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Influence of surface phenomena in oxidative desulfurization with WO_x/ZrO_2 catalysts

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ABSTRACT Oil refinery related catalysis, particularly hydro desulfurization is viewed as a mature technology, but still we view that more efforts have to be made to boost the efficiency of the existing catalysts. So in this article we report the use of WO_x/ZrO_2 catalysts for the oxidation of dibenzothiophene (DBT) as a more effective material in nanometer scales. The WO_x/ZrO_2 samples were prepared by solid impregnation of $ZrO_{2-x}(OH)_{2x}$ with ammonium metatungstate solution maintaining the pH at 10. Detailed structural and surface morphological analyses were carried out using Raman spectroscopy and Atomic force microscopy. In order to understand the catalytic activity which is largely influenced by the surface morphology, an interpretation based on the experimental results is given. The results showed an important correlation between the catalytic efficiency with the morphology of the surface which is identified as arrays of planes with steps of around 10 nm with the structures showing faceting with a preferential angle of 90°. It was established that when the number of W atoms in the surface increase the catalytic efficiency also increases. Thus we conclude that the material efficiency as a catalyst is directly related with the surface structure.

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1   Introduction

In the field of heterogeneous catalysis, specifically in the, zirconia-supported systems, tungsten oxide-based catalysts, have received a great deal of attention in the past decade, because they are strong acids, and thus are active for isomerization and alkylation of hydrocarbons [1–3]. Although numerous published studies have been devoted to alkane isomerization on the tungsten/zirconia system, some areas of investigations still remain open. The main recent issue now, is the necessity of producing clean fuels which has been pointed out by the Environmental Protection Agency (EPA), USA. EPA has released a new regulation that establishes a limit of 15 ppm of sulfur content in diesel fuel, which will be effective from June 1, 2006 [4]. To produce fuels satisfying the new environmental legislations concerning sulfur levels, refineries need to consider desulfurization of all

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streams that are used in the end products of the fuel. This regulation has stimulated many researchers around the world to make enormous stride in desulfurization technologies and recently, a general review on this has been reported [5]. One of the traditional options to remove sulfur from diesel has been the hydro treatment process (HDT). It is well known that, producing ultra low sulfur diesel (< 15 ppm of sulfur) with the existing processes, needs the use of high temperature, high hydrogen pressure, more active catalysis and longer residence times than the actual procedure. This implies increased costs to refineries because of reduced catalyst life, increased hydrogen consumption and ultimately leading to the loss in total yield. So, in this work we have made an attempt to use the WO_x/ZrO_2 catalysts for the oxidation of sulfur compounds present in diesel like DBT and related the catalytic activity with the surface morphology.

It is well known that the surface properties have an imperative role in the control of catalysis process. Furthermore, it is common to relate it with crystalline distribution or other factors involving the structural configurations like preferential orientations, presence of individual elements, etc., in the synthesized material. In order to develop optimal solution to remove sulfur from fuels, new catalyst compositions have been used to identify better responses. Structure manipulation has been demonstrated to be an important parameter to develop efficient catalysts [6]. Both composition and structure affect the electronic distribution together with the atomistic configuration, producing significant variations in the chemical potential, which is related to the selectivity and activation energies during the catalyst design [7]. In addition to these factors, in order to have optimum materials for catalysts it is indispensable to have the maximum effective area to induce reactions, which introduce a higher number of active sites per unit area and per unit volume [8]. Hence in this work, we report the influence of the surface morphology producing important improvements in the catalytic efficiency of WO_x/ZrO_2 in the reactions of oxidative desulfurization, where internal structure was maintained constant.

2   Experimental methods

The WO_x/ZrO_2 samples were prepared by impregnation of $ZrO_{2-x}(OH)_{2x}$ with ammonium metatungstate $((NH_4)_6(H_2W_{12}O_{40}) \cdot nH_2O)$ solution (Strem Chemicals, 99.9%) maintaining the pH at 10. The whole mixture was

stirred and heated in order to evaporate the water contents in it and this was followed by calcination in air for 3 h at 800 °C (tungsten content up to 30 wt. %. High-surface-area $ZrO_{2-x}(OH)_{2x}$ (320 m^2/g) was prepared by hydrolysis of 0.5 M zirconyl chloride solution ($ZrOCl_2 \cdot 8H_2O$, Aldrich, > 98 wt. %, Hf 0.5 wt. %) with NH_4OH solution (Baker 28%) at pH = 10 [9]. After thermal treatment the catalysts were characterized by surface area determination (Micromeritics, Model ASAP-2000) and diffuse optical reflectance spectra with a Varian (Cary 5E) spectrophotometer. The Kubelka–Munk function was used to convert reflectance measurements into equivalent absorption spectra. For the measurement of vibrational spectra of the samples, Raman spectrometer (SPEX Mod. 1403) with a double monochromator, using an Ar$^+$ ion laser (30–40 mW) of incident radiation was used, and the excitation line of the laser was 514.5 nm. Surface morphology was studied using a Nanoscope4 Scanning Probe Microscope by Digital Instrument, applying the contact mode. Section analysis was applied in order to get information about structural distribution and aerial view of the surface.

