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SiO₂@V₂O₅@Al₂O₃ core-shell catalysts with high activity and stability for methane oxidation to formaldehyde

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ABSTRACT

The stable tetrahedral geometry and high C–H bond dissociation energy of methane complicate its direct catalytic conversion; for example, the selective oxidation of methane to formaldehyde, which avoids the production of carbon dioxide by full oxidation and is therefore important for the versatile utilization of natural gas, is still viewed as challenging. Here, we utilize hydrothermal synthesis followed by atomic layer deposition (ALD) to prepare an efficient and thermally stable catalyst based on novel SiO₂@V₂O₅@Al₂O₃ core@shell nanostructures, showing that the thickness of Al₂O₃ shells over SiO₂@V₂O₅ cores can be tuned by controlling the number of ALD cycles. Catalytic methane oxidation experiments performed in a flow reactor at 600 °C demonstrate that SiO₂@V₂O₅@Al₂O₃ nanostructures obtained after 50 ALD cycles exhibit the best catalytic activity (methane conversion = 22.2%; formaldehyde selectivity = 57.8%) and outperform all previously reported vanadium-based catalysts at 600 °C. The prepared catalysts are subjected to in-depth characterization, which reveals that their Al₂O₃ shell provides new surfaces for the generation of highly disperse T_d monomeric species with a V–O–Al bond by promoting interactions between Al₂O₃ and V₂O₅ nanoparticles during ALD. Moreover, the surface Al₂O₃ shell is found not only to protect V₂O₅ nanoparticles against sintering at 600 °C, but also to anchor the produced T_d monomeric vanadium species responsible for the high catalytic performance.

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1. Introduction

Methane, the main component of natural gas, is mainly used for heating and electricity generation [1–3]. Recent progress in shale gas collection technology based on hydraulic fracturing presents a further stimulus for converting abundant methane to more valuable chemical feedstocks and thus reducing dependence on petroleum resources [1]. Nevertheless, the four strong C–H bonds of methane (bond energy = 413 kJ mol^{−1}) present a serious obstacle to its chemical conversion. At elevated temperatures, methane can be catalytically converted to syngas, which can be used as a feedstock for the catalytic production of added-value hydrocarbons or alcohols. Although a number of indirect processes for the oxidative conversion of methane to formaldehyde (HCHO), methanol (CH₃OH), and ethylene (C₂H₄) have been developed and applied industrially [4–8], direct conversion of methane by partial oxida-

tion is still challenging in view of the abovementioned high C–H bond energy and the need to avoid the production of carbon dioxide as a greenhouse gas [9]. Previous studies on methane oxidation to HCHO demonstrated that temperatures above 600 °C are required to break the strong C–H bonds and identified supported V₂O₅ and MoO₃ as the best partial oxidation catalysts for producing HCHO or CH₃OH [10–12]. However, HCHO easily undergoes further oxidation to CO and H₂O, which requires the development of efficient partial oxidation catalysts, for example, by modifying the above catalysts while preserving their high-temperature active sites. Notably, the use of noble metals such as Pt or Pd for C–H bond activation results in the complete oxidation of methane to CO, CO₂, and H₂O [13–16]. For these reasons, the partial oxidation of methane to HCHO is still regarded as a challenging reaction, and the best methane-to-HCHO conversion achieved so far at 600 °C is less than 10%. Parmaliana et al. reported that conversions of 1–3% obtained at 600 °C for V₂O₅/SiO₂ catalysts prepared by impregnation further increased to 25% at 700 °C, although the HCHO selectivity was less than 30% [10]. Nguyen et al. used mesoporous silicas to prepare several impregnated V₂O₅/SiO₂ catalysts [11],

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