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# Synthesis and performance of vanadium-based catalysts for the selective oxidation of light alkanes

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## ABSTRACT

Vanadium compounds have attracted much attention because they have widely been used for homogeneous and heterogeneous catalysis field, especially in the selective oxidation of light alkanes, where vanadium-based catalysts were announced to be one of the most efficient catalysts. The present mini-review analyzed the recent developments for the preparation using new synthesis approaches of vanadium based catalysts, and their catalytic performances in the selective oxidation reactions of light alkanes. The influences of several synthesis strategies on the catalytic performances were illustrated in detail, while the samples characterizations were briefly presented.

## 1. Introduction

In the last decades, a lot of achievements were obtained in the fields of new polymer materials, new biomaterials, new catalysts for depollution and treatment of exhaust gases and others [1,2]. Remarkable advances in the fields of nano materials, nano science and nanotechnology have also been frequently reported [3–9], which greatly simulate the synthesis strategy and performance improvement for new efficient heterogeneous catalysts [10–16].

In the effective utilization of natural resources, there were a few new industrialized developments [15,17]. However, the developments of new efficient catalysts for the selective oxidation of light alkanes were still challenging subjects to be explored [18–30]. Among the tasks, one way was the production of light olefins from hydrocarbons, where the oxidative dehydrogenation (ODH) reactions could be applied for the production of ethylene, propylene, iso-butene, butadiene from the corresponding alkanes [20,25,26,28,31]. The second way was the oxygenates production, while the selective oxidations of alkanes or light olefins could produce maleic anhydride (MA), acrylic acid (AA), methacrylic acid, acetic acid, acroleine, acronitrile, propylene oxide, etc. [32–34], which are important chemicals or monomers in the petrochemical industry. The alkanes are more economical raw materi-

als than the corresponding olefins, available in abundance and with low toxicity as compared to aromatics [30].

The accelerating demand for propylene and other light olefins in the modern petrochemical industry requires the development of new technologies, which would overcome the disadvantages of the actual processes. The oxidative dehydrogenation (ODH) of propane or other light paraffins could be feasible options [25,28,35], which could overcome the drawbacks (coke deposition etc.) of the direct dehydrogenation (DDH) processes of light alkanes. The inconveniences of DDH process by using metal oxide catalysts were: low equilibrium constants, deactivation by the coke formation, the necessity of catalyst regeneration, and the exothermicity of the reaction. The design and elaboration of efficient heterogeneous catalysts for the oxidative dehydrogenation (ODH) of alkanes are very important because of the economic benefits of using light paraffins for the production of value-added chemicals. However, the yields of light olefins over the actual catalysts were not satisfactory, because of the side reactions leading to the formation of CO<sub>x</sub> [20].

In the aspect of oxygenates production from selective oxidations of alkanes or light olefins, the maleic anhydride (MA), acrylic acid (AA), methacrylic acid, acetic acid, acroleine, acronitrile and propylene oxide could be the main value-added products. For each of the targeting

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products and related processes, there was specific preferable catalytic system with better selectivity and yield for each desired product. For example, for the production of maleic anhydride (MA), the V-P-O based catalysts were better systems [36,37]; whilst for the reaction of propane to acrylic acid, mixed metal oxides based on MoVNbTe(Sb) with strong synergetic effect seemed to be outstanding [34,38–40]. Before going to the new developments, the related achievements obtained in the last decades were presented briefly in the following paragraphs, as a mini-review.

## 2. Brief earlier works of selective oxidation catalysts

The technical development of the alkane oxidation process is generally limited due to insufficient production of the targeting chemicals. In that case, in point of view for the efficient utilization of feedstocks and energies, the selectivity to the desired reaction product is still one of the essential factors in the oxidation catalysis [41–43]. The energy barrier makes it possible for subsequent or simultaneous insertion of oxygen that is generally more reactive to the unsaturated intermediates under certain temperature, while prevents partial or total oxidation of the carbon oxides [44–47]. Complex design of catalyst is required to activate the carbon-hydrogen bond reduction in non-polar hydrocarbon molecules. In most of the metal oxides, vanadium in the oxidation state of 5+ is considered to be necessary in the activation of alkanes. The supports for vanadia also play an important role for the properties and catalytic performances for oxidation of light alkanes [48–51]. Khodakov and co-workers have previously made elaborate work on the influences of support on the vanadium-based catalysts, where the surface density of vanadia was found to be greatly changed according to different carriers [52]. The turnover rate of ODH was also reported to be independent of the supports. It was concluded that the primary reaction and secondary reaction during propane oxidative dehydrogenation required similar  $\text{VO}_x$  surface sites. The Raman spectra analysis as shown in Fig. 1 suggested the transformation between  $\text{V}_2\text{O}_5$  and polyvanadate concerning different surface density of vanadia and the specific supports. It is also indicated by the figure that the weak bands between support and vanadia can be observed on the  $\text{HfO}_2$  and  $\text{ZrO}_2$  supports (772 and 977  $\text{cm}^{-1}$ ). The work of Iglesia and colleagues suggested that the ODH turnover rates was positively related with the surface density of vanadia species up to 7.2  $\text{V}/\text{nm}^2$  as well as the structure of vanadia species, where polyvanadate was demonstrated more reactive than the monovanadate structures [53]. However, the turnover rates ultimately decreased at higher surface densities due to the incipient formation of three-dimensional structures. They also suggested that  $\text{VO}_x$  with intermediate size should be compromised for a balance between site reactivity and accessibility during ethanol ODH.

Wang et al. [54] studied a series of Ni-Mo-Mg-O catalysts with mesoporous structure prepared by sol-gel method, and subsequently

used for the oxidative dehydrogenation of propane. It was found out that the catalytic performances volcanically increased with the incremental content of Mo, where the Mo/Ni atomic ratio of 1/1 exhibited a much better activity with propene selectivity of 81.4% at conversion of 11.3% under 600 °C.

## 3. Synthesis of efficient vanadium-based catalysts for the selective oxidation

In order to synthesis efficient vanadium-based catalysts with high selective oxidation of light alkanes, a lot of attempts