A model solution was prepared with heptane (C_7H_{16}, 99.0 mol %) and DBT, (98.0 mol %), with 490 ppm of total sulfur. The quantities of the reactants employed were: 50 ml of model solution, 50 ml of acetonitrile (CH_3CN, 99.93 mol %), 0.2 ml of hydrogen peroxide (H_2O_2 at 30 wt. %) and 100 mg of WO_x/ZrO_2 catalyst. The reaction was carried out in a 250 ml glass batch reactor, equipped with a magnetic stirrer (1000 rpm) and a heated circulating bath. The temperature in the reactor was 60 °C. Samples at intervals 5, 15 and 30 min were taken and measured by a total sulfur analyzer (Horiba SFLA 1800) with an X-ray fluorescence detector and the accuracy of the reported values is estimated to be around 5%. The experimental details have already been reported by our group [10].

3   Results and discussion

The catalytic activities of the WO_x/ZrO_2 system for reaction of oxidative desulfuration were examined and the results are shown in Fig. 1. From the plot we can observe that the maximum efficiency for the reaction study (about 12 W/nm^2) correspond to the sample of 20 wt. % W. From this plot it is possible to identify that if the surface possesses 6.5 W atoms per nm^2 the sulfur removal is more effective after 15 min. It is also clear from the plot that for 6.5 W atoms per nm^2 the sulfur removal is effectively 9% from 5 to 15 min but increases to 16% from 15 to 30 min. But for the samples possessing 16.4 W atoms per nm^2 the sulfur removal is about 22% during the time period 5 to 15 min and remaining 5% was removed in another 15 min. It is more explicit that for the samples possessing 12 W atoms per nm^2 the removal of sulfur is gradual and 100% removal was also achieved in 30 min. Hence we initially conclude that the samples possessing 12 to 15 W atoms per nm^2 on the surface will be a more efficient catalyst.

Figure 1 also shows the variation of absorption edge energy and the evaluated catalytic efficiency with surface density of W atoms, obtained at constant temperature (60 °C) and at constant atmospheric pressure. It is clear that when the W atom density increases the efficiency of the system for the oxidation and for reducing sulfur based products becomes more effective, and the edge energy is reduced from 3.62 to
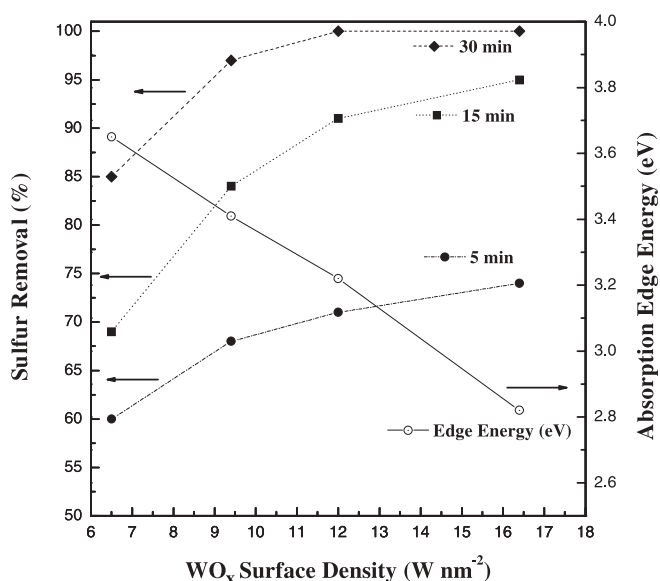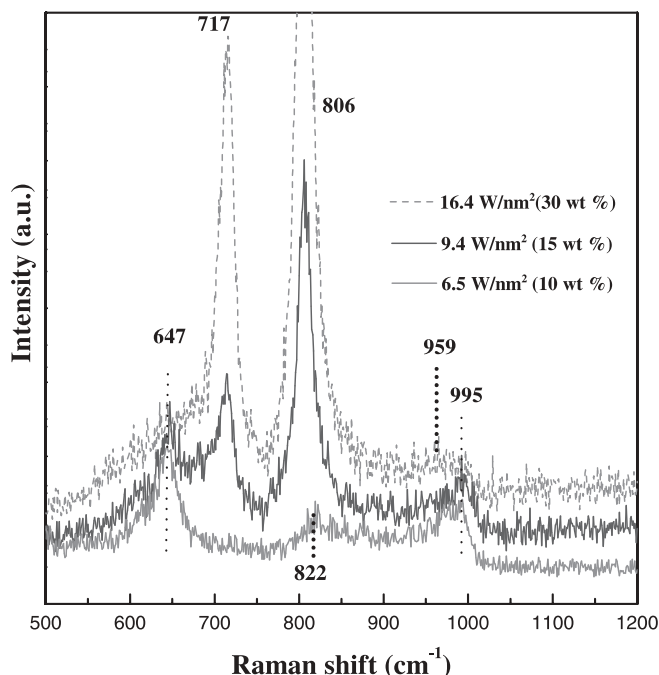

