Selective photo-assisted oxidation of methane into formaldehyde on mesoporous VO_x/SBA-15 catalysts

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Mesoporous VO_x/SBA-15 samples have been prepared by different impregnation methods, characterized by N_2 adsorption and diffuse reflectance UV–visible spectroscopy, and their photocatalytic reactivity evaluated for the selective oxidation of methane with oxygen at 220 °C under UV irradiation. Vanadium in dehydrated VO_x/SBA-15 samples was found to be predominantly as isolated four-coordinated V^{5+} species, especially at V loading below 2.5 wt%. VO_x/SBA-15 catalysts prepared by impregnation with an aqueous solution of ammonium metavanadate (AMV) showed a maximum rate of formation of formaldehyde of 525 μmol g^{-1} h^{-1} (selectivity of 93.8 mol%) at a vanadium content of 2.65 wt%. Both the rate of formation and selectivity of formaldehyde were improved when vanadium was impregnated on the SBA-15 support from a vanadyl sulfate methanolic solution (rate of formation of HCHO = 733 μmol g^{-1} h^{-1}, selectivity = 95.4 mol%). VO_x/SBA-15 catalysts were seen to be more effective for the selective photo-assisted oxidation of methane than VO_x/SiO_2 catalysts.

KEY WORDS: photo-oxidation of methane; vanadium oxide; SBA-15; formaldehyde.

1. Introduction

The partial oxidation of methane (POM) into methanol and formaldehyde offers an attractive route for the synthesis of high-value chemicals from relatively inexpensive feedstocks, *i.e.*, natural gas [1]. Among the different POM catalysts studied, better results have usually been reported for V and Mo oxides supported on silica [2–4]. However, at the relatively high reaction temperatures used (typically above 600 °C) the over-oxidation of the intermediate oxygenates into carbon oxides is a serious competing reaction leading to low product selectivities. Deep oxidation reactions can be minimized by working at very low per-pass methane conversions, making the process economically unattractive.

There are, therefore, strong incentives for searching for new routes for the selective activation of methane at low temperatures [1,5]. In this sense, the photocatalytic activation of light alkanes has been investigated in the past two decades as an alternative pathway for the selective formation of oxygenated products at mild temperatures [6–10]. The photoreactivity of different transition metal oxides supported on porous Vycor glass [11–14] or incorporated on microporous and mesoporous zeolitic materials [15–17] has been extensively studied by Anpo and co-workers. In the case of vanadium-containing catalysts, these authors have shown by using different *in situ* spectroscopic techniques, such as dynamic photoluminescence, ESR, XAFS, UV–vis and FTIR, that the photocatalytic reactivity of the catalysts is closely related with the charge transfer excited triplet of surface vanadyl species, $(V^{4+}-O^{-})^{*}$, associated with highly dispersed surface tetrahedral vanadium entities [11–17]. Recently, Wada *et al.* [18] reported high activities for the selective photo-oxidation of methane on a V_2O_5/SiO_2 catalyst under UV irradiation. The photo-oxidation of methane on V_2O_5/SiO_2 was suggested to occur only on highly dispersed isolated tetrahedral V^{5+} species having a V=O group [18]. These authors reported a maximum yield of formaldehyde of 34 μmol h^{-1} at 220 °C for a V_2O_5/SiO_2 catalyst containing 0.6 mol% V, corresponding to a selectivity of 76 and 0.48 mol% one-pass yield. Higher vanadium loading resulted in a decreased formaldehyde yield as a result of a poorer dispersion of the vanadium oxide species on the low surface area amorphous silica support favoring the formation of accumulated V–O–V species that were not active for the photo-oxidation of methane [18].

