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# Structural Effect of One-Dimensional Samarium Oxide Catalysts on Oxidative Coupling of Methane

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We report an interesting structural effect of one-dimensional  $Sm_2O_3$  catalysts such as nanorods, nanobelts and nanotubes synthesized by a simple solvothermal method on oxidative coupling of methane. The  $Sm_2O_3$  nanobelts showed the 28% CH<sub>4</sub> conversion and 42% C<sub>2</sub> selectivity at 500 °C. The different spatial structures and surface structures of these  $Sm_2O_3$  catalysts indeed brought about the distinct exposed facets, surface active oxygen species and surface active sites, which could account for their diverse activity and products selectivity in OCM reaction. Otherwise, the  $Sm_2O_3$  nanobelts doped with Sr increased the C<sub>2</sub> selectivity to 48% at 500 °C, which enhanced the C<sub>2</sub> yield sharply.

Keywords: Samarium Oxide, Oxidative Coupling of Methane, One-Dimensional Structure.

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# **1. INTRODUCTION**

Over the past few decades, researchers have concentrated on the direct conversion of methane,<sup>1</sup> whose conversion to more useful carbon chemicals is highly desired. Oxidative coupling of methane (OCM) is a considerably attentive reaction to produce high valuable hydrocarbons such as ethylene and ethane ( $C_2$ ) from methane directly.<sup>2,3</sup> However, methane is a symmetrical molecule and a very stable hydrocarbon and most of methane conversions are thermodynamically unfavorable at 298 K. Until now the yield toward ethylene cannot meet the industrial requirement  $(C_2 \text{ yield is about } 25\%)$  in a real world, due to the undesirable surface reaction and gas-phase combustion reaction to improve the deeper oxidation of methane and C<sub>2</sub> products, although researchers endeavored to enhance the selectivity of C<sub>2</sub> hydrocarbons. In particular, the direct conversion of methane to form ethylene and ethane is not easy at mild temperatures, and the activation of CH4 and coupling of methyl radicals to produce C<sub>2</sub> are usually proceeding at  $\sim 800$  °C.<sup>4-6</sup> Among all kinds of catalysts for OCM, the rare earth oxides<sup>7-11</sup> have exhibited excellent properties. The OCM reaction has been found to be structure sensitive,<sup>12</sup> whereas one-dimensional structure catalyst performed excellently.<sup>13, 14</sup> Our previous studies<sup>15</sup> also investigated that La<sub>2</sub>O<sub>3</sub> with one-dimensional nanorods had higher catalytic activity and C2 selectivity at low temperatures compared to conversional spherical particles. No further significant advance in the correlate other one-dimensional structures like belt, tube, and wire with catalysis in OCM reaction has no reported in the related literature. Therefore, it is worthwhile exploring the structure effect of one-dimensional morphologies of rare earth oxides on the catalytic activity and C<sub>2</sub> selectivity. Sm<sub>2</sub>O<sub>3</sub> with well-defined one-dimensional structure has rarely been considered in this catalytic reaction, and their catalysis for OCM is not unheard. Based on these questions, herein we elaborately controlled the synthetic conditions of Sm2O3 catalysts to obtain different one-dimensional structures, and study the effect of the different one-dimensional structure of the catalysts on the methane conversion and  $C_2$ selectivity. Our studies indicate that belt-like Sm<sub>2</sub>O<sub>3</sub> catalyst achieved higher conversion of methane and selectivity of C<sub>2</sub>, when compared with rod-like and tube-like ones, which is attributed to the more surface activity specites and sites of the former induced by the structural factor.

In this work, one-dimensional  $\rm Sm_2O_3$  nanocatalysts including belt, rod and tube were synthesized to catalyze the oxidative coupling of methane. Methane activity

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and  $C_2$  hydrocarbons selectivity descend as the following sequence:  $Sm_2O_3$  nanobelts  $>Sm_2O_3$  nanorods  $>Sm_2O_3$  nanotubes. The enhanced catalysis of  $Sm_2O_3$  nanobelts should be attributed to the more open exposed face, more relative amount of active oxygen species and stronger surface basic sites, compared to  $Sm_2O_3$  nanorods and nanotubes.

