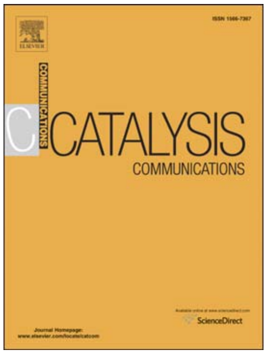

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On the role of WO_3 surface hydroxyl groups for the photocatalytic partial oxidation of methane to methanol

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Abstract

The photocatalytic partial oxidation of methane to methanol has been investigated on WO_3. The surface fluorination of the catalyst has given an insight on the reaction mechanism which proceeds mainly through the interaction with surface hydroxyl groups.

Keywords

Surface fluorinated WO_3; Photocatalysis; CH_4 conversion; Mechanism

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], [2] and [3]. Given the low reactivity of methane, this reaction requires high temperatures and pressures to proceed [4] and [5]. Nevertheless, previous research has demonstrated that 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 (WO_3) 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 CH_4 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], [10], [11] and [12]. Based on this approach, the purpose of the present work is to evaluate the performance of WO_3 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 WO_3 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 350ºC for 4h to decompose the precursors, and then further at 550 ºC for 6h to obtain WO_3 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 WO_3 catalyst was separated by centrifugation, washed sequentially with water and ethanol and dried at room temperature. The WO_3/F was prepared by treatment of the surface of the as-prepared mesoporous WO_3 with hydrofluoric acid. First, 33 µL of 50% HF were added into 15 mL of the aqueous slurry containing 0.3 g of WO_3 under magnetic stirring for 4 h. Later, the suspension was centrifuged, rinsed with water for several times, and finally, the powder was dried at 50ºC.

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 properties were measured using UV–vis diffuse reflectance spectrophotometer (Perkin Elmer Lamba 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 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 WO_3 and WO_3/F. All the diffraction peaks of both samples indicate the formation of monoclinic structure of WO_3 (JCPDS Card No. 43-1035). Clearly, the fluorination process does not affect the crystal structure of WO_3. The crystal size was estimated to be 11.7 nm and 11.9 nm for WO_3 and WO_3/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 WO_3, the WO_3/F exhibits a slightly higher visible light absorption. Therefore, fluorination affected the optical absorption edge of WO_3. This influence in the light absorption characteristics has also been reported for fluorinated surface TiO_2 and $SrTiO_3$. In the latter, it has been explained that the substitution of F^- to O^{2-} must be compensated for by changing an equivalent number of Ti^{4+} to Ti^{3+} to maintain the electroneutrality of the sample. As a result, the presence of Ti^{3+} shifts the absorption edge of $SrTiO_3$ to visible light range [15] and [16].

The photocatalytic conversion of methane to methanol was studied from aqueous suspension containing the as-synthesized WO_3 and WO_3/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 (185nm) leads to the generation of hydroxyl radicals by photolysis [17] and [18].

$$\mathrm{H_2O} \xrightarrow{\mathrm{hv}\ (\lambda \geq 185\mathrm{nm})} 1/2\mathrm{H_2} + \mathrm{HO}^{\bullet} \tag{1}$$

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, CO_2 and other minor products.

$$\mathrm{CH_4} + \mathrm{HO}^{\bullet} \rightarrow \mathrm{CH_3}^{\bullet} + \mathrm{H_2O} \tag{2}$$

As can be seen in Fig. 3 when the photocatalytic reaction is carried out in the presence of WO_3, the yield of methanol increases 2.4-fold. The reaction is initiated by irradiation of the WO_3 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 I*. 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 WO_3 is not negative enough to reduce H^+ to H_2, the formed electrons react with WO_3 to reduce the W^{6+} to W^{5+}. 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.

<u>Scheme I</u>

$$\mathrm{WO_3} \overset{\mathrm{hv}}{\rightarrow} \mathrm{e^-_{CB}} + \mathrm{h^+_{VB}}$$

$$\mathrm{e^-_{CB}} \overset{\mathrm{hv}}{\rightarrow} \mathrm{e^-_{tr}} + \mathrm{W^{6+}} \rightarrow \mathrm{W^{5+}}$$

$$\mathrm{h^+_{VB}} + \mathrm{H_2O_{ads}} \rightarrow \mathrm{HO^\bullet_{ads}} + \mathrm{H^+}$$

$$\mathrm{h^+_{VB}} + \mathrm{HO^-_{ads}} \rightarrow \mathrm{HO^\bullet_{ads}}$$

$$\mathrm{CH_4} + \mathrm{HO^\bullet_{ads}} \rightarrow \mathrm{CH_3^\bullet} + \mathrm{H_2O}$$

$$\mathrm{CH_3^\bullet} + \mathrm{H_2O_{ads}} \rightarrow \mathrm{CH_3OH} + \frac{1}{2}\mathrm{H_2}$$

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 H_2O_2, would increase the production of CH_3OH. Taylor and Nocetti [7] reported a remarkable increase in the CH_3OH 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 WO_3/H_2O_2 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 radical generator. However, although the lamp used in these experiments exhibits the same energy distribution of the lamp described by Taylor and Noceti, it was not observed such an increase of yield of CH_3OH after the addition of H_2O_2.