The concentration of isolated tetrahedral vanadium species and thus the photocatalytic activity of vanadium-supported catalysts might be increased, in principle, by spreading the vanadium precursor on a high-surface-area-support. In this respect, Anpo and co-workers have already demonstrated the high photoreactivity of V species incorporated within a high-surface-area mesoporous molecular sieve (HMS) [15,16]. Recently, the synthesis of a new highly-ordered mesoporous silica SBA-15 material has been achieved using a triblock copolymer template under acidic conditions [19]. SBA-15 material possesses

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high surface area (600–1000 m^2/g) and is formed by uniform hexagonal channels with pore diameters in the range of 5–30 nm, which are significantly larger than those of MCM-41 materials (3–8 nm).

In this work, we have investigated for the first time the photocatalytic activity of vanadium-supported SBA-15 catalysts for the selective oxidation of methane to formaldehyde under UV irradiation. The influence of the method of vanadium impregnation and vanadium loading is addressed. Finally, the photo-oxidation activity of VO_x/SBA-15 is compared with that of VO_x/SiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

An all-silica SBA-15 sample was synthesized according to the procedure described in ref. [20] with slight modifications, using Pluronic triblock copolymer (Aldrich, EO_{20}–PO_{70}–EO_{20}, P123) as the structure-directing agent and tetraethyl orthosilicate (TEOS, Merck-Schuchardt) as silica source from a gel of the following molar composition:

$$SiO_2 : 0.0168\,P123 : 5.866\,HCl : 193\,H_2O.$$

First, the triblock copolymer is dissolved in a solution of water and HCl under stirring, and then the required amount of TEOS is added to the above solution at 36 °C and kept with stirring for 20 h. Then, the gel mixture is transferred into polypropylene bottles and heated at 80 °C for 3 days in static. After the synthesis, the solid obtained is filtered, exhaustively washed with distilled water until neutral pH, dried at 80 °C and finally calcined in a flow of air at 500 °C for 6 h.

Vanadium was loaded into siliceous SBA-15 by impregnation using three different methods: (i) incipient wetness impregnation from an aqueous solution of ammonium metavanadate (AMV, Riedel-deHaën) (method A), (ii) impregnation in excess solvent (liquid : solid ratio = 8 cm^3/g) from an aqueous AMV solution followed by evaporation to dryness (method B), and (iii) impregnation in excess solvent using a methanolic solution containing the required amount of vanadyl sulfate (VS, Aldrich) followed by evaporation to dryness (method C).

VO_x/SBA-15 samples with variable vanadium loading (1.26–5.54 wt% V) were prepared by method B. A series of VO_x/SiO_2 catalysts with vanadium loading from 0.57 to 2.38 wt% V was also prepared for comparison by impregnation using method A. The silica support used for the preparation of VO_x/SiO_2 catalysts was a fumed silica (Aldrich) with low alkali content (90 ppm Na, 50 ppm K). After impregnation the V-containing samples were dried at 100 °C overnight and finally calcined at 650 °C for 16 h.

2.2. Characterization techniques

The textural properties of the SBA-15 and amorphous SiO_2 supports and the V-containing materials were determined by N_2 adsorption at −196 °C in Tristar 3000 equipment (Micromeritics) after pretreating the samples at 400 °C in vacuum overnight. The nature of the V species was studied by UV–vis spectroscopy in a Varian Cary 5G equipment. The UV–vis spectra of dehydrated samples were obtained after pretreating the solids at 400 °C in a flow of Ar (20 cm^3/min) for 2 h. The vanadium content was determined by atomic absorption spectrophotometry in Spectra-A 10 Plus (Varian) apparatus.

