sub>2</sub> support. Combining catalytic kinetics, electron paramagnetic resonance and control experiment results, methane conversion mechanism was proposed as a methyl radical pathway to form CH<sub>3</sub>OH and CH<sub>3</sub>OOH first, and then the generated CH<sub>3</sub>OH is further oxidized to HOCH<sub>2</sub>OOH and HCOOH.

Methane is one of the most promising building blocks for producing basic chemicals because of its abundant and inexpensive.<sup>[1-2]</sup> However, methane is the most inert hydrocarbon due to the strong C-H bond strength (434 kJ/mol) and its tetrahedron structure.<sup>[3]</sup> Activation of methane is a big challenge and has been regarded as the "holy grail" in catalysis.<sup>[4]</sup> In the conventional approaches that has been implemented on a large scale, methane is converted into liquid hydrocarbons through the indirect route, such as steam-reforming<sup>[5]</sup> and Fischer-Tropsch (FT) synthesis<sup>[6]</sup>. These processes are usually operated at high temperature and are highly energy intensive.<sup>[7]</sup> As an alternative approach, the direct route for methane conversion into liquid hydrocarbon products with oxidants (H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, etc.) has attracted great attention in recent years due to the advantages in mild reaction condition and environmentally-benign.

Several kinds of catalysts, including homogeneous and heterogeneous catalysts, have been developed for direct

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methane oxidation under mild conditions. Homogeneous molecular catalysts are usually highly active and selective, but usually highly corrosive acids were used and it was hard to recover the catalysts.<sup>[8]</sup> Many impressive heterogeneous catalysts, such as Cu and Fe-exchanged zeolites<sup>[9]</sup>, Au-Pd colloids<sup>[10]</sup> and single atom catalysts of Rh<sup>[11]</sup> and Fe<sup>[12]</sup>, were also developed for direct methane conversion under mild conditions in recent years. For example, Hutchings et al. reported that aqueous Au-Pd colloidal catalysts exhibited better catalytic performance than the same nanoparticles supported on TiO2 for oxidation of CH4 to methanol with high selectivity (92%) at 50°C and 3 MPa pressure with H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> as co-oxidants.<sup>[10a]</sup> Lee et al. reported a singleatom Rh catalyst dispersed on zirconia surface for selective activation of CH<sub>4</sub> at 70°C with H<sub>2</sub>O<sub>2</sub> as an oxidant.<sup>[9]</sup> Very recently, Deng et al. reported that graphene-confined single iron atoms could activate CH<sub>4</sub> conversion at room temperature with H<sub>2</sub>O<sub>2</sub> as an oxidant, and the highest selectivity of C1 oxygenated products (CH<sub>3</sub>OH, CH<sub>3</sub>OOH, HOCH<sub>2</sub>OOH and HCOOH) was around 94%.<sup>[12c]</sup>

Although much progress has been achieved with heterogeneous catalysts for direct methane conversion with oxidants, two major issues are still needed to be addressed. First, the newly emerged single-site catalysts have shown impressive catalytic performance for kinds of reactions.<sup>[13]</sup> However, only a few metals were reported for direct methane conversion so far. It is worth of developing and investigating other single-site metals, especially non-noble metal catalysts for this reaction. Second, the oxygenated products are hard to be preserved during the reaction because it is much easier for them to be further oxidized to CO or CO<sub>2</sub> thermodynamically<sup>[14]</sup>. Therefore, it is highly important to control the extent of methane oxidation to selectively obtain the oxygenated products.<sup>[15]</sup>

Herein, we report single site chromium atoms supported on titanium dioxide nanoparticles (denoted as Cr<sub>1</sub>/TiO<sub>2</sub>) can be used as an efficient heterogeneous catalyst for direct methane oxidation to C1 oxygenated products with  $H_2O_2$  as an oxidant under mild conditions. With optimized catalyst, the highest yield for C1 oxygenated products can be reached as 57.9 mol/mol<sub>Cr</sub> with high selectivity of around 93% at 50°C for 20 h, which is significantly higher than those of most reported catalysts. The superior catalytic performance can be attributed to the synergistic effect between Cr single atoms and TiO<sub>2</sub> support. Combining catalytic kinetics, electron paramagnetic resonance and control experiment results, a possible reaction pathway for methane conversion with Cr<sub>1</sub>/TiO<sub>2</sub> catalyst is proposed as: CH<sub>4</sub> is first oxidized through a radical pathway to form CH<sub>3</sub>OH and CH<sub>3</sub>OOH, and then the generated CH<sub>3</sub>OH is further oxidized to HOCH<sub>2</sub>OOH and HCOOH.

