# Investigation of non-thermal plasma treatment on vanadium oxide-based catalysts

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**Abstract:** The modification of supported vanadium oxide catalysts was carried out in a direct current hollow cathode discharge plasma sustained in  $O_2$  gas. The modified catalysts were characterized using different techniques such as BET, XPS, and SEM. The results showed that the surface active sites of these catalysts were enhanced with plasma, which improved the dispersion of the catalysts and confirms that plasma is an effective tool to manipulate the catalyst surface properties, which may contribute to an increasing catalyst activity.

Keywords: plasma modification, vanadium oxide, catalyst performance, morphology.

## 1. Introduction

Catalysis has been considerably utilized in the chemical industry. At present, almost all major chemicals are produced by catalytic processes. Due to the development of renewable energy and increasing concern about the environment, catalysts will play an even more prominent role in the future. Various methods and efforts have been performed in order to modify and obtain catalysts with controllable structure and properties: thermal treatment (in  $O_2$ ,  $H_2$ , or inactive gas), electrochemical treatment, wet impregnation, plasma treatment, ion or cluster bombardment, supercritical fluids, etc. [1, 2].

Plasma is a quasi-neutral gas composed of energetic free radicals, ions, electrons, photons, and neutrals. The active species in the plasma can simultaneously interact with the catalyst surface to alter its chemical and physical properties. Thus, non-thermal plasma (NTP) techniques are dry processes and plasma modifications are restricted to the top surface of the material, leaving the bulk unaltered. This makes plasma based processes more convenient than other processes for the incorporation of surface functional groups [1].

The application of NTP in the preparation of catalysts has been considered as a promising way for improving the catalysts' performance. This method can be used in any step of the catalyst preparation, including treatment of the support, drying, decomposition, oxidation, reduction, activation and also the regeneration of deactivated catalysts in order to allow improving dispersion and enhancing the low-temperature activity and stability of catalysts [3, 4]. In recent years, few works have been done on modifying the surface of catalysts using NTPs such as plasma treatment of silica supports for improving Fischer–Tropsch synthesis (FTS) activity [3, 5], improvement of MnO<sub>x</sub> catalysts for the catalytic oxidation of nitrogen oxide and increase of the carbon based catalyst's activity for  $H_2O_2$  reduction in a fuel cell using a low-pressure radio frequency discharge [3]. In many cases it is highly complicated to reach a high catalyst activity, selectivity and excellent stability. The purposes of such catalyst surface modifications include the generation of surface vacancies and roughed surfaces, the increase in active sites, and the modification of the surface functional groups. This can lead to a change in surface properties of the catalyst in order to improve its performance and achieve the optimum catalytic properties [5-7]. There are many factors that can affect catalytic reactions like size, phase structure, shape, catalyst-support interaction, interface, surface properties, reaction conditions and others.

Supported metal oxide catalysts are of great importance because of their numerous applications in the chemical and environmental industries. In particular, supported vanadium oxide materials are widely used in various selective oxidation reactions as well as in the manufacturing of important chemicals (e.g. sulfuric acid, phthalic anhydride) and in the reduction of environmental pollution (e.g. nitrogen oxides from flue gas of power plants). These catalysts consist of an active vanadium oxide phase deposited on the surface of an oxide support, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> in order to improve their activity, selectivity, mechanical strength, thermal stability and lifetime [8]. In the present study, the catalyst was first prepared with a specific content of vanadium, which has been measured by ICP-OES device (Varian, Vista MPX) (inductively coupled plasma optical emission spectroscopy) after preparation. Next, a direct current hollow cathode discharge plasma sustained in O2 gas was used to investigate the effect of NTP on this catalyst at different plasma conditions. The variations of surface active groups, chemical composition, and topography were examined by Brunauer-Emmett-Teller (BET) surface area analysis, field emission gun scanning electron microscopy (FEG-SEM), scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) and X-ray photoelectron spectroscopy (XPS).