# 2. EXPERIMENTAL DETAILS

# **2.1. Catalyst Preparation**

Synthesis of  $Sm_2O_3$  nanobelts: The 4.44 g Samarium nitrate  $(Sm(NO)_3 \cdot 6H_2O)$  was dissolved into 75 mL deionizer water with stirring, the precursor was obtained after the 5 mL ammonia (28%~30%) being added slowly and stirring for 1 h. The precursor solution was transferred into a 100 mL Teflon-lined autoclave and kept 110 °C for 12 h in an oven. When the solution was cooled to room temperature, the precipitate was centrifuged and washed by ethanol and ultra-pure water several times before being dried in a vacuum drying oven at 60 °C. Finally the powder samples were calcined in air at 800 °C for 1 h to obtain the product.

Synthesis of  $Sm_2O_3$  nanotubes: The 0.5460 g CTAB was put into 30 mL deionized water, and then the 0.7372 g samarium nitrate was added into the solution under stirring at room temperature and stirred for about 1 h. The 0.2 mL ammonia (25%~28%) was added dropwise into the above solution and stirred for 2 h to get the precursor. Then we put the precursor into a 50 mL Teflon-lined autoclave and kept it at 120 °C for 24 h in an oven. The nanotubes were centrifuged and dried at 60 °C, then the final nanotubes was calcined at 800 °C for 1 h to obtain.

Synthesis of  $Sm_2O_3$  nanorods: After we obtained the precursor of nanotubes, 1.8 mL ammonia (25%~28%) was put into it and stirred for 10 min, and then we got the precursor of nanorods. Next, the nanorods precursor was put into a 50 mL Teflon-lined autoclave and heated at 120 °C for 24 h. Nanorods were also gotten by centrifuging and calcining at 800 °C for 1 h in the same way.

#### 2.2. Catalyst Characterization

The crystalline microstructure of the as-prepared catalyst was characterized by X-ray powder diffraction (XRD) with a RigakuD/Max-RB X-ray diffractometer with Cu K $\alpha$  radiation. SEM characterization was detected by ZEISS Supra 55. TEM characterization was observed using JEOL JEM-2100 Electron Microscope (JEOL). The Brunauer-Emmett-Teller (BET) was recorded by nitrogen adsorption–desorption isotherm measurements at 77 K (ASAP 2010). X-ray photoelectron spectra (XPS) were performed by a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. The binding energy values were corrected using the C1*s* peak at 284.80 eV. CO<sub>2</sub> temperature-programmed desorption measurements were measured on Micromeritics AutoChem II 2920 instrument.

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The catalyst power (170 mg) was heated a He flow from 60 to 800 °C with a heating rate of 10 °C/min and then keep for 60 min at 700 °C, and cooled down to 60 °C. The  $CO_2$  was injected at 60 °C for 60 min. after that He was injected and flow for 60 min, finally the temperature was raised to 800 °C with a rate of 10 °C/min.

### 2.3. Catalytic Activity Measurement

The catalytic activity test of the oxidative coupling of methane (OCM) was evaluated in fixed bed quartz tubular reactor under atmospheric pressure. In a typical test, 0.2 g fresh Sm<sub>2</sub>O<sub>3</sub> catalyst (40-60 mesh) and 0.8 g silica sand were mixed together and placed in quartz. The catalyst was treated in N2 atmosphere with 30 mL/min flow rate at 800 °C for 2 h prior to the reaction. When the feed temperature was cooled to room temperature, a flow (240 mL/min) of mixed reactant gas, consisting of methane and oxygen (CH<sub>4</sub>/O<sub>2</sub> = 3) passed the catalyst bed. In order to separate the condensed water vapor produced during the reaction, a cold trap was needed at the outlet of the quartz tube. The outlet products were detected by a micro gas chromatogragh (3000 Micro GC; Inficon) with two thermal conductivity detectors (TCD), one Molecular sieve 5A and one Plot U columns.

