

Low temperature catalytic conversion of methane to methanol by barium sulfate nanotubes supporting sulfates: $\text{Pt}(\text{SO}_4)_2$, HgSO_4 , $\text{Ce}(\text{SO}_4)_2$ and $\text{Pb}(\text{SO}_4)_2$

Fengbo Li and Guoqing Yuan*

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Barium sulfate nanotubes perform excellently in supporting sulfates ($\text{Pt}(\text{SO}_4)_2$, HgSO_4 , $\text{Ce}(\text{SO}_4)_2$ and $\text{Pb}(\text{SO}_4)_2$) for low temperature catalytic conversion of methane to methanol under strongly acidic conditions in a conventional gas-phase reactor.

Methane is one of the most abundant and low cost feedstocks, but its full exploitation remains a great challenge to scientists. Currently, methane is converted to liquid products mainly by a multistep and energy intensive process that involves the generation of syngas and the following formation of higher products.¹ Direct methods, which partially oxidize and functionalize the C–H bond efficiently through low temperature routes, have attracted great attention because of the potential of high pay-off. Methane is a very unreactive molecule and can be made to be converted to functionalized methyl products such as methanol,² sulfonic acid,³ methanesulfonyl chloride,⁴ methyl bisulfate⁵ and acetic acid⁶ in strong acid solvents with oxidants and radicals. However, the separation of products is difficult. Other routes through complicate metal complexes⁷ and enzymes⁸ are possible to realize methane conversion efficiently under mild conditions. Such processes may be practical in very small-scale synthesis of specialized chemicals, but problematic in large-scale conversion. This communication reports a heterogenized route for converting methane to methanol at low temperature. This route is different from general high temperature methane oxidation processes over some solid catalysts.⁹ Methane is activated by sulfates ($\text{Pt}(\text{SO}_4)_2$, HgSO_4 , $\text{Ce}(\text{SO}_4)_2$ and $\text{Pb}(\text{SO}_4)_2$) supported over barium sulfate nanotubes, which are acidified by concentrated sulfuric acid. Oxygen molecules are used as oxidants.

Barium sulfate nanotubes were prepared by a surfactant templating route.¹⁰ Sodium dodecyl benzene sulfonate (0.0258 mol) was used as organic structure directing agents and barium sulfate was generated by the hydrolysis of dimethyl sulfate (0.0561 mol) in barium chloride aqueous solution (Ba^{2+} : 0.0364 mol, 150 ml). After 36 hour vigorous agitation at 76 °C, the reaction mixture was kept at ambient temperature for 72 hours. The resulting solid materials were filtered. The surfactant molecules were extracted by a mild method. They were first twice extracted by diethyl ether (20 ml), and then, they were stirred in diethyl ether and ethanol mixture (2:1) for hours, filtered and dried at room temperature. Finally, hot acetone steam was used to extract the fresh samples for two hours. Sulfates supported over barium sulfate nanotubes were introduced by impregnating the fresh nanotubes in $\text{Pt}(\text{SO}_4)_2$ and HgSO_4 diluted sulfuric acid

aqueous solution, $\text{Ce}(\text{SO}_4)_2$ aqueous solution, $\text{Pb}(\text{SO}_4)_2$ acetic acid aqueous solution, followed by drying them in a vacuum at room temperature. XPS was used to determine the surface atomic ratio of the introduced metal ions to Ba^{2+} and the value is in the range of 0.1–0.16. The XPS intensity ratio of the signals from metal elements of sulfates and the support (M^{n+}/IBa^{2+}) reflects the dispersion of the sulfates over the support. Good dispersion leads to high intensity ratio (M^{n+}/IBa^{2+}).