### 2. Experimental

#### 2.1. Catalyst preparation

Silica gel (Kieselgel 60) was obtained from Merck. This silica was first thermally pretreated in air for 17 h at 400°C. At this temperature, the specific area of the silica has a constant value of 367.38 (cm<sup>2</sup>/gr). In this study, the catalyst was prepared by adsorption and calcination of vanadyl acetylacetonate complexes on the surfaces of silica. Vanadyl acetylacetonate was supplied by Fluka, dried at 120°C and dissolved under vacuum in an appropriate amount of acetonitrile solvent. Afterwards, silica was added to the vanadium solution and was filtered, washed and dried under vacuum. Calcination was performed at 400°C for 17 h in air. The amount of vanadium in untreated catalyst (V<sub>2</sub>O<sub>5</sub>) was found to be 3.85 mg/gr, as obtained from ICP-OES device.

### 2.2. Non-thermal plasma treatment

The plasma modification process was produced in a direct current hollow cathode discharge plasma reactor operating at low pressure  $(2.5 \times 10^{-1} \text{ mbar})$  (Fig. 1). The plasma was generated at a discharge output voltage of 0.5-1.1 kV. All dried catalyst powders (0.5 g) were placed into the rotating bed rotating at a speed of 5 rpm. During the plasma treatment process, a mass flow controller (Bronkhorst F201) was used to send a constant oxygen gas flow of 10 standard cubic centimetre per minute (sccm) into the reactor. The plasma exposure time was varied between 10 and 20 min. After plasma treatment, the treated catalysts were stored in an airtight container for further measurements.



Fig. 1. Schematic representation of the used experimental set-up.

# 2.3. Catalyst characterization

The textural properties of the prepared catalysts were determined by nitrogen adsorption. This technique was used to examine the surface area and the pore size distribution. The measurements were carried out by a Tristar 3000 (Micrometrics) device using liquid N<sub>2</sub> at -196°C. Before starting the measurements, each sample was first pretreated at 120°C for 16 h while degassing. The BET surface area has been measured making use of the BET equation.

XPS measurements were carried out to analyse the elemental composition on a PHI 5000 Versaprobe II spectrometer equipped with a monochromated Al  $K_{\alpha}X$ -ray source operating at 23 W. All measurements were

conducted in vacuum of at least  $10^{-6}$  Pa and at an angle of  $45^{\circ}$  with respect to the normal of the sample surface. Elements present on the catalyst surfaces were identified from XPS survey scans, measuring 4 points per sample and quantified by Multipak (V 9.5.0) software.

The surface morphology of the untreated and plasma treated samples were examined using a FEG-SEM (JEOL JSM-7000F) instrument. Samples were first coated with a thin layer of carbon making use of a sputter coater in order to take SEM images.

The distribution of vanadium through the catalyst particles was studied by SEM-EDS (JEOL JSM-5600) equipped with an electron microprobe JED 2300. The different particular elements present on the catalysts can also be identified using SEM-EDS.

The loading of vanadium was only performed for the untreated catalyst using an ICP-OES device which has been mentioned in section 2.1.

# **3. Results and discussion 3.1. BET results**

According to the IUPAC classification, the adsorption isotherms of treated and untreated catalysts exhibited typical type IV isotherms of mesoporous silica [9]. This observation indicated that the performed plasma treatment did not change the catalyst structure. Table 1 shows the textural properties of untreated and treated samples at different plasma conditions. These results showed that the surface area was enhanced after plasma treatment. In addition, the surface area was only increased slightly at lower applied voltage (0.5 kV) in comparison with 0.85 kV.

Although functional groups are present in the pores of the catalyst, NTP can destroy the present chemical bonds. This can cause the observed increase in surface area, together with the etching effect produced during the NTP treatment [10]. The increase in surface area after plasma treatment can also be due to the incapability of the particles to agglomerate, hence no pore plugging can be occurred. In addition, Table 1 also showed that the average pore diameter remained constant after plasma treatment at different working conditions, which is similar to the results obtained by Liu et al. [5].