# 3. RESULTS AND DISCUSSION

To gain insight into the influence of the precise structure of Sm<sub>2</sub>O<sub>3</sub> on the nature of catalytic active sites, the catalysts were evaluated for the oxidative coupling of methane. As presented in Figure 1(a), the activities of  $Sm_2O_3$  catalysts for OCM process descend as the following sequence: nanobelts > nanorods > nanotubes. Although the initial ignition temperature of methane over the three catalysts was 500 °C, Sm<sub>2</sub>O<sub>3</sub> nanobelts could give rise to 28% conversion of methane and 42% selectivity toward C<sub>2</sub> hydrocarbons at 500 °C. At that condition, Sm<sub>2</sub>O<sub>3</sub> nanorods gave 38% C<sub>2</sub> selectivity and tube-like catalyst exhibited only 34%  $C_2$  selectivity in Figure 1(b). From Figures 1(c) and (d), the selectivity for CO and CO<sub>2</sub> over Sm<sub>2</sub>O<sub>3</sub> nanotubes is the highest among the three catalysts, revealing that the deep oxidation process is easy to be carried out on the tube-like catalyst. The possible reason might be ascribed to the presence of the surface active species on the tubes to favor the complete oxidation of methane or  $C_2$ products, which will be confirmed by the following studies. If the feed temperature is high, C2 hydrocarbons are put at a serious disadvantage, since methane is more thermodynamic stable than C<sub>2</sub> products. This phenomena has been proved by this result that with the increase of feed temperature, the C2 selectivity decreased while CO2 selectivity went up for the three catalysts. Therefore, it is worth noting that valuable products such as ethylene and ethane can be improved by keeping the reaction temperature at a favorable range.



Figure 1. Catalytic performance of  $\text{Sm}_2\text{O}_3$  catalysts with different one-dimensional catalysts for oxidative coupling of methane (space velocity: 72000 mL  $\cdot$  g<sup>-1</sup>  $\cdot$  h<sup>-1</sup>, CH<sub>4</sub>/O<sub>2</sub> = 3:1, 1 atm).

We now turn to find the reasons why  $Sm_2O_3$  nanobelts showed better catalytic performance for OCM reaction in comparison of nanorods and nanotubes. Above all, the focus on the surface structures of the three catalysts shows that their crystal facets are indeed different. Figure 2(a) shows that the average width of  $\text{Sm}_2\text{O}_3$  nanobelts is about 200 nm and the length is up to 1–2  $\mu$ m with thickness of 30 nm. For the  $\text{Sm}_2\text{O}_3$  nanorods, the diameter is



Figure 2. SEM images (a, b, c), TEM images (d, e, f) and HRTEM images (g, h, i) of Sm<sub>2</sub>O<sub>3</sub> catalysts.



Figure 3. XRD patterns of Sm<sub>2</sub>O<sub>3</sub> catalysts.

approximate 20 nm and not longer than 400 nm shown in Figure 2(b). Especially, the nanotube is constructed with many tunnels rather than one tunnel. Each tube is up to several micro-scale meters and the diameter of a tunnel is in the range of 50-100 nm. XRD patterns of these catalysts shown in Figure 3 display dominating diffraction peaks at the  $2\theta$  of 28.1, 32.6, 47.0 and 55.6°, which are typically indexed as the (222), (400), (440), and (622)diffractions well matching with Sm<sub>2</sub>O<sub>3</sub> with face centered cubic phase (JCPDS, PDF No. 43-1029). Further TEM and HRTEM images of these catalysts were analyzed to make clear the distinct surface faces. According to the crystal lattice fringes and the measure angles between the faces, shown in Figure 2(g), the belt was detected along the [111] direction, which means that (111) crystal planes are mainly exposed in Sm<sub>2</sub>O<sub>3</sub> thick-nanobelts. Here we need to take the vertical faces into account, consisting of the side and terminal ends of the nanobelts. Based on the formula:  $\mathbf{r}_1^* \cdot \mathbf{r}_2^* = r_1^* \cdot r_2^* \cdot \cos \alpha$  ( $\alpha$ : angle between crystal facets,  $M^*$ : reciprocal vector,  $M = \mathbf{r}_1, \mathbf{r}_2$ ).

