

Liquid phase oxidation of n-Octane in the presence of vanadium based materials

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Introduction

The oxidation of alkanes to ketones and alcohols is an interesting process for both academic and industrial chemists, and thus controlled oxidation of alkanes is of particular interest [1–2]. Saturated hydrocarbons are abundant in nature, they are the main constituents of crude oil and of natural gas, and consequently they are important feedstocks for chemical production. The development of improved catalytic systems for this reaction is thus necessary and the vanadium based catalysts, constitute an alternative for transformation of octane into valuable oxygen-containing products.

The most important goals of this contribution are: i) a better understanding of the physico-chemical and catalytic properties of the vanadium based catalysts in the selective oxidation process and ii) their control by designing new structures at the nonometric scale. More specifically, the following parameters were investigated: the support; the vanadium content; the substrate to oxidizing agent molar ratio; the solvent; the reaction temperature.

Materials and Methods

Catalysts containing different vanadium loadings (1, 3, 5 and 7%) were supported on different materials (Al_2O_3 , SiO_2) by wet and dry impregnation method and calcined at different temperatures.

The oxidation reactions were carried out in a batchwise glass reactor. Typically, 0.05 g of catalyst, different solvents, and different molar ratios octane : H_2O_2 (30%) were used. The reaction was performed for different time at different temperatures (318, 333, and 348 K). Reaction products were analyzed on a Shimadzu GC using a 5% phenylmethylsiloxane capillary column and a FID detector.

Results and Discussion

The materials obtained exhibit a specific area between 263–412 m^2g^{-1} as function of the support and vanadium loading.

UV–VIS diffuse reflectance spectroscopy has been used to investigate the structures and oxidation states of vanadium that possess the ligand-to-metal charge transfer (LMCT) transition of V^{5+} in the region of 550–200 nm and d–d transitions of V^{4+} and V^{3+} in the range of 400–1000 nm [3]. All calcined V-containing samples show strong UV–VIS absorption bands around 220, 250, and 340 nm due to the charge transfer (CT) transition between metal and ligand (figure 1). The absorption band in the region of 333–500 nm is associated with the lower-energy charge transfer (LCT) of O–V5C electron transfer for octahedral coordination. In the case of V^{4+} , the LCT transition is expected to show at a higher wavelength of 250–285 nm. In the samples with higher V content, octahedral V species occur, which is revealed by the pale yellow or bright orange colors of the samples, and a broad absorption band around

400–480 nm. The area of the bands at 250 and 301 nm increases almost linearly as a function of the vanadium loading. The latter band is attributed to a charge transfer transition occurring between six oxygen ligands and a central V ion in a distorted octahedral coordination. The sample with the highest loading (7%) shows an additional absorption above 400 nm, indicating the presence of polymeric chains.

The oxidation reaction of octane with H_2O_2 over V/SiO_2 and $\text{V}/\text{Al}_2\text{O}_3$ yields octanols, octanone and octanoic acid. As a general tendency the octane conversion increases with the vanadium loading, achieving a maximum for the samples containing 5% of vanadium. Also an optimal catalytic activity was obtained when silica was used as support, due probably to a better dispersion, and higher concentration of vanadium monomer species. During this study was optimized a range of polar (acetonitrile, nitromethane) and apolar solvents (dioxane, toluene, cyclohexane). Water as solvent was weakly active and afforded ca. 1% conversion. All polar solvents, such as acetonitrile and nitromethane, greatly influenced the catalytic performance, typically giving higher activity and less selectivity to 3-octanol.

In summary, vanadium based catalysts are very active, stable, recyclable catalyst for the liquid phase oxidation of n-octane with hydrogen peroxide. The higher yield of the products can be achieved by increasing the value of reaction parameters such as reaction time and octane/ H_2O_2 molar ratios. The highest activity was obtained for the catalysts containing 5% V/SiO_2 and the reactions carried out in acetonitrile, achieving 80% conversion and almost 80% selectivity in 3-octanol.

Significance

The ketones and alcohols are important as starting materials in the chemical and pharmaceutical industry, therefore the functionalization of alkanes is an interesting process for both academic and industrial chemists. This reaction may be a basis for a new technology for the transformation of alkanes into valuable oxygen-containing products.

References

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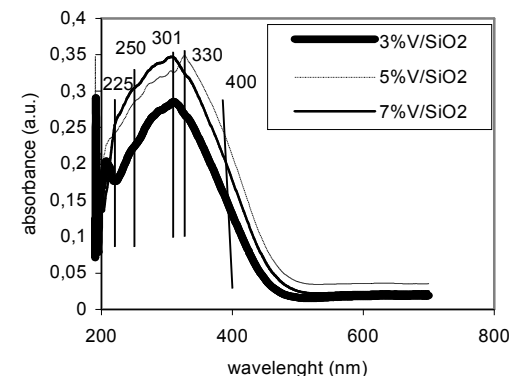


Figure 1 DR-UV-VIS Spectra of samples supported on silica containing different content of vanadium