Table 1. Textural properties of supported vanadium oxide

| Sample          |                  | surface area | Total pore            | Average<br>pore<br>diameter<br>(Å) |  |
|-----------------|------------------|--------------|-----------------------|------------------------------------|--|
| Voltage<br>(kV) | Exposure<br>Time | (cm²/gr)     | (cm <sup>3</sup> /gr) |                                    |  |
|                 | (min)            |              |                       |                                    |  |
| Untreated       | 0                | 364,8820     | 0.002152              | 11.7815                            |  |
| 0.5             | 10               | 366,581      | 0.00229               | 11.745                             |  |
|                 | 15               | 374,821      | 0.00173               | 11.763                             |  |
|                 | 20               | 376.776      | 0.00412               | 11.786                             |  |
| 0.85            | 10               | 431.9320     | 0.002546              | 11.6895                            |  |
|                 | 15               | 404.5059     | 0.00221               | 11.5902                            |  |
|                 | 20               | 453.8516     | 0.001936              | 11.6023                            |  |
| 1.1             | 10               | 388.9235     | 0.007467              | 11.5086                            |  |
|                 | 15               | 381.2062     | 0.006741              | 11.5387                            |  |

# 3.2. XPS results

The XPS survey spectra exhibited prominent peaks attributed to C1s, O1s, Si2p and V2p3. Table 2 summarizes the elemental compositions (at. %) of the samples over the sampling depth of several atomic layers from the surface. As can be observed in Table 2, the percentage of vanadium in pure vanadyl acetylacetonate was detected to be higher than 3%. In the untreated and treated catalysts, a lower amount of vanadium was detected, as could be expected.

| Table 2. | Surface | elemental | analysis | of samp | ples. |
|----------|---------|-----------|----------|---------|-------|
|          |         |           |          |         |       |
|          |         |           |          |         |       |

| sample                  | C1s | O1s  | Si2p | V2p3 |
|-------------------------|-----|------|------|------|
| vanadyl acetylacetonate | 3.4 | 23.4 |      | 3.1  |
| Untreated catalyst      | 9.6 | 59.1 | 31.1 | 0.2  |
| Catalyst 0.5kV          | 10  | 62.6 | 27.3 | 0.1  |
| Catalyst 0.85kV         | 7.6 | 65.5 | 26.9 | 0.1  |
| Catalyst 1.1kV          | 6.4 | 64.8 | 28.5 | 0.2  |

The percentage of oxygen increased from 59.1% for the untreated catalyst to 65.5% for treated catalyst at 0.85 kV. The significantly higher oxygen percentage indicates that plasma active species successively react with the catalyst surface, which is in agreement with the results obtained by Tang et al., who performed plasma treatment of  $MnO_x$  catalysts using a dielectric barrier discharge at atmospheric pressure [2]. XPS results thus revealed that the performed NTP treatment increased the oxygen functional groups on the catalyst's surface, which may in turn contribute to an increased catalyst activity.

### 3.3. FEG-SEM and SEM-EDS results

As shown in Fig. 2, plasma treatment does not greatly affect the external  $V_2O_5$  located on the silica catalyst's surface. The surface of the untreated sample is covered with irregular shapes of  $V_2O_5$  agglomeration, whereas homogeneous and well dispersed  $V_2O_5$  is observed on the catalyst's surfaces after plasma treatment due to etching effect.





Fig. 2. Morphology of different catalysts: (a) untreated (b) 0.5 kV, 20 min (c) 0.85 kV, 20 min and (d) 1.1 kV, 15 min at two different magnifications:1500x (left side), 30000x (right side)

In order to confirm the results obtained with XPS, the catalyst composition was also analyzed by SEM-EDS. As can be seen in Fig. 3, a low percentage of vanadium (0.08%) was obtained in untreated and treated catalysts, which is consistent with the XPS results. In addition, the percentage of oxygen also increased from 33.3% for untreated sample to 41.2 % after 15 min of plasma treatment at 1.1 kV, which is also consistent with the XPS analysis results.



Fig. 3. SEM-EDS analysis of (a) untreated catalyst (b) treated catalyst at 1.1 kV for 15 min

### 4. Conclusion

In this work,  $V_2O_5/SiO_2$  catalysts were fully synthesized and the effect of plasma treatment on their structure was investigated. It has been demonstrated that the plasma has a beneficial effect on the textural and chemical properties of the catalyst surface. The surface active sites were enhanced, which in turn improved the dispersion of  $V_2O_5$ on the silica. This might in turn result in an increased catalyst activity, which will be examined in the near future.

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