Not only the angle between the vertical side face and (110) is 30°, but also the angle between the vertical side face and (011) planes is 30°, which implies the presence of (121) facets in vertical sides. In addition, the terminal ends are enclosed by (110) facets since they are parallel to the (110) facets combining the TEM and HRTEM from Figures 2(d) and (g). In terms of the nanotubes, they



Figure 5. O1s XPS spectra of Sm<sub>2</sub>O<sub>3</sub> catalysts.

look like multi-faced pillars with inner tunnels. The lattice fringes of nanotubes are 0.32 nm and 0.26 nm apart, which agree with the *d* values of (111) and (200). It is obvious that the side enclosed facets are paralleled to the lattice fringes of (111), in that (111) facets are mainly exposed on nanotubes. For nanorods, it's clearly that there is more than one kind of diffraction lattice inset the Figure 2(h), revealing that the nanorods were formed with multi crystals. As a result, nanobelts enclosed by (110) facets are more effective for methane activation than nanorods and nanotubes, which is well agreement with the results reported.<sup>16–18</sup>

Further SEM also offered insight into the structural information of spent  $Sm_2O_3$  catalysts after catalytic tests. Three structures of  $Sm_2O_3$  samples appeared to have no significant aggregation after catalytic reaction (Fig. 4).

The electronic properties of the three catalysts were also recorded via X-ray photoelectron spectroscopy (XPS). In the O1s profiles in Figure 5, four components, i.e., superoxide ions  $O_2^-$ , peroxide ions O<sup>-</sup>, lattice oxygen O<sup>2-</sup> and carbonate CO<sub>3</sub><sup>2-</sup>, can be decomposed from the two peaks observed for the three catalysts. It is well known that surface-absorbed oxygen species (O<sup>-</sup> and O<sub>2</sub><sup>-</sup>) benefit to



Figure 4. SEM images of  $Sm_2O_3$  nanobelts (a), nanorods (b), and nanotubes (c) after the OCM reaction.

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exposed facets of Sm <sub>2</sub> O <sub>3</sub> samples.					
Catalyst	$\frac{S_{\rm BET}}{({\rm m}^2\cdot{\rm g}^{-1})}$	Pore size (nm)	Pore volume $(cm^3 \cdot g^{-1})$	(O <sup>-</sup> +O <sub>2</sub> <sup>-</sup> ) /O <sup>2-</sup>	Exposed facets
Nanobelt	17.2	14.5	0.06	1.4	(121), (101) and (111)
Nanorod Nanotube	27.6 8.2	38.5 11.1	0.27 0.02	1.1 0.9	(111)

Table I. Surface area, porous textures, surface oxygen species, and

enhance the C<sub>2</sub> selectivity, whereas lattice oxygen might result in the formation of CO and CO<sub>2</sub> through complete oxidation process. The relative amount ratio of the electrophilic oxygen species (O<sup>-</sup> and O<sub>2</sub><sup>-</sup>) to lattice oxygen (O<sup>2-</sup>), which is pointed to be relative effectivity on C<sub>2</sub> selectivity,<sup>19-21</sup> is calculated as 0.90 for nanotubes, 1.11 for nanorods and 1.38 for nanobelts, respectively, listed in Table I. As a comparison of the above ratio values, it can be concluded that nanobelts should show higher selectivity toward ethane and ethylene, which is in accordance with

The surface area and pore feature of catalysts could play a significant role on the catalytic activities. Thus, the information of specific surface area, pore size and pore volume of catalysts were obtained from the N<sub>2</sub> absorption– desorption characterization. See from Figure 6 and Table I, the specific surface area of nanobelts, nanorods and nanotubes are 17.2, 27.6 and 8.2 m<sup>2</sup>/g, respectively. It is

the catalytic results.



