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Redox-driven restructuring of lithium molybdenum oxide nanoclusters boosts the selective oxidation of methane

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ABSTRACT

Selective methane oxidation is one of the key challenges in modern chemistry. To increase the value-added chemical production, the oxidation state of active metals should be easily converted to oxidized or reduced states in order to adsorb or provide an oxygen atom efficiently into methane. Here, we firstly report that lithium incorporating molybdenum oxide with silica supports significantly enhances HCHO production in virtue of redox-driven restructuring of active molybdenum sites. In reduction conditions under CH₄ flow, lithium ions are inserted into the molybdenum-oxide phase by forming lithium molybdenum oxide (Li_yMoO₃) nanoclusters and conversely extracted by O₂ oxidation. Due to the redox migration of lithium ions and reconstruction of Li_yMoO₃ nanoclusters under the reaction process, the oxidation state of active molybdenum centers is effectively controlled to both oxidized and reduced states. These findings provide insight into the distinct role of lithium ions in various catalytic systems and suggest new strategies for developing active sites for selective oxidation area.

1. Introduction

Direct conversion of methane, the primary component of shale gas, to value-added chemicals has been actively studied due to the growing interest in the efficient use of non-renewable resources [1–6]. Its simple reaction pathway is also considered to be one of the “Holy Grails in Chemistry” [7]. Methane is the least reactive alkanes with C–H binding energy that can be as high as 440 kJ mol^{−1}. Therefore, current industrial systems use harsh operation conditions (above 850 °C and 10–100 bar) and multi-step processes that proceed through the production of syngas from methane to the subsequent conversion of syngas to chemical commodities [8]. In this regard, the direct oxidation of methane to C1 oxygenates has been vigorously researched in recent years in order to promote the efficient and universal use of natural gas as a feedstock [9–15].

Flexibility in the electronic structure of an active metal is one of the key factors in designing active sites for selective oxidation, because the

entire reaction pathway entails a reduction of the active center by providing oxygen species to reactants, which allows their regeneration with oxidants [16–18]. Although various catalytic models have been suggested for modifying the electronic properties of active sites, the oxidation state can be controlled in only one direction — either highly oxidized or reduced [19,20]. However, selective oxidation of light alkanes requires an active center for the effective conversion of its oxidation state to both states over the entire redox cycle [21,22].

Silica-supported molybdenum oxide catalyst (MoO_x/SiO₂) is commonly used to convert methane to formaldehyde, because of the multiple oxidation states of the active metal [23–25]. Interestingly, molybdenum oxide is also known as a lithium insertion compound, and has recently been tested in numerous studies for use as a cathode material in lithium-ion batteries because of its high capacity for reversibility in redox reactions with lithium ions [26–28]. Intercalation and de-intercalation of lithium ions are triggered either by the discharge or charge of a cathode material [29]. During the process, a lower

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