2.3. Photocatalytic experiments

The photo-oxidation of methane was carried out in a quartz glass reactor equipped with a flat cell (10 mm × 35 mm, 1.0 mm inner thickness) for UV irradiation. The irradiation window was loaded with catalyst particles of 0.10–0.25 mm size confined between two quartz glass plugs. Before starting the irradiation the catalysts were pretreated at the reaction temperature (220 °C) in nitrogen flow for about 30 min. Then, the reactant gas mixture (N_2:CH_4:O_2 molar ratio of 10:3:1) was fed at the top of the reactor (downflow system) after passing through a preheater kept at a constant temperature of 170 °C. Heating of the catalyst bed was accomplished by means of two cartridge heaters inserted in respective metallic elements surrounding the irradiation cell perpendicular to the direction of the light. The temperature in the catalyst bed was measured by a thermocouple inserted at the middle of the bed. The maximum temperature gradient in the bed was determined to be 14 °C, which is similar to the 15 °C gradient observed by Wada *et al.* [18] in their irradiation cell. For UV irradiation two high-pressure mercury vapor lamps (250 W, 60 mm arc length) with a water filter and equidistant *ca.* 75 mm from the irradiation window were used. The total number of photons irradiated by the two lamps to the catalyst bed was estimated to be 16.8×10^{-7} einstein s^{-1} for 250–500 nm range by using the ferric potassium oxalate chemical actinometry method. All the experiments were carried out at 220 °C reaction temperature and at a GHSV of 31 500 l kg^{-1} h^{-1} (catalyst mass of 0.050–0.150 g). The irradiation times typically varied between 2 and 5 h. The liquid oxygenated products (formaldehyde and methanol) were condensed and accumulated at the reactor exit in a receiver containing a small and known amount of water (*ca.* 2–3 g) immersed in an ice bath at *ca.* 0 °C. Gaseous products (N_2 diluent, unconverted CH_4 and O_2, CO and CO_2) were collected in a gas sampling bag. Both liquid and gas products were analyzed in a gas chromatograph (HP 6890 Series Plus) equipped with both thermal conductivity (TCD) and

flame ionization detectors (FIDs) and two packed columns (molecular sieve 5 Å and Hayesep-Q).

3. Results and discussion

3.1. Characterization of catalysts

The chemical composition and textural properties of the V/SBA-15 and V/SiO_2 samples are given in table 1. The shape of the N_2 adsorption isotherm of calcined siliceous SBA-15 sample (not shown) confirmed the presence of a uniform mesopore structure characteristic of a good-quality SBA-15 material. Vanadium-supported SBA-15 samples show N_2 adsorption isotherms similar to Si-SBA-15 but with a decreased BET surface area and pore volume, as observed in table 1. Moreover, a decrease of surface area and pore volume with increasing V loading is observed for VO_x/SBA-15 samples prepared by aqueous impregnation in excess AMV solution (method B). It is also seen in table 1 that the sample prepared by method A (incipient wetness impregnation from an aqueous AMV solution) shows surface area and pore volume similar to a VO_x/SBA-15 sample prepared by method B and having similar V content. However, the 2.5V/SBA(C) sample impregnated from a methanolic solution of vanadyl sulfate precursor (method C) shows higher surface area and pore volume than samples obtained by aqueous impregnation (at similar V loading), indicating that the mesoporous structure of SBA-15 was better preserved in the former case. Furthermore, at similar vanadium loading VO_x/SBA-15 samples present much higher surface area than VO_x/SiO_2 (table 1).

The UV–vis spectra of calcined VO_x/SBA-15 samples with different vanadium loading and prepared by method B are presented in figure 1. Dehydrated VO_x/SBA-15 samples (figure 1(a)) show a main strong absorption band centered at about 280 nm, which can be assigned to isolated V^{5+} species in a tetrahedral coordination [21]. Besides this band, a shoulder at higher wavelengths (300–400 nm) is also observed in the UV–vis spectra of dehydrated VO_x/SBA-15 samples, suggesting the presence of some polymeric vanadium species. The relative concentration of those polymeric V species appears to increase with increasing vanadium loading. Formation of significant amounts of V_2O_5 in VO_x/SBA-15 samples is unlikely as dehydrated bulk V_2O_5 gives strong absorption bands at *ca.* 340 and 460 nm, although the presence of some dispersed microcrystalline V_2O_5 particles cannot be excluded.