In addition, a treatment of the surface of WO_3 with hydrofluoric acid was carried out to partially occupy the interaction sites of WO_3. As shown in *scheme II*, the surface OH would be replaced by fluoride, then, on this WO_3/F, the holes photogenerated, directly would react with water molecules to produce only free hydroxyl radicals [21] and [22].

Scheme II

$$\mathrm{W-OH+H^+ + F^- \rightarrow W-F+H_2O}$$
$$\mathrm{W-F+h^+ + H_2O \rightarrow W-F+HO^{\bullet}_{free}+H^+}$$

As can be seen from Fig. 3, the fluorination of WO_3 led to a decrease in the yield of methanol. Strikingly, the methanol generated (2.4 µmol h^{-1}) was almost the same that the blank experiment without catalyst (2.1 µmol h^{-1}). This result suggests that about 6% of the methanol photogenerated is due to direct hole oxidation (solution bulk) and 94% due to adsorbed hydroxyl radicals. Hence, a surface catalyst with active sites is essential for the improvement of the generation of methanol under UVC-visible light irradiation with water. On the other hand, considering the yields of ethane corresponding to each system (Fig. 3), it seems clear that increasing the content of free OH radicals in the aqueous slurry leads to a high formation of methyl radicals that stimulate the increase of ethane. Hence, in the system WO_3/H_2O_2 is observed the highest selectivity toward C_2H_6.

(See the Supplementary data, Table S1).

Based on the above, the reaction scheme shown in Fig. 4 has been proposed for the photocatalytic conversion of CH_4 on WO_3. It can be assumed that although methane is not adsorbed on the catalyst (See the Supplementary data, Fig. S1), the mechanism in this photocatalytic conversion would imply a synergistic effect between water and catalyst that improves the generation of methanol. Thus, the hydroxyl radical formed in the photolysis of water activate the methane by hydrogen abstraction to produce mainly methyl radicals and then these reactive species would react with OH radicals adsorbed on the catalyst to increase the yield of methanol. On WO_3/F the reaction proceeds almost entirely through homogeneous hydroxyl radicals. As a result, the generation of ethane and total oxidation is favored.

4. Conclusions

Summing up the results, it can be concluded that the modification of the surface of WO_3 by fluorination affects negatively the yield of methanol. This effect is attributed to a change in the reaction mechanism that favors the free OH radical formation in the aqueous medium. Also, the addition of a hydroxyl radical generator to the reaction results in a decrease of the generation of methanol compared to pure WO_3. Then, our findings describe for the first time that OH radical groups on the catalyst surface are the main responsible to enhance the performance of WO_3 in the selective oxidation of methane to methanol while a larger amount of free OH radicals favor the formation of ethane.

Acknowledgements

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Figure captions

Fig. 1. XRD patterns of WO_3, WO_3/F and the corresponding diffraction pattern of monoclinic phase (JCPDS 43-1035).

Fig. 2. Diffuse reflectance spectra of WO_3 and WO_3/F samples and spectral energy distribution of the quartz mercury-vapor lamp.

Fig. 3. Yields of products in the photocatalytic oxidation of CH_4 on blank, WO_3/F, WO_3/H_2O_2 and WO_3 at ~50 ºC under UVC-visible light irradiation. Catalyst dosage is $1 g\cdot L^{-1}$. Data corresponding to 2 h of irradiation in continuous methane flow of 4.5 mL min^{-1}. Error bars represent standard deviation.

Fig. 4. Proposed reaction pathway for the selective oxidation of methane to methanol on WO_3 and WO_3/F.

