

Direct methane electrochemical oxidation over a multifunctional nanoelectrocatalyst

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1. Introduction

Methane is present in large amounts on the earth, being the main constituent of natural gas and coming from many other sources [1]. Moreover, CH₄ is a greenhouse gas whose negative effects on the environment are over 30 times more potent than CO₂. More and more attention for fruitful methane oxidation and conversion versus an effective utilization and emission reduction is thus desirable. The methane combustion produces a smaller amount of CO₂ compared to emissions from the other fossil fuels, making the use of methane a promising intermediate step before a total replacement with renewable sources. On the other hand, methane availability encourages for upgrading methane into value-added products, too. However, the use of methane as chemical raw materials is still insufficient. Indeed, methane is inherently difficult to activate, this is due to its lack of polarity and chemical inertness. Moreover, for CH₄ conversion to syngas or other products, large scale production facilities and/or high temperatures and energy still constitute significant drawbacks. Despite its direct transformation, via conventional heterogeneous and homogeneous catalysis, has been the object of a lot of studies, it still remains a challenge.

Electrocatalytic approaches represent promising alternatives [1], overcoming the methane chemical inertness thanks to the rapid generation of highly reactive species, and supplying partially oxidized stable products at relatively low temperatures. An efficient catalyst for this process must be able to fulfil different functions: activate oxygen; adsorb and activate methane; and, allow the formation of methanol, avoiding subsequent oxidation. In this scenario, the use of multi-components, with different functionality to optimize activities, selectivity and costs, is the way forward. Supported single-atom metals [2], maximizing atom efficiency, have been demonstrated promising materials for C–H bonds activation. Transition metal oxides show high catalytic performances also at low temperatures. V₂O₅ catalyst [3] exhibited the highest current efficiency and methanol selectivity, since the vanadium species were considered to provide active sites for the formation of the active oxygen species. Ni-based materials [4], although inactive on oxygen molecules, are active for adsorption and hydrocarbon activation in both their metallic and oxide forms.

Herein, to develop an enhanced catalyst for direct and selective oxidation of methane at low temperature, single atoms dispersed on a mixed oxides nanocomposite (based on NiO and V₂O₅), was prepared. We found that the prepared nanocatalyst can catalyse efficiently the selective oxidation of CH₄ to higher alcohols (i.e. 1-Propanol, 2-Propanol).

2. Methods

Different methods performed the materials characterization: FEI Tecnai electron microscope, equipped with an EDX probe, was used to obtain transmission electron microscopy (TEM) images. Phenom electron microscope was used for scanning electron microscopy (SEM) characterization. X-ray diffraction patterns were acquired by means of a Bruker D8 X-ray diffractometer. N₂ adsorption-desorption (Kelvin 1042 V3.12,

COSTECH Instruments) at 77 K permits to obtain surface area, after 250 °C for 3 h pretreatment in He. PHI-550 Multitechnique spectrometer was used for XPS measurements. A gas diffusion layer (TGP-H-090) was coated with the mixture by dropping. A two-electrode setup (Figure 1) was used for the evaluation of CH₄ electrochemical conversion. The cell assembly was placed between two alumina tubes gas chambers. Mixtures (30 mL/min), of 1 vol. % O₂ (Ar balance) and 10 vol. % methane and 1 vol. % H₂O (Ar balance), were fed to the cathode and anode chambers. For galvanostatic and cyclic voltammetry (CV) tests a PGSTAT302N from Autolab potentiostat/galvanostat was used. A quadruple mass spectrometer was used for the gas from the anode chamber analysis.

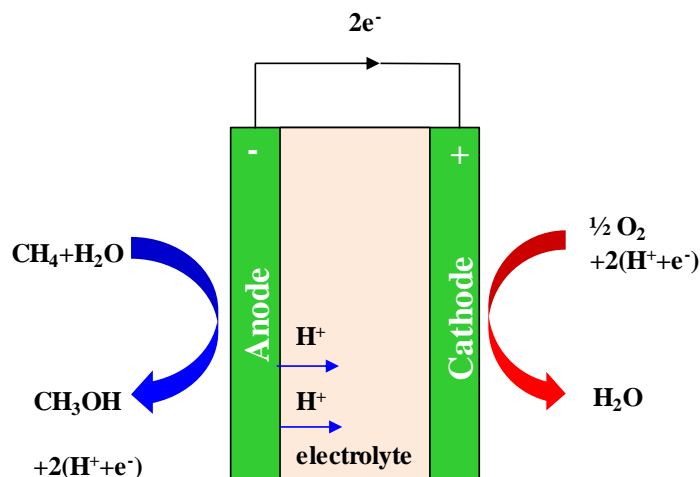


Figure 1. Methane electrochemical oxidation apparatus

3. Results and discussion

TEM analysis revealed the formation of flat nanoparticles of V₂O₅. The in-plane V₂O₅ NPs sizes are in the large range 200-6 nm. They are covered by nickel oxide nanoparticles as evidenced by the high resolution TEM image. Rh single atoms was homogeneously distributed, as revealed by the element mapping images.

To determine the optimal potential for methane oxidation, the difference in the current density of the sample in Ar- and CH₄-saturated electrolyte was calculated. Based on the curves, 2.0 V was selected as the suitable potential for CH₄ electrochemical oxidation to obtain high current density and low competition with water oxidation. ¹H-NMR spectrum of the products, obtained after the electrochemical reaction, was acquired. The main products were 1-Propanol and 2-Propanol, no significant by-products were found.

4. Conclusions

The synthesis of a V, Ru and single metal based nano-structured catalyst was successfully carried out. Homogeneous nanoparticles, with a mean diameter of 8-10 nm, were obtained and characterized. 1-Propanol and 2-Propanol were observed for direct methane oxidation when a small amount of O₂ was flown together with methane at 150 °C and atmospheric pressure.

References

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