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Table 1. Comparative catalytic performance of the catalysts for CH<sub>4</sub> oxidation.

Entry	Catalyst	Metal [wt%]	т [°С]	P [MPa]	HCOOH [µmol]	HOCH₂OOH [µmol]	CH₃OOH [µmol]	CH₃OH [µmol]	CO₂ [µmol]	SUM [µmol]
1 <sup>a</sup>	Cr <sub>2</sub> O <sub>3</sub>	68.4	50	3	0.2	0.6	1.7	0.1	*	2.4
2	Cr/SiO <sub>2</sub>	1	50	3	0.4	3.7	6.3	0.8	*	11.2
3	Cr/Fe <sub>2</sub> O <sub>3</sub>	1	50	3	1.3	12.2	13.2	2.1	*	28.8
4	Cr/CeO <sub>2</sub>	1	50	3	1.4	7.7	10.0	1.1	*	20.2
5	Cr/ZrO <sub>2</sub>	1	50	3	0.5	9.4	7.5	0.9	*	18.3
6	Cr/TS-1	1	50	3	2.6	15.0	16.1	3.1	*	36.8
7 <sup>[a]</sup>	TiO <sub>2</sub>	1	50	3	0	0	0	0	*	0
8	Cr/TiO <sub>2</sub>	1	50	3	2.2	20.8	17.5	3.4	*	43.9
9	Cr/TiO <sub>2</sub>	0.25	50	3	0.7	12.2	26.5	2.5	*	41.9
10	Cr/TiO <sub>2</sub>	0.5	50	3	1.5	15.8	24.1	3.8	*	45.2
11	Cr/TiO <sub>2</sub>	2	50	3	2.0	13.2	7.9	2.1	*	25.2
12	Cr/TiO <sub>2</sub>	4	50	3	1.0	7.5	4.9	1.2	*	14.6
13	Cr/TiO <sub>2</sub>	8	50	3	0.3	2.1	1.8	0.4	*	4.6
14	Cr/TiO <sub>2</sub>	1	50	0.1	0.4	1.2	1.1	0.1	*	2.8
15	Cr/TiO <sub>2</sub>	1	25	3	0.4	1.3	3.0	0.5	*	5.2

Typical reaction conditions: 0.5 mL H<sub>2</sub>O<sub>2</sub> (30%), 9.5 mL deionized water, 3 MPa CH<sub>4</sub>, catalysts (Cr: 0.1mg), in a stainless steel auto-clave with a Teflon liner vessel at 50 °C for 1 h. [a] Catalyst (10 mg).

In a typical reaction, the oxidation of CH<sub>4</sub> is performed in water with H<sub>2</sub>O<sub>2</sub> as an oxidant at 50°C and 3 MPa pressure in a stainless-steel autoclave with a Teflon liner vessel. Initially, we investigated the activity of commercial Cr<sub>2</sub>O<sub>3</sub> for oxidation of CH<sub>4</sub>, and the result showed that about 2.5 µmol C1 oxygenated products was detected in the liquid phase in an hour based on the <sup>1</sup>H-NMR analysis. The peaks can be ascribed to CH<sub>3</sub>OH, CH<sub>3</sub>OOH, HOCH<sub>2</sub>OOH and HCOOH, respectively, which were similar with those reported in the literatures (Figure S1). Encouraged by this, 1 wt% Cr supported on commercial SiO<sub>2</sub>, ZrO<sub>2</sub>, TS-1 zeolite, TiO<sub>2</sub> nanoparticles and flowerlike  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CeO2 were prepared by incipient wetness followed by calcinations in air in order to enhancing the dispersion and catalytic activity. All these supported catalysts were then test for oxidation of CH4 under the same conditions. As shown in Table 1 and Figure S2, the supported catalysts exhibited much better activities and 1 wt% Cr/TiO<sub>2</sub> showed the best performance with nearly 43.9 µmol C1 oxygenated products, which is about 17 times than that of bare commercial Cr<sub>2</sub>O<sub>3</sub>.