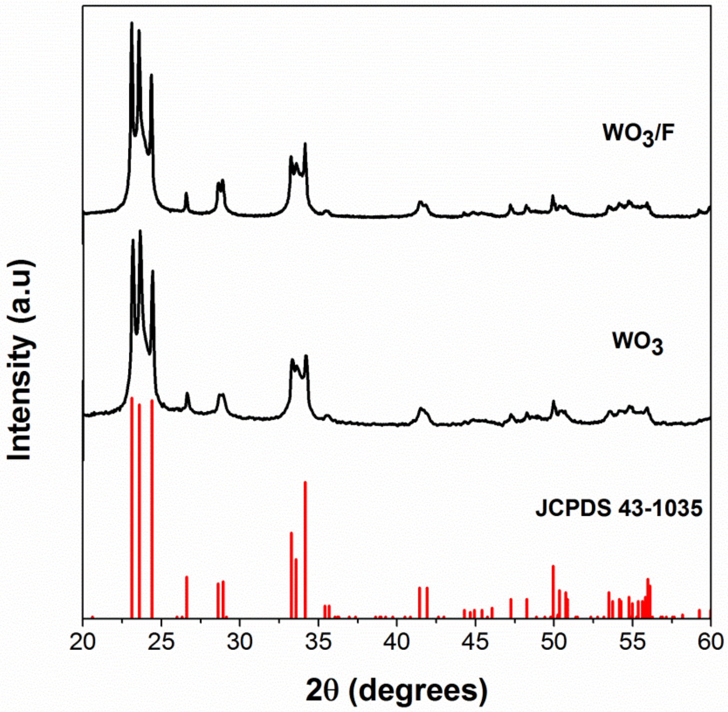

WO3/F
WO3
JCPDS 43-1035
Intensity (a.u)
2θ (degrees)
20
25
30
35
40
45
50
55
60

Figure 1

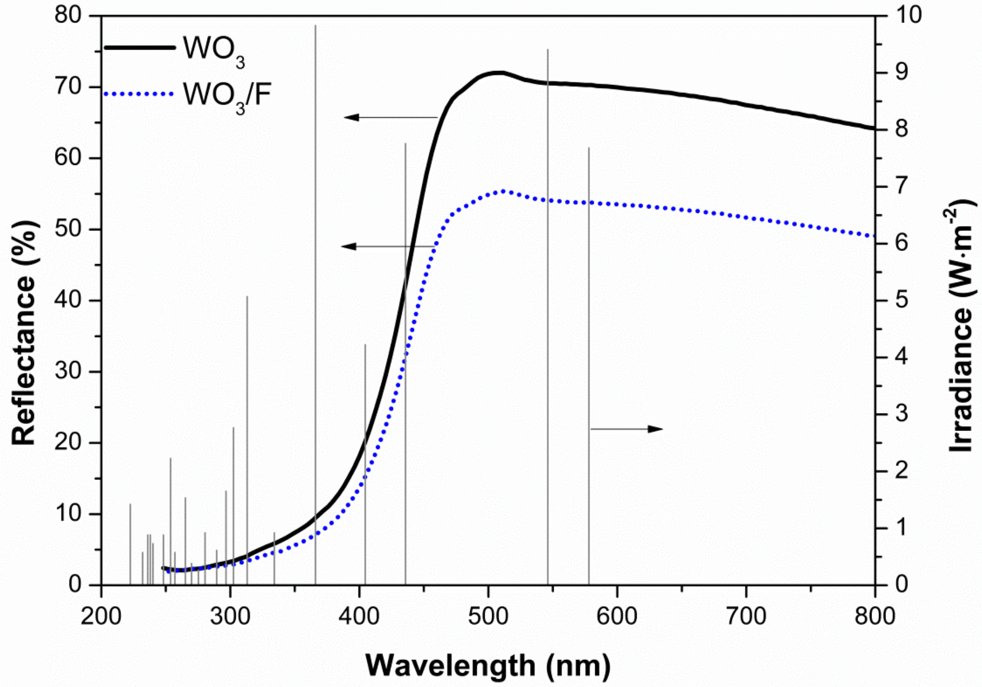

80
70
60
50
40
30
20
10
0
Reflectance (%)
WO$_3$
WO$_3$/F
10
9
8
7
6
5
4
3
2
1
0
Irradiance (W·m^{-2})
200
300
400
500
600
700
800
Wavelength (nm)

