



Short Communication

On the role of WO₃ surface hydroxyl groups for the photocatalytic partial oxidation of methane to methanolKatherine Villa ^{a,*}, Sebastián Murcia-López ^a, Teresa Andreu ^a, Joan R. Morante ^{a,b}^a Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Sant Adrià de Besòs, Spain^b Department of Electronics, University of Barcelona (UB), Martí i Franquès 1, 08028 Barcelona, Spain

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ABSTRACT

The photocatalytic partial oxidation of methane to methanol has been investigated on WO₃. The surface fluorination of the catalyst has given an insight on the reaction mechanism which proceeds mainly through the interaction with surface hydroxyl groups.

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1. Introduction

For several years great effort has been devoted to the study of the partial oxidation of methane into useful oxygenates compounds such as methanol [1–3]. Given the low reactivity of methane, this reaction requires high temperatures and pressures to proceed [4,5]. Nevertheless, the previous research has demonstrated that it is possible to perform this methane conversion under mild conditions by photocatalysis [6]. Among the candidate materials that have been examined as possible photocatalysts, tungsten oxide (WO₃) is one of the most promising, due to its relative chemical stability, non-toxicity, and moderate oxidizing power, as previously reported by Taylor and Nocetti [7] and Gondal et al. [8].

The mechanism of this photocatalytic process involved the generation of hydroxyl radicals that are responsible for the activation of methane through the H-abstraction. However, the contribution of the bulk or surface of the catalyst in the mechanism is neither fully understood nor reported earlier. The fact that CH₄ is not adsorbed on the catalyst tends to support the assumption that the oxidation of methane is essentially a bulk reaction, but there is no direct evidence about this procedure. In the literature, several studies have demonstrated that surface fluorination of photocatalysts gives information about the influence of free OH radicals in the solution bulk and surface OH groups in the mechanism reaction [9–12]. Based on this approach, the purpose of the present work is to evaluate the performance of WO₃ surface modified by

fluorine anions and their implications in the mechanistic process of the selective oxidation of methane to methanol.

2. Experimental

2.1. Catalyst synthesis

KIT-6 mesoporous silica material was synthesized following the procedure reported in literature [13]. Ordered mesoporous WO₃ was prepared as follows: a solution of 5 mmol of phosphotungstic acid hydrate (Alfa-Aesar) in ethanol (Aldrich) was incorporated into 0.75 g of as-prepared KIT-6 silica under stirring. The sample was dried and then calcined at 350 °C for 4 h to decompose the precursors, and then further at 550 °C for 6 h to obtain WO₃ inside the hosting silica. Later, the obtained material was suspended under stirring in a 10 wt.% HF solution to remove the KIT-6 silica template. Finally, the mesoporous WO₃ catalyst was separated by centrifugation, washed sequentially with water and ethanol and dried at room temperature. The WO₃/F was prepared by the treatment of the surface of the as-prepared mesoporous WO₃ with hydrofluoric acid. First, 33 μL of 50% HF were added into 15 mL of the aqueous slurry containing 0.3 g of WO₃ under magnetic stirring for 4 h. Later, the suspension was centrifuged, rinsed with water for several times, and finally, the powder was dried at 50 °C.

2.2. Catalyst characterization

The crystallinity was determined by X-ray powder diffraction (XRD) using a diffractometer with Cu-Kα radiation source, a LYNXEYE super speed detector and a Ni filter (Bruker D8 Advance). The light absorption

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properties were measured using a UV–vis diffuse reflectance spectrophotometer (Perkin Elmer Lambda 950 UV–vis) with a wavelength range of 250–800 nm.

2.3. Photocatalytic setup

The photocatalytic partial oxidation of methane tests were performed in a photochemical reactor (Ace Glass) of 500 mL volume equipped with gas inlet and outlet. A medium pressure quartz mercury-vapor lamp (immersion-type Ace Glass) inside the reactor was used to provide UVC–visible light irradiation. The reaction temperature was maintained at 55 °C by the recirculation of cold water in the outer jacket of the lamp. A mixture of methane (4.5 mL min⁻¹) and helium (17.9 mL min⁻¹) was sparged continuously through the photocatalytic reactor. In every experiment, 0.3 g of the photocatalyst was added into 300 mL of water (Milli-Q). Prior to irradiation, the suspension was magnetically stirred in the dark for 30. After that, the lamp was turned on and gas samples were periodically taken for analysis. Blank test with water under UVC–visible irradiation was conducted to examine the products due to photolysis. The products were analyzed using a Shimadzu GC-2010 chromatograph equipped with a capillary column (HP-PLOT Q), a thermal conductivity detector (TCD) and a flame ionization detector (FID).

3. Results and discussion

Fig. 1 shows the powder XRD patterns of pure WO₃ and WO₃/F. All the diffraction peaks of both samples indicate the formation of monoclinic structure of WO₃ (JCPDS Card No. 43-1035). Clearly, the fluorination process does not affect the crystal structure of WO₃. The crystal size was estimated to be 11.7 nm and 11.9 nm for WO₃ and WO₃/F, respectively, based on the Scherrer equation [14].