FIGURE 1   Correlation plot of the catalytic efficiency vs. W atoms density and absorption edge energy

2.81 eV (approximately 0.9 eV.) We can explain this behavior based on the hardness of the system, because when the material becomes softer, the catalysis activities are more favorable. This is supported in the Pearson theory that involves the HOMO–LUMO energy gap with the selectivity and the reactivity of the material [11]. Numerically the corresponding hardness can be calculated in terms of the frontier orbital Eigen-values as $\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO}$, which is directly related with the observed catalytic efficiency [12]. The determination of absorption edge energy takes in to account the number of atoms per unit area and also the production of hot point (implying high energy zones in the materials) which is directly related to the structure and the surface morphology of the sample and in turn influencing the catalytic efficiency.

Figure 2 shows the Raman spectra of WO_x/ZrO_2 samples with different densities of W atoms on the surface. The ZrO_2 tetragonal phase can be identified from the peak at 647 cm^{-1}, which is significantly decreased in intensity and resolution, when the quantity of tungsten is increased. The signals corresponding to the surface tungsten oxospecies are expected in the 700–1060 cm^{-1} region for W–O–W modes and W=O stretching modes [13–18]. For the samples with 6.5 W atoms per nm^2, a peak is observed at 822 cm^{-1} which relates to W–O–W stretching. Similarly a peak at 960 cm^{-1} is observed for the samples with 16.5 W atoms per nm^2 which corresponds to W=O bond and is related to the existence of hydrates state. It is observed that a shoulder appears around 995 cm^{-1}, which is assigned to the symmetric stretch mode of the W=O bonds at the borders which are related to the surface polytungsten oxide [13]. The strong bands at 717 and 807 cm^{-1} are characteristic of WO_3 for bulk. Above 800 °C the lattices collapse with the formation of its corresponding oxides, ZrO_2 and WO_3.

The structure of ZrO_2 in WO_x/ZrO_2 was similar to pure ZrO_2 calcined slightly above the glow exotherm [7, 19]. The stabilized surface area of WO_x/ZrO_2 in calcined samples was about 30–60 m^2/g. Below 800 °C, the Raman spectra
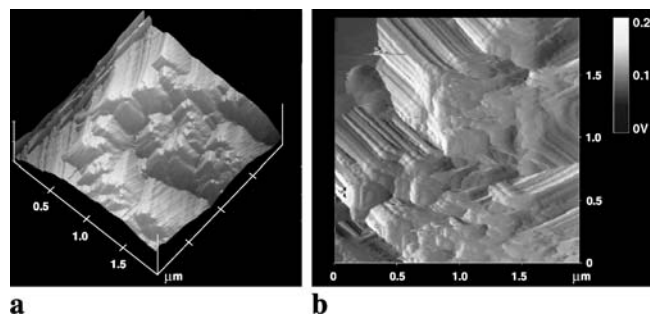
FIGURE 2 Raman spectra of WO_x/ZrO_2 samples with different W atoms density on the surface

In order to substantiate our claim on the influence of surface morphology on the catalytic activity, topographic sectional analyses was done. Figures 4a and 4b, show a detailed transversal section analysis of the WO_x/ZrO_2 material. In the first analysis (Fig. 4a), a section of one of the observed structures is shown, which clearly depicts the profile of the planes with changes around 5–10 nm. It is also clear that big planes dominate the borders of the structure. However in the middle of the profile it is observed that there are important amount of perturbations on the plane, which must influence the catalytic activity of the material. A more detailed analysis is shown in Fig. 4b, which indicate how the structure is basically composed of many laminar structures arranged to produce a bigger change in the surface morphology of the material. In the section profile curve it is clear that the multiple steps of 10 nm corresponds to less than 30 atoms on each of the longitudinally exposed layers as indicated by a line in Fig. 4.