Figure 2

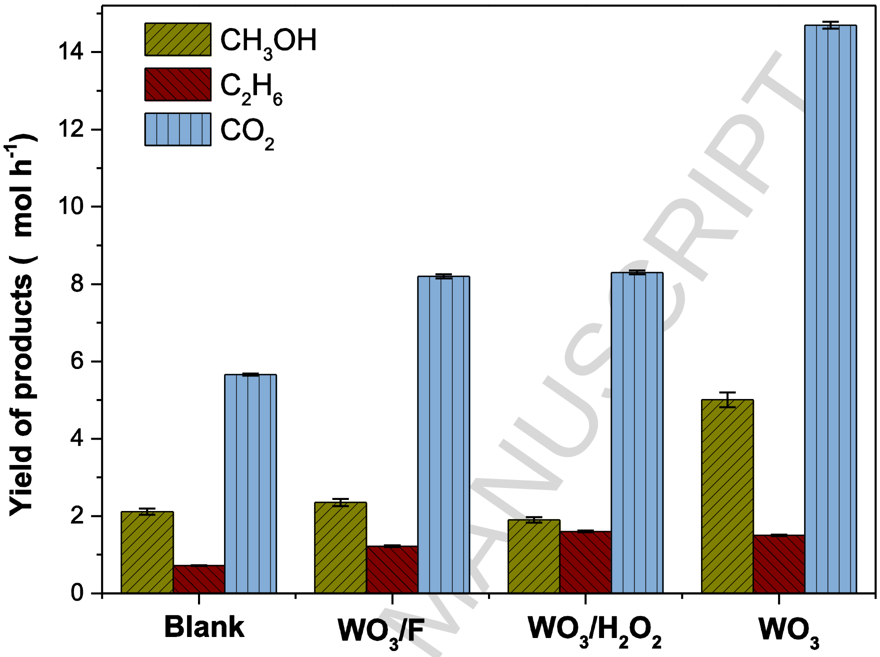

CH$_3$OH
C$_2$H$_6$
CO$_2$
Yield of products (mol h^{-1})
0
2
4
6
8
10
12
14
Blank
WO$_3$/F
WO$_3$/H$_2$O$_2$
WO$_3$

Figure 3

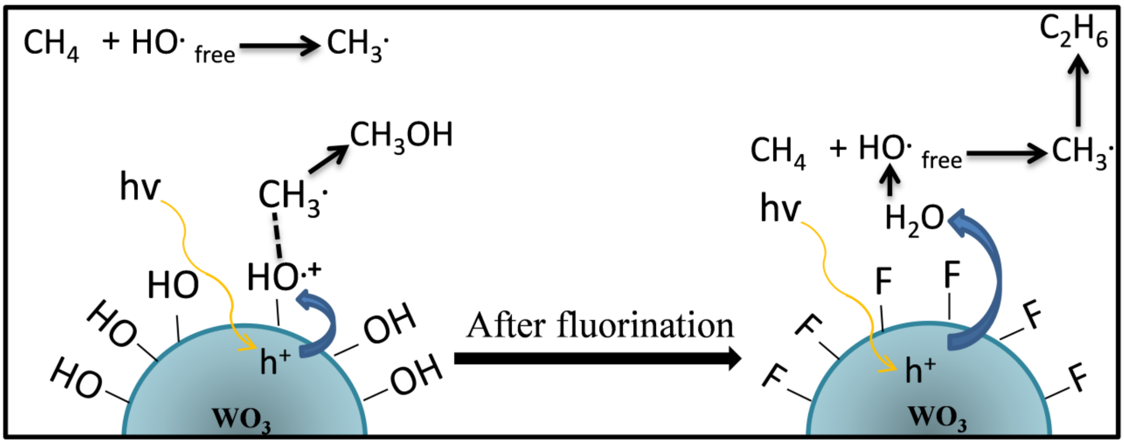
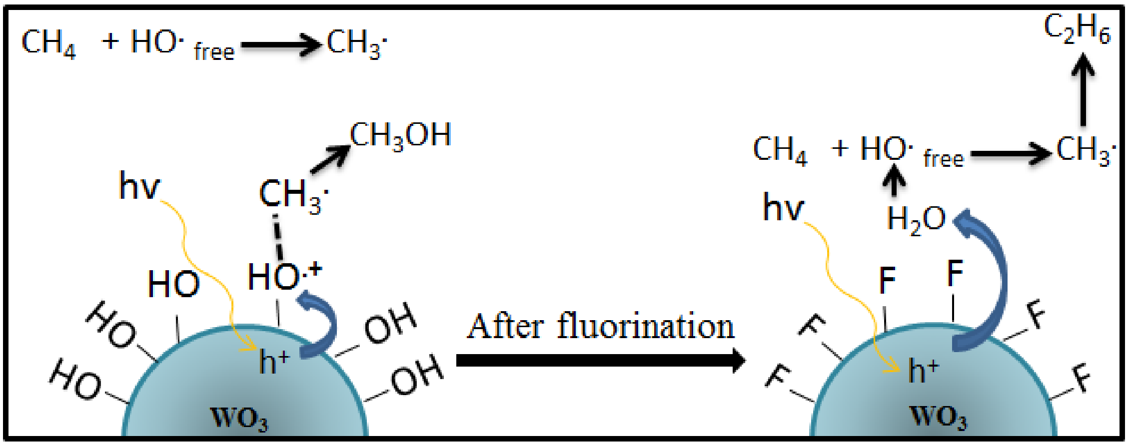

CH_4 + HO· free → CH_3·
CH_3OH
hv
CH_3·
HO·+
HO
HO
HO
OH
OH
h+
WO_3
After fluorination
C_2H_6
CH_4 + HO· free → CH_3·
hv
H_2O
F
F
F
F
F
F
h+
WO_3

Figure 4



Graphical abstract

Highlights

- Photocatalytic conversion of CH_4 over WO_3 and WO_3/F was studied.
- Surface fluorinated WO_3 led to low yield of methanol.
- Reaction pathway was proposed for the photocatalytic conversion of CH_4 on WO_3.