

Catalytic performance of vanadium incorporated MCM-41 catalysts for the partial oxidation of methane to formaldehyde

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Abstract

The catalytic performance of incorporated V-MCM-41 catalysts for the partial direct oxidation of methane to formaldehyde with molecular oxygen has been investigated. V-MCM-41 catalysts containing 0.56–1.86 wt.% V have been prepared by incorporating the vanadium ions into the framework of mesoporous siliceous MCM-41, resulting in a highly ordered structure with large BET surface area and high surface density of isolated vanadium atoms. The structure of the V-MCM-41 catalysts was studied by N₂ physisorption. The influence of the main reaction parameters, i.e. reaction temperature, reaction pressure, CH₄:O₂ ratio, gas hourly space velocity (GHSV) and vanadium content, on the selectivity and space time yield (STY) of formaldehyde were studied. A formaldehyde selectivity of 59.4% using a 0.56 wt.% vanadium loading V-MCM-41 catalyst was achieved at a temperature of 873 K, pressure of 12 psi, CH₄:O₂ molar ratio of 13:1, GHSV of 2.0×10^3 l kg⁻¹ h⁻¹. The highest STY_{HCHO} of 2103 g kg⁻¹ h⁻¹ with a high HCHO selectivity of 53.2% was obtained with the V-MCM-41 catalyst containing 1.86 wt.% vanadium loading at 933 K, CH₄:O₂ ratio of 13:1, GHSV of 1.3×10^6 l kg⁻¹ h⁻¹. The improved catalytic performance of the V-MCM-41 catalysts is related to the highly dispersed vanadium oxide species forming a high concentration of isolated active sites, which are crucial to minimize the consecutive oxidation of formaldehyde to carbon oxides.

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1. Introduction

The world's known reserves of gas are large enough to be comparable to those of liquid fuels [1,2] and the reserves are increasing much faster than that of oil. Methane, as the principle component of the natural gas and by product of oil refining and chemical processing, has been considered as an important sustainable feedstock for the chemical industry. The effective single-step catalytic conversion of methane into useful oxygenated products, such as formaldehyde and methanol in sufficient yield remains as a great challenge for catalysis in the new century [2–4].

Industrially, formaldehyde is produced from methane by a three-step process including: (i) high temperature steam reforming of methane to syngas (CO and H₂), (ii) high pressure conversion to methanol and (iii) oxidative dehydrogenation of methanol to formaldehyde. The conventional three-step process

clearly has some disadvantages, e.g. the energy requirements of the endothermic steam reforming of the first step, the high pressure operation of the second step and the elimination of the energy of the strongly exothermic oxidation of the last step [5]. Consequently, the direct conversion of methane to formaldehyde via partial oxidation would be highly attractive, and has been the subject of extensive research. However, in spite of the various efforts made, the low selectivities and yields obtained by all of these works have prevented the direct application for commercial consideration [5–7].

Since Blair and Wheeler first demonstrated the catalytic partial oxidation of methane [8], intensive efforts have been made to develop a heterogeneous catalyst system for the partial oxidation of methane, and many reviews have been published outlining the issues for commercial processes [3,4,6,7,9–17]. Many catalyst systems have been investigated for the direct conversion of methane to methanol or formaldehyde, with the majority of the studies involving supported metal oxide catalysts [18–27] primarily molybdenum [12,17,19,25,26] and vanadium oxides [7,12,20,26,27]. Surface vanadium oxide species have been reported to be more reactive and lead to

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higher methane conversion at lower temperature than the molybdenum oxide species, whereas, the latter exhibit higher selectivity to formaldehyde at similar methane conversion [26]. As a support for the transition metal oxide catalysts, silica was reported to be the most effective for the selective partial oxidation [28,29]. Moreover, the silica support itself can also act as a catalyst for the formation of formaldehyde [30]; however, the activity is much lower than the metal oxide catalysts studied.

The active site was proposed to be the isolated tetrahedral vanadium oxide species with terminal oxygen sites ($V=O$) [31–33], whereas, the surface species without terminal $V=O$ sites leads to the over oxidized products. Thus, the dispersion and nature of the metal oxide species have great influence on the reactivity and selectivity of the catalysts for the selective oxidation of methane. The relationship between methane conversion and formaldehyde selectivity and the dispersion of the surface species have been reported by Banares and Fierro [25], Faraldos et al. [26] and Kartheuser and Hodnett [34]. A decrease of formaldehyde selectivity could be seen when the vanadium loading was higher than 2 wt.% in V_2O_5/SiO_2 catalysts, due to the formation of polyvanadates or aggregated vanadium species [34]. Monolayer coverage has been shown to produce the optimized formaldehyde selectivity and productivity for silica stabilized isolated vanadium catalysts [25,35,36] and mesoporous silica supported catalyst, i.e. $VO_x/SBA-15$ catalyst [37].