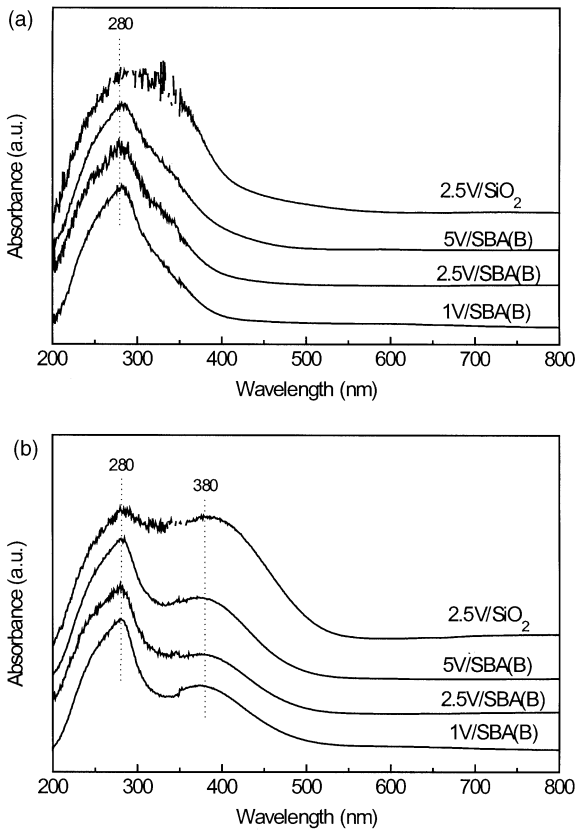

Figure 1. Diffuse reflectance UV–vis spectra of dehydrated (a) and hydrated (b) VO_x/SBA-15 samples with different vanadium loading prepared by method B. The spectra of a VO_x/SiO_2 sample (2.38 wt% V) are also included for comparison.

Table 1
Physicochemical properties of VO_x-supported catalysts.

Sample[a]	V content (wt%)	BET (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
Si-SBA-15	–	915	1.07	45.8
1V/SBA (B)	1.26	569	0.58	43.3
2.5V/SBA (B)	2.65	507	0.56	46.6
4V/SBA (B)	3.85	480	0.54	45.9
5V/SBA (B)	4.51	449	0.58	53.9
6V/SBA (B)	5.54	336	0.49	56.4
2.5V/SBA (A)	2.36	523	0.60	46.1
2.5V/SBA (C)	1.71	604	0.89	55.6
SiO_2	–	375	0.67	79.1
0.5V/Si (A)	0.57	294	0.72	97.2
1V/Si (A)	1.20	312	0.75	97.1
2.5V/Si (A)	2.38	306	0.74	89.8

[a] Method of vanadium impregnation in parentheses (see experimental section).

On the other hand, hydrated VO_x/SBA(B) samples (figure 1(b)) show, besides the band at *ca.* 280 nm of tetrahedral V^{5+} species, a broad absorption band at *ca.* 380 nm, indicating that part of the tetrahedral species were transformed into penta- or octahedral V^{5+} ions by additional coordination to water molecules [21]. The fact that some vanadium species still remain in a tetrahedral coordination upon hydration may suggest that they are located inside the siliceous walls of SBA-15. It is also seen in figure 1(b) that the relative intensity of the 380 nm band with respect to that at *ca.* 280 nm increases with the vanadium content. Similar features have been

Table 2
Photo-oxidation of methane on VO_x/SBA-15 catalysts.

Sample [a]	V content (wt%)	CH_4 conversion rate (μmol h^{-1} g^{-1})	Selectivity (mol%)			HCHO formation rate (μmol h^{-1} g^{-1})
			HCHO	CH_3OH	CO_x	
Si-SBA-15	–	0.4	–	–	–	–
1V/SBA (B)	1.26	382	93.4	0.3	6.3	357
2.5V/SBA (B)	2.65	560	93.8	0.4	5.8	525
4V/SBA (B)	3.85	499	89.2	0.6	10.2	445
5V/SBA (B)	4.51	318	77.4	1.4	21.2	246
6V/SVA (B)	5.54	482	51.7	1.0	47.3	249
2.5V/SBA (A)	2.36	629	85.7	0.4	13.9	539
2.5V/SBA (C)	1.71	810	95.4	0.2	4.4	773