We further evaluated the effect of Cr loading in Cr/TiO<sub>2</sub> on the catalytic performance. Without Cr, bare TiO<sub>2</sub> nanoparticles could not catalyze CH<sub>4</sub> oxidation, indicating Cr species were the active sites. A series of Cr/TiO<sub>2</sub> catalysts with different Cr lording from 0.25 to 8 wt% were prepared by the same incipient wetness method. The Cr loadings were close to the theoretical values as measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Table S1). As shown in Table 1 and Figure S3, it could be found that the Cr/TiO<sub>2</sub> catalysts with loading of less than 1 wt% showed the highest yields of C1 oxygenated products. However, the yields significantly decreased as further increasing the Cr loading. That is probably because of the agglomeration of active sites with higher Cr content. Therefore,



**Figure 1.** (a) <sup>13</sup>C-NMR and <sup>13</sup>C DEPT-135 of oxygenated products in liquid phase with 1 wt%  $Cr/TiO_2$  catalyst by using <sup>13</sup>CH<sub>4</sub> as the reactant gas. (b) Catalytic performance of the 1 wt%  $Cr/TiO_2$  catalysts for CH<sub>4</sub> oxidation with different reaction time. (c) EPR experiments oxygenated products in liquid phase with different catalysts. (d) Catalytic performance with CH<sub>4</sub> (3 MPa) and CH<sub>3</sub>OH (~15.8 µmol) as reactants over 1 wt%  $Cr/TiO_2$ .

1 wt%  $\mbox{Cr/TiO}_2$  was selected as the optimum catalyst for the following study.

 $^{13}\text{C-NMR}, \,^{13}\text{C}$  DEPT-135 (distortionless enhancement by polarization transfer) and 2D  $^{1}\text{H-}^{13}\text{C}$  HMQC (heteronuclear multiple-quantum correlation) were measured by using  $^{13}\text{CH}_4$  as the reactant gas to further confirm the C1 oxygenated products in

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liquid phase with 1 wt% Cr/TiO<sub>2</sub> catalyst. Combined <sup>1</sup>H-NMR and <sup>13</sup>C-NMR results, the featured points matched well with CH<sub>3</sub>OH, HOCH<sub>2</sub>OOH, CH<sub>3</sub>OOH and HCOOH in 2D <sup>1</sup>H-<sup>13</sup>C HMQC spectrum (Figure 1a and Figure S5). No other liquid products were detected from NMR analysis and no CO<sub>2</sub> was detected from gas chromatography, indicating the selectivity of C1 oxygenated products was nearly 100% at 1 h. Compared with the previous reports, 1 wt% Cr/TiO<sub>2</sub> catalyst shows significant higher catalytic activity and selectivity for direct oxidation of CH<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> (Table S2)<sup>[10-11,12b,c]</sup>. Especially, it still worked well even at room temperature or ambient pressure (Table 1 and Figure S4).

The evolution of products with reaction time was then investigated to elucidate the catalytic kinetics and the reaction pathway. As shown in Figure 1b, the overall yields of C1 oxygenated products first increased and then started to decline with the highest value at the reaction time of 20 h. Meanwhile,  $CO_2$  appeared and increased after 8 h, suggesting the liquid C1 oxygenated products were further oxidized to  $CO_2$  with prolonged reaction time. The highest C1 oxygenated products could be reached as 57.9 mol/mol<sub>Cr</sub> with high selectivity of around 92.8% in 20 h.