The diffuse reflectance spectra of the present two samples are shown in Fig. 2. Compared with pure WO₃, the WO₃/F exhibits a slightly higher visible light absorption. Therefore, fluorination affected the optical absorption edge of WO₃. This influence in the light absorption characteristics has also been reported for fluorinated surface TiO₂ and SrTiO₃. In the latter, it has been explained that the substitution of F⁻ to O²⁻ must be compensated for by changing an equivalent number of Ti⁴⁺ to Ti³⁺ to

maintain the electroneutrality of the sample. As a result, the presence of Ti³⁺ shifts the absorption edge of SrTiO₃ to visible light range [15,16].

The photocatalytic conversion of methane to methanol was studied from aqueous suspension containing the as-synthesized WO₃ and WO₃/F samples under UVC–visible light irradiation. A blank experiment consisting on the irradiation of methane in the presence of water (no catalyst) evidences the product formation (Fig. 3). It is well-known that the irradiation of water with a deep-UV lamp (185 nm) leads to the generation of hydroxyl radicals by photolysis [17,18].

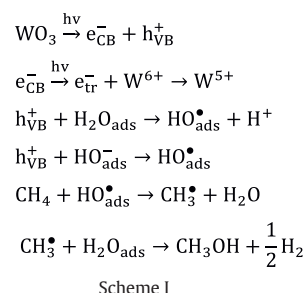


These free hydroxyl radicals can initially perform the activation of methane to produce methyl radicals and then, a series of subsequent reactions involve the production of methanol, ethane, CO₂ and other minor products.



As can be seen in Fig. 3 when the photocatalytic reaction is carried out in the presence of WO₃, the yield of methanol increases 2.4-fold. The reaction is initiated by the irradiation of the WO₃ slurries with light energy higher than ~2.7 eV (that is, wavelengths of <459 nm) that generates an electron (e⁻) and hole (h⁺) pair in the catalyst as described in Scheme 1. In principle, these photogenerated pairs can undergo reductive and oxidative reactions on the catalyst surface and in the bulk.

Since the conduction band (CB) potential of WO₃ is not negative enough to reduce H⁺ to H₂, the formed electrons react with WO₃ to reduce the W⁶⁺ to W⁵⁺. On the other hand, this process also involves the production of HO[•] by the reaction of photogenerated holes with water or hydroxide ions adsorbed on the surface. According to Hameed et al., methane is an inert molecule that is not adsorbed on the catalyst, then, the photocatalytic oxidation reactions occur in the bulk of the catalyst [19]. However, the mechanism of the generation of methanol in the presence of the catalyst with water under UVC–visible irradiation is not clear.



Scheme 1.

In fact, if the mechanism of photocatalytic conversion of methane occurs via homogeneous radical reaction in bulk solution, the addition of a source of OH radicals as H₂O₂, would increase the production of CH₃OH. Taylor and Nocetti [7] reported a remarkable increase in the CH₃OH production after addition of this chemical to the suspension. Even though, in reference [20] and in the present work, the opposite effect was observed (Fig. 3). Gondal et al. suggested that the decrease of the production of methanol in the system WO₃/H₂O₂ is due to its type of irradiation (visible laser). Since the laser irradiation emits a high flux density monochromatic light, it is not necessary to add external hydroxyl radicals generator. However, although the lamp used in these

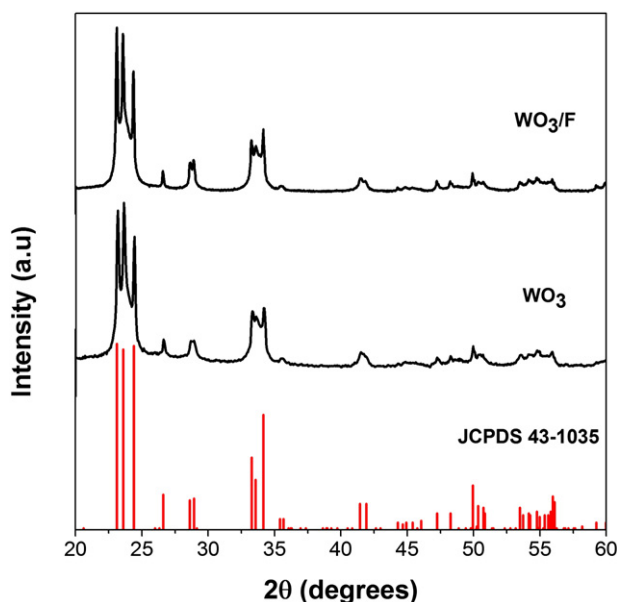


Fig. 1. XRD patterns of WO₃, WO₃/F and the corresponding diffraction pattern of monoclinic phase (JCPDS 43-1035).

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