**Figure 6.**  $N_2$  absorption–desorption isotherm of the three  $Sm_2O_3$  catalysts, and insets are the corresponding pore size distribution.

obviously that the specific surface area is not consistent with the catalytic performance trends, which suggests that catalytic activities are not mainly influenced by the specific area on OCM reaction but by the active sites of the catalysts, which is in keeping with the speculation in our previous work.<sup>22</sup> In this work, it is estimated that the poor catalytic performance for OCM might be attributed to a higher specific surface space exceeding certain optimal condition, which means a higher residence time of the intermediate species at the surface of the catalyst and destroy of surface, leading to the complete oxidation of methane to yield relative high amount of CO<sub>2</sub> and CO. In view of above analysis, next we transfer our point to the surface basic sites for powerful explanation of the distinct properties of the three catalysts.

The roles played by surface basic sites, which made such a significant effect on OCM reaction, are clarified by CO<sub>2</sub>-TPD analysis. The description by CO<sub>2</sub>-TPD told us the nature surface basic sites on the surface of catalysts. Generally speaking, the weak, medium and strong basic sites can be found by the CO<sub>2</sub> detected at low temperature (<200 °C), middle temperature (300-600 °C), and high temperature (>600 °C), respectively. From Figure 7, medium strong basic sites are existed on the surface of the three Sm<sub>2</sub>O<sub>3</sub> catalysts, obtained from two peaks around 250-600 °C, in which one is located at 250-300 °C, and the other is located at 500 °C. It should point out that the value of peak area represents the quantity of surface basic sites, following as the order: nanobelts > nanorods > nanotubes. The result has expressed a fact that Sm<sub>2</sub>O<sub>3</sub> nanobelts have moderately strong surface basic sites which are crucial for OCM.23-26

In addition, the above result also gave us a clue to improve  $C_2$  selectivity of OCM reaction to add the basic metal as a promoter. The three  $Sm_2O_3$  catalysts doped with Sr indeed gave the enhanced methane conversion and  $C_2$ hydrocarbons selectivity, which has been approved by our experiments (Fig. 8). It's clearly that the conversions of methane of  $Sm_2O_3$  nanorods and nanotubes go up to 28%, nanobelts lift the conversion of methane to 29% after doping with Sr at 500 °C. Moreover, the  $C_2$  selectivity of  $Sm_2O_3$  nanobelts doped with Sr have been boosted from 42% to 48% at 500 °C, in the meantime, both nanorods



Figure 7.  $CO_2$ -TPD profiles of the three  $Sm_2O_3$  catalysts.

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Figure 8. Catalytic performance of Sm<sub>2</sub>O<sub>3</sub> catalysts doped Sr with different one-dimensional catalysts for oxidative coupling of methane (space velocity: 72000 mL  $\cdot$  g<sup>-1</sup>  $\cdot$  h<sup>-1</sup>, CH<sub>4</sub>/O<sub>2</sub> = 3:1, 1 atm).

and nanotubes doped with Sr have strengthen the  $C_2$  selectivity a lot. So, it's demonstrated that increasing the surface of 1, E. McFarland, Science 338, 340 (2012). basic sites could enhance the C2 selectivity of Sm2O3 catalysts and then improve the C<sub>2</sub> yield, which is in accordance with the previous jobs.<sup>15</sup>

# 4. CONCLUSIONS

In summary, one-dimensional Sm<sub>2</sub>O<sub>2</sub> catalysts including nanobelts, nanorods and nanotubes prepared by hydrothermal routes catalyzed the oxidative coupling of methane to produce hydrocarbons. Sm<sub>2</sub>O<sub>3</sub> nanobelts exhibited the highest yield of ethane and ethylene at the temperature of 500 °C. The exposed facets, relative amount of adsorbed oxygen species, as well as medium strong basic sites on the surface of catalysts could account for the different catalytic behavior of the three catalysts. The model onedimensional Sm<sub>2</sub>O<sub>3</sub> catalysts are of promise in the correlation of exact structures and catalytic properties for the OCM process and such well-defined catalysts also will provide a new opportunity for improving C<sub>2</sub> selectivity at low temperature to meet the industrial requirement.

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