The presence of CH<sub>3</sub>OH, CH<sub>3</sub>OOH, HOCH<sub>2</sub>OOH, HCOOH and CO<sub>2</sub> suggests a consecutive pathway for CH<sub>4</sub> oxidation, which were observed and proposed previously by many groups. Basically, for direct CH<sub>4</sub> conversion in heterogeneous system, the activation of oxidants produces oxidative species that can attack C-H bond of CH<sub>4</sub> nucleophilically to form methyl radicals, which are then reacted with oxygenated species to form oxygenated products. In order to clarify the reaction mechanism on 1 wt% Cr/TiO<sub>2</sub>, electron paramagnetic resonance (EPR) experiments were carried out after the reaction. As shown in Figure 1c, both 'CH<sub>3</sub> and 'OH radicals were detected in the reaction. As TiO<sub>2</sub> is well-known for activating  $H_2O_2$  to produce surface-stabilized peroxo- or hydroperoxo species (TiO<sub>2</sub>-O<sub>2</sub><sup>-</sup> or Ti-OOH)<sup>[16]</sup>, the generated 'CH<sub>3</sub> may interact with Ti-OOH to form CH<sub>3</sub>OOH, which is also confirmed as the primary product in the initial stage.

At the same time, the generated 'CH<sub>3</sub> and 'OH could also react to form CH<sub>3</sub>OH, which was also observed in the product. Apparently, CH<sub>4</sub> is first oxidized to CH<sub>3</sub>OH and CH<sub>3</sub>OOH. After 30 min, CH<sub>3</sub>OOH and HOCH<sub>2</sub>OOH increased significantly while CH<sub>3</sub>OH remained. In addition, HCOOH and CO<sub>2</sub> increased significantly after 8 h. These results suggest that CH<sub>3</sub>OH formed in the initial CH<sub>4</sub> oxidation stage is further oxidized to HOCH<sub>2</sub>OOH and HCOOH. In order to confirm this, we used CH<sub>3</sub>OH as the reactant instead of CH<sub>4</sub>. Indeed, HOCH<sub>2</sub>OOH and HCOOH were observed in the products, which agrees well with the hypothesis (Figure 1d). These observations agreed well with Deng *et al.* on FeN<sub>4</sub>/GN catalyst. CH<sub>4</sub> is first oxidized to CH<sub>3</sub>OH and CH<sub>3</sub>OOH, and then the generated CH<sub>3</sub>OH is further oxidized to HOCH<sub>2</sub>OOH and HCOOH.<sup>[12c]</sup>

The morphology and structure of 1 wt%  $Cr/TiO_2$  was then investigated to elucidate the excellent catalytic performance. Under bright-field transmission electron microscopy (TEM), only pure TiO<sub>2</sub> nanoparticles were observed and there was no obvious  $CrO_x$  particles or clusters found on TiO<sub>2</sub> (Figure S6). However, energy-dispersive spectroscopy EDS mapping images showed that Cr element was uniformly dispersed on TiO<sub>2</sub> nanoparticles (Figure S6h). Thus, aberration-corrected high-angle annular dark-

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Figure 2. (a) HAADF-STEM image of 1 wt% Cr/TiO<sub>2</sub>. The red circles show single Cr atoms in the matrix of TiO<sub>2</sub>. (b) H<sub>2</sub>-TPR results of catalysts.

field scanning transmission electron microscope (HAADF-STEM) was further performed to confirm the dispersion state of Cr atoms. As shown in Figure 2a, isolated bright dots corresponding to individual Cr atoms dispersed on the TiO<sub>2</sub> support were observed.