These analytical data's showed how the superficial surface phenomenon contributes to the catalytic activity when we have a large quantity of exposed active sites and also the contribution of energy to a specific catalytic reaction producing improved results.

of WO_x/ZrO_2 in the catalyst indicated that the tetragonal phase of ZrO_2 was dominant and was composed of nanometric crystallites of about 20 nm [20]. Furthermore, the absence of bands in the region between 717 and 809 cm^{-1} for the samples with 6.5 W/nm^2 implies the existence of different species like polytungstate. The presence of Raman bands (Fig. 2) at 809 cm^{-1} and 717 cm^{-1} for samples with 9.4 W/nm^2 and 16.4 W/nm^2 W loading suggests the presence of crystalline domains of WO_x in octahedral environment as it has been reported earlier [21, 22]. The analysis of UV-visible optical absorption spectra, shows a direct relation between the WO_x domain sizes and the tungsten surface density (Fig. 1), which is related to the number of W atoms sharing a neighboring common oxygen atom [22, 23].
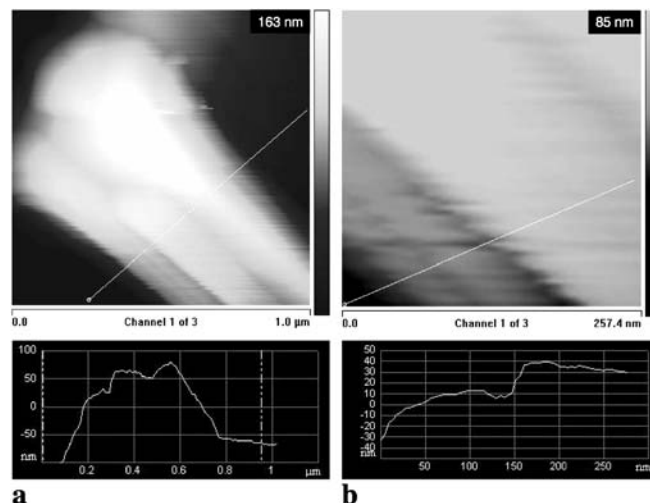
From the above discussions it is clear that the results on the structural analysis, Raman spectra analysis and other optical interpretations are perfectly coinciding with the earlier reported results except for the catalytic interpretations. Since, the surface morphology was considered to be a very important factor to relate it with the catalytic activity; the study was focused on the surface characterization. Figure 3 shows the AFM images of the surface of WO_x/ZrO_2 composite. Figure 3a shows a 3D representation of the common structures found in the samples showing well faceted domains with angles near to 90° and the planes that are usual for crystalline materials. However it is also evident from the Fig. 3b, which corresponds to a deflection image and the observed structures correspond to materials formed of smaller pieces with laminar assembling and these laminar arrays produce a high degree of exposed surface area. It must be noticed from the scale that these observed layers are of less than 100 nm thick, which will increase the active sites in the materials. In fact the surface structure can be shown to be arrays of small layers with steps in the order of a few nanometers.

FIGURE 3 AFM micrographs of the sample surface. **a** A 3D representation of the surface morphology shows well faceted structures with shapes of square corners which are produced by layers. **b** Image of deflection signal which clearly shows the multiple planes forming the material

FIGURE 4 Transversal section analysis of the surface and the corresponding plots in bottom show the profile of the line marked on the images. **a** Using a 1 μm scan, it is possible to observe how the structure is composed of multiple steps, while in the (**b**) magnified image (scan of 257 nm) it is observed that the step size correspond to 10 nm

4   Conclusions

WO_x/ZrO_2 material was synthesized using conventional methods and its catalytic efficiency was evaluated for oxidative desulphurization reactions. The results indicate that using WO_x/ZrO_2 catalysts and appropriate oxidants like hydrogen peroxide (H_2O_2), model compounds such as dibenzothiophene (DBT) can be quantitatively oxidized and eliminated in very short time (around 30 min). Based on the analytical measurements, the results indicate a direct relation between the catalytic activity and the density of W atoms on the surface ie., higher the exposed W atoms higher the sulfur removal. From the surface analysis, it is possible to identify the material as an array of aggregates produced by small planes of 10 nm-steps; these surface arrangements show faceted structures with angles which tend to be preferentially near to 90°. This implies that, atoms at vortex structures have unsatisfied coordination sites with high surface energy, becoming preferential reactive points contributing to increased catalytic activity. This means that there must be a large quantity of hot points per unit area which is directly related with the chemical potential and catalysis activity. Hence, we conclude that there exists an important relation between the surface morphology, the density of W atoms and the corresponding energy gap between the frontier orbital and the chemical potential with the catalytic activity of WO_x/ZrO_2 for oxidative desulfurization reactions.

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