The barium sulfate nanotubes were characterized clearly by TEM. Their outer diameters are from 20 to 30 nm and the tube wall thickness is 5–8 nm. Fig. 1a shows that the nanotubes are of very uniform size and shape and that they are arrayed in the same direction. Fig. 1b depicts a single nanotube. It is clearly demonstrated that the resulting nanostructure is well organized as a cubic tubular structure. The strong contrast between the wall and the center reveals that the tube center is hollow. Fig. 1c shows barium sulfate nanotubes impregnated with sulfates ($\text{Ce}(\text{SO}_4)_2$). The introduced sulfates are in a highly dispersed state. No agglomeration is detected.

The methane conversion was performed in a conventional fixed-bed reactor and the products were analyzed by on-line chromatography. Before the test, the fresh catalysts were pretreated by being immersed in concentrated sulfuric acid (100%) at 120 °C for 3 hours. The reported catalytic activity data were determined after 50 min on the stream. The activity fluctuated markedly in the first 50 min. In the following test periods, the activity fluctuation was negligible. Table 1 summarizes the results of methane conversion over four typical catalysts. From Table 1, we learn that at given reaction conditions the one-pass conversion of methane is all above 30% and the selectivity to methanol is above 60%. Platinum(IV) is the most active oxidation state of the four typical metal elements for methane activation. Fig. 2 shows the influence of reaction temperature on the selectivity and conversion of the Pt catalyst ($\text{Pt}(\text{SO}_4)_2/\text{BaSO}_4$). Methane conversion increases from 9.3% to 50% when the reaction temperature is elevated from 170 °C to 230 °C, but the change of the selectivity is not so patent. Generally, when oxygen molecules are used as oxidant for methane oxidation over solid-state catalysts, methanol and formaldehyde are the intermediate products of the methane oxidation process (from methane to carbon dioxide) and it has been proved that the selectivity of intermediate products of any consecutive reaction is increased markedly with the decrease of the conversion.^{9f} But in our experimental observation, the selectivity at the conversion of 9.3% is almost equal to the value at 50%. It is clearly indicated that methanol is not evolved *via*

*Yuangq@iccas.ac.cn

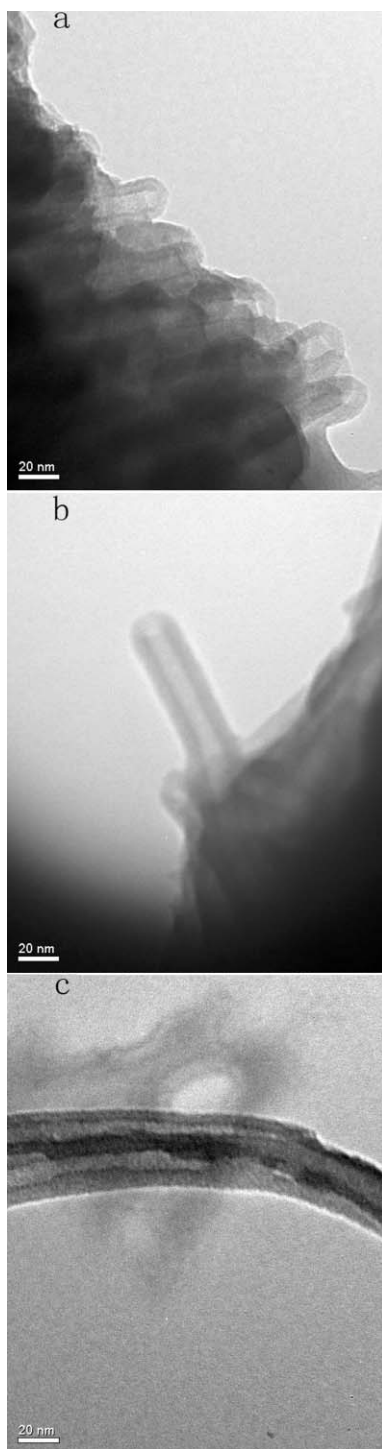


Fig. 1 (a) TEM image of the as-synthesized BaSO₄ nanotubes in array. (b) TEM image of the tip of a single tube. (c) TEM image of barium sulfate nanotubes impregnated with Ce(SO₄)₂.

direct reaction between methane and oxygen molecules on these solid catalysts.