[a] Method of vanadium impregnation in parentheses (see experimental section).
Reaction conditions: $T = 220\,^{\circ}C$, $N_2 : CH_4 : O_2$ molar ratio = 10 : 3 : 1, methane feed rate = 25 mmol h^{-1}, GHSV = 1.28 mol g^{-1} h^{-1}.

reported for VO_x/SBA-15 samples prepared by a different impregnation method [22]. The most accessible V species which can achieve coordination higher than four were suggested to be coordinated on the interior wall surface of SBA-15 [22].

For comparison purposes, the diffuse reflectance UV–vis spectra of a VO_x/SiO_2 sample containing 2.38 wt% V (Si/V = 34) are also presented in figure 1. Dehydrated VO_x/SiO_2 (figure 1(a)) shows a broad absorption band in the 250–350 nm range, which suggests a wide distribution of vanadium oxide species with a significant contribution of polymeric V^{5+} species (V–O–V) on the silica surface. After hydration a strong absorption band at *ca.* 380 nm of octahedral vanadium appears in the UV–vis spectrum of VO_x/SiO_2 (figure 1(b)).

3.2. Photo-oxidation of methane on VO_x/SBA-15 catalysts

The photocatalytic reactivity for methane oxidation and product selectivities of the VO_x/SBA-15 catalysts are given in table 2. The rate of methane conversion on a vanadium-free Si-SBA-15 sample under the same reaction conditions was below 1 μmol h^{-1} g^{-1}, indicating that the presence of vanadium in the catalyst was essential for obtaining photocatalytic activity. Furthermore, we also checked in a blank experiment that at 220 °C the reaction did not proceed in the absence of UV irradiation. As observed in table 2, a maximum methane conversion rate of 560 μmol h^{-1} g^{-1} was obtained for the VO_x/SBA-15 sample (method B) containing 2.65 wt% V. For all the VO_x/SBA(B) catalysts the main product formed from the photo-oxidation of methane under the reaction conditions used was formaldehyde, whereas methanol was formed in small amounts. Moreover, a strong dependence of the selectivity to formaldehyde on the vanadium content was clearly observed. Thus, formaldehyde selectivity was very high (above 93 mol%) for samples with vanadium content up to 2.65 wt%, and then a decrease was noticed for higher vanadium loading in favor of carbon oxides produced by overoxidation of the aldehyde.

According to the UV–vis results discussed before (figure 1), most of the vanadium in VO_x/SBA-15 was present as dispersed tetrahedral V^{5+} entities, though some polymeric V–O–V species and microcrystalline V_2O_5 could also be formed on the surface of SBA-15 at high vanadium loading (>2.5 wt%). Taking this observation into consideration, the photocatalytic results presented above suggest that the selective formation of formaldehyde on mesoporous VO_x/SBA-15 catalysts proceeds on highly dispersed tetrahedral V^{5+} species, while polymeric vanadium species are probably responsible for the decomposition of formaldehyde into carbon oxides. These results are in good agreement with those previously reported by Anpo and co-workers [11–17] which related the photocatalytic activity of vanadium-containing catalysts to the charge transfer excited triplet state of tetrahedrally coordinated V species. Moreover, according to Wada *et al.* [18] only isolated tetrahedral V species on the surface of VO_x/SiO_2 samples displayed photocatalytic activity toward methane oxidation.