High active site dispersion is considered to be the key to optimize the productivity of formaldehyde and avoid the consecutive oxidation of formaldehyde to undesired carbon oxides. The dispersion of metal oxide species at moderate loading on the support with high surface area is crucial to improve the catalyst system and thus, enhance the formaldehyde yield. Recently, the mesoporous siliceous material MCM-41 has been used as the support for highly dispersed vanadium oxide species by Berndt et al. [38]. By impregnation, a high concentration of isolated vanadium active species was obtained compared to amorphous silica, resulting in significantly higher formaldehyde space time yield (STY_{HCHO}) of $2255 \text{ g kg}^{-1} \text{ h}^{-1}$ at 895 K and GHSV of $280,000 \text{ l kg}^{-1} \text{ h}^{-1}$ over $VO_x/MCM-41$ with 2.5 wt.% V, albeit, with a low HCHO selectivity of only 26.3%. More recently, Fornes et al. [37] reported the catalytic performance of mesoporous $VO_x/SBA-15$ catalysts by impregnation of vanadium species on the ordered mesoporous material SBA-15. A space time yield of formaldehyde reached about $2383 \text{ g kg}^{-1} \text{ h}^{-1}$ at 891 K and GHSV of $417,000 \text{ l kg}^{-1} \text{ h}^{-1}$ over $VO_x/SBA-15$ with vanadium loading of 3.85 wt.%, again, with a relatively low HCHO selectivity of 39.9%.

Almost all of the heterogeneous catalysts investigated for the partial oxidation of methane are impregnated catalysts, and no studies of this reaction have been published to date using incorporated catalysts (catalyst with V atomically dispersed in a silica matrix) with high dispersion. One study has compared partial oxidation reactions of a range of small alkanes over an MCM-41 catalyst with vanadium dispersed on the wall surface and one in which vanadium was incorporated into the

framework [39], which showed that the two types of catalysts behaved profoundly different. For example, the MCM-41 supported vanadium catalyst showed moderate selectivity for ethane to ethylene and propane to propylene whereas the V-MCM-41 catalyst showed high selectivity for propane to propylene and isobutane to isobutene [39]. In addition, a highly ordered vanadium incorporated MCM-41 catalyst has been successfully synthesized and developed in our previous work [40] such that the physical and chemical properties can be controlled precisely. Our previous work has already shown that V-MCM-41 is a good catalyst for the gas phase conversion of methanol to formaldehyde showing up to 98% selectivity [41]. The aim of this work is to develop V-MCM-41 catalysts with a high density of isolated active sites and to optimize the catalytic reaction conditions for the partial oxidation of methane directly to formaldehyde in order to enhance both the formaldehyde selectivity and the yield. In this work, a series of catalysts with highly ordered structure and highly dispersed vanadium active species are synthesized by direct incorporation of vanadium into the silica framework, characterized by N_2 physisorption and evaluated for the partial oxidation of methane to formaldehyde using molecular oxygen.

2. Experimental

2.1. Catalyst preparation

The sources of silica were Cab-O-Sil (Cabot) and tetramethylammonium silicate (Aldrich). The vanadium source was $VOSO_4 \cdot 3H_2O$ (Sigma–Aldrich). Hexadecyl trimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, Sigma–Aldrich) surfactant was used as a template material. The surfactant solutions were prepared by ion-exchanging the 20 wt.% $C_{16}H_{33}(CH_3)_3NBr$ aqueous solution with equal molar exchange capacity of Amberjet-4400(OH) ion-exchange resin (Sigma) by overnight batch mixing. The resulting solution was filtered and ready for use. The anti-foaming agent was Antifoam A (Sigma), which is a silane polymer alkyl terminated by methoxy groups. Acetic acid (Fisher Scientific) was used for pH adjustment of the synthesis solution.

All of the samples studied in this work are based on C16 V-MCM-41 (16 carbon chain length surfactant). The fumed silica Cab-O-Sil (2.5 g) was added into tetramethylammonium silicate aqueous solution (10.4 g of 16.9 wt.% sol. containing 1 g of SiO_2) and stirred vigorously for 30 min. Deionized water (50.7 ml) was added to improve mixing. The vanadium aqueous solution ($VOSO_4 \cdot 3H_2O$, 2.0 wt.%) was added with continued stirring for another 30 min. Two drops of antifoam agent (0.2 wt.% of surfactant) were added, followed by adding the surfactant ($C_{16}H_{33}(CH_3)_3N \cdot OH$ 20 wt.%) solution (28.7 g) slowly and continuously. The pH was adjusted to 11.5 by adding acetic acid. After additional mixing for about 120 min, this synthesis solution was poured into a polypropylene bottle and placed in the autoclave at 373.2 K for 6 days. After cooling to room temperature, the resulting solid was recovered by filtration, washed with deionized water and dried under ambient conditions. The pre-dried solid was heated at a constant rate

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