X-ray photoelectron spectroscopy (XPS) was then used to characterize the Cr oxidation state. The main peaks located at 586.4 eV and 588.4 eV in Cr 2p spectrum (Figure S7a) can be ascribed to Cr (III) and Cr (VI), respectively.<sup>[17]</sup> The presence of Cr oxidation species was also confirmed by temperature programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR). As shown in Figure 2b, the peaks at around 245°C and 305°C were corresponding to the reduction of Cr (VI) and Cr (III), respectively. Compared to pure TiO<sub>2</sub>, Ti 2p peaks of 1 wt% Cr/TiO<sub>2</sub> shift to lower binding energies. Especially, with the increase of Cr loading, the binding energies of Ti decreased progressively (Figure S7a), suggesting the interaction between Cr oxidation species and TiO<sub>2</sub> nanoparticles. Raman spectra also confirmed their interaction, as shown in Figure S7b. There were progressively blue-shift for the B<sub>1g</sub> and MP modes, and red-shift for the  $E_g$  and  $A_{1g}$  modes of TiO<sub>2</sub> with the increase of the Cr loading on the  $\text{TiO}_2^{\,[18]}$ 

Based on the structure characterizations and compared catalytic results, we can ascribe the high efficiency of 1 wt% Cr/TiO<sub>2</sub> catalyst for direct CH<sub>4</sub> oxidation to their synergistic effect. EPR results showed that only very weak 'OH radicals were generated with bare TiO<sub>2</sub> nanoparticles. Introducing Cr species, much higher 'OH radicals as well as 'CH<sub>3</sub> radicals were produced, suggesting single Cr atoms play roles not only in activating C-H bonds of CH<sub>4</sub> to form 'CH<sub>3</sub> radicals, but also activating H<sub>2</sub>O<sub>2</sub> to form 'OH radicals. 'CH<sub>3</sub> radicals could react with surface bound – OOH of TiO<sub>2</sub> to form CH<sub>3</sub>OOH. Moreover, the synergistic effect between TiO<sub>2</sub> and Cr species lies in TiO<sub>2</sub> is a more suitable support for the formation of highly dispersed single Cr atoms, which have the maximum atomic efficiency and highest activity.

Besides high activity and selectivity, 1 wt% Cr/TiO<sub>2</sub> also exhibited good recyclability for methane oxidation. After reaction, the catalyst was separated through centrifugation and directly used for the next cycle, its catalytic activity decreased greatly. H<sub>2</sub>-TPR result showed that the peak at around 220 °C corresponding to Cr(VI) was nearly disappeared (Figure 2b). However, after calcinations in air at 400 °C for 2 h, its catalytic activity was similar with the fresh catalyst and the peak of Cr(VI) in H<sub>2</sub>-TPR curve was recovered, suggesting Cr (VI) species in 1 wt% Cr/TiO<sub>2</sub> catalyst played a vital role in direct methane oxidation. Although slightly activity loss was observed during each cycle, the catalyst

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maintained high activity after re-used for 4 times (Figure S8a). In addition, HAADF-STEM confirmed Cr species still kept single atoms state after re-used and calcinations (Figure S8b).

In conclusion, we have produced synergistic catalysts with single chromium atoms supported on TiO<sub>2</sub> nanoparticles for direct methane oxidation to C1 oxygenated products with  $H_2O_2$  as oxidant under mild conditions. The optimized catalyst shows high activity and selectivity with the highest yield for C1 oxygenated products of 57.9 mol/mol<sub>Cr</sub> at 50°C. During the reaction, methane is activated to form the methyl radical, which is first converted into CH<sub>3</sub>OH and CH<sub>3</sub>OOH, and CH<sub>3</sub>OH is further oxidized to HOCH<sub>2</sub>OOH and HCOOH. This study provides a new non-noble metal single-site catalyst with superior catalytic performance for direct conversion of methane under mild conditions.

#### Acknowledgements

The authors thank the National Key Research and Development Program of China (Grant No. 2018YFA0208504), National Natural Science Foundation of China (NSFC 21932006, 21573245) and the Youth Innovation Promotion Association of CAS (2017049). The help from Dr. Jie Cui (NMR measurement and discussion) was acknowledged.

**Keywords**: Methane • single atom • chromium • heterogeneous catalysis • synergistic catalysis

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## COMMUNICATION

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A new kind of single chromium atoms supported on titanium dioxide nanoparticles as an efficient synergistic heterogeneous catalyst for direct methane oxidation to C1 oxygenated products with  $H_2O_2$  as oxidant under mild condition.



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Single chromium atoms supported on titanium dioxide nanoparticles for synergic catalytic methane conversion under mild condition