The rate of formation of formaldehyde on VO_x/SBA-15 and VO_x/SiO_2 catalysts is compared in figure 2 as a function of vanadium loading. A maximum in the rate of formation of formaldehyde of 525 μmol h^{-1} g^{-1} was observed for the 2.5V/SBA(B) sample containing 2.65 wt% vanadium. The rate of formation of the aldehyde decreased to *ca.* 250 μmol h^{-1} g^{-1} for vanadium contents up to about 4.5 wt% and then remained practically unchanged at higher metal loading. By contrast, the maximum rate of formation of HCHO was 391 μmol h^{-1} g^{-1} for VO_x/SiO_2 catalysts, this maximum being observed at a much lower vanadium content (1.20 wt% V) as compared with VO_x/SBA-15. In a previous work, Wada *et al.* [18] also reported a maximum rate of formation of formaldehyde by photo-oxidation of methane on VO_x/SiO_2 at a vanadium content of 0.6 mol% for a series of samples prepared by incipient wetness impregnation and at 1.0 mol% V for a series of

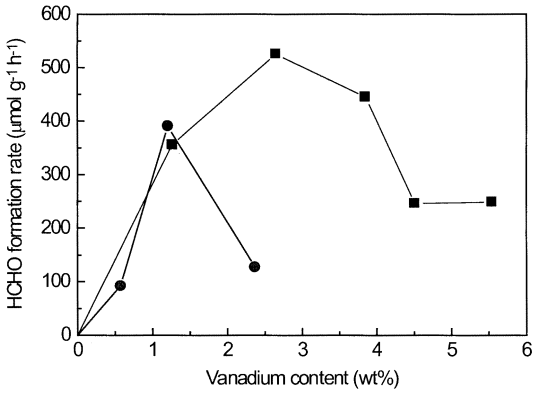

Figure 2. Influence of vanadium content on the rate of formation of formaldehyde: (■) VO_x/SBA-15 (method B), (●) VO_x/SiO_2 catalysts. Reaction conditions: $T = 220\,^{\circ}C$, $N_2:CH_4:O_2$ molar ratio = 10:3:1, methane feed rate = 25 mmol h^{-1}, GHSV = 1.28 mol g^{-1} h^{-1}.

samples obtained by a sol–gel procedure. If, as has been suggested, the formation of formaldehyde occurs on isolated tetrahedral V entities, the data in figure 2 would clearly indicate a better dispersion of the vanadium oxide on the mesoporous SBA-15 support, especially at relatively high V contents, as could also be deduced from the UV–vis results in figure 1.

Finally, the effect of the method of vanadium impregnation on the catalytic behavior of VO_x/SBA-15 was also examined. At a similar V content, the catalyst prepared by incipient wetness impregnation from an aqueous solution of AMV (method A) displayed a similar rate of formation of HCHO (539 μmol h^{-1} g^{-1}) to the sample obtained in excess aqueous solution (method B) (table 2). However, both a higher photocatalytic activity and HCHO selectivity (95.4 mol%) were obtained for the catalyst prepared by impregnation with a methanolic solution of vanadyl sulfate precursor (method C), resulting in a significantly higher rate of HCHO formation (773 μmol h^{-1} g^{-1}). As shown before, the VO_x/SBA-15 sample prepared by method C had a higher surface area and pore volume than those prepared by methods A and B (table 1), which could favor the dispersion of the vanadium oxide species resulting in a higher photocatalytic activity for methane oxidation.

4. Conclusions

VO_x/SBA-15 mesoporous catalysts displayed high photocatalytic activity for the selective oxidation of methane to formaldehyde at mild temperatures. For the series of samples prepared by method B a maximum in the rates of methane conversion and formation of formaldehyde was obtained at a vanadium loading of 2.65 wt%. Selectivity to formaldehyde was very high (above 93 mol%) for samples with V loading below 2.65 wt% and decreased for higher vanadium contents. A further improvement in photo-oxidation activity and HCHO selectivity (*ca.* 95 mol%) was achieved by impregnating the Si-SBA-15 support with a vanadyl sulfate methanolic solution, which led to better mesostructured materials. VO_x/SBA-15 catalysts displayed a higher photocatalytic activity and produced higher yields of formaldehyde than VO_x/SiO_2, especially at a vanadium loading above 1 wt%.

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