The formation mechanism of methanol in the present work may proceed *via* methyl bisulfate as shown in Scheme 1.^{11,2a} Periana *et al.* have reported a high-yield system for the low temperature conversion of methane to methyl bisulfate based on Pt(II) catalysts that operate in liquid sulfuric acid,^{5a} another three salts

Table 1 Experimental results of catalytic oxidation conversion of methane to methanol

Entry	Catalysts ^a	Methane conversion (%)	Selectivity to methanol (%)
1	Pt(SO ₄) ₂ /BaSO ₄	43.0	70
2	HgSO ₄ /BaSO ₄	36.9	66
3	Ce(SO ₄) ₂ /BaSO ₄	32.2	64
4	Pb(SO ₄) ₂ /BaSO ₄	30.3	61

^a 6g catalyst samples were immersed in concentrated sulfuric acid (100%) at 120 °C for 40 min. After filtration, they were mixed with glass beads (100 mesh) of the same volume and packed in a conventional fixed bed reactor. The test was carried out at 200–220 °C under atmospheric pressure. Argon was used as carrier gas ($P_{\text{CH}_4}/P_{\text{O}_2} = 2.0$, $P_{\text{CH}_4} = 20$ kPa, flow rate: 20 ml min⁻¹).

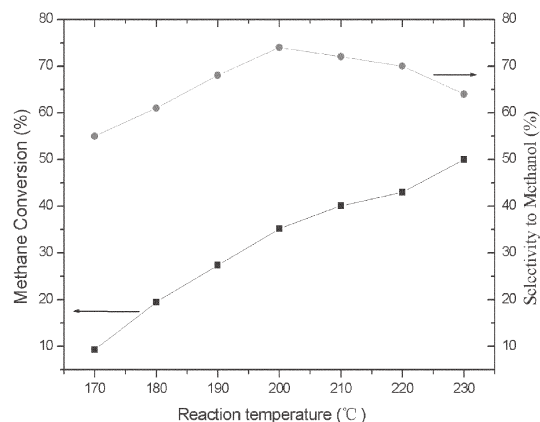
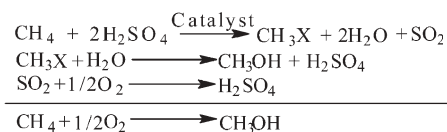


Fig. 2 The influence of reaction temperature on the selectivity and conversion of the Pt catalyst (Pt(SO₄)₂/BaSO₄).



Scheme 1 Possible methanol formation mechanism. X = OSO₃H.

impregnated into barium sulfate nanotubes have also been shown to be active for synthesis of methyl bisulfate at elevated temperature and sulfuric methane at lower temperature.^{12,13} From a certain angle, what is presented in this communication is a heterogenized version of the experiments in liquid sulfuric acid through application of novel barium sulfate nanotubes as supports. The homogeneous processes involve difficulty in the separation of methyl bisulfate and the following hydrolysis to methanol. But in these heterogeneous processes, separate hydrolysis of methyl bisulfate and reoxidation of the sulfur dioxide with oxygen molecules provide a novel route for the oxidation of methane to methanol with oxygen molecule. This may also lend great possibility to development of a methane-to-methanol process on a large scale. However, some related mechanistic issues raised here need further investigation. We hope to address these points in future studies.

In summary, we have developed a low-temperature and high-selectivity process to convert methane to methanol with oxygen molecules. Barium sulfate nanotubes were synthesized by a surfactant templating route and performed excellently in

supporting sulfates (Pt(SO₄)₂, HgSO₄, Ce(SO₄)₂ and Pb(SO₄)₂) and concentrated sulfuric acid for methane conversion. The conversion reaction proceeds below 250 °C and presents selectivity to methanol of above 60%.

Fengbo Li and Guoqing Yuan*

Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China. E-mail: Yuangq@iccas.ac.cn; Fax: +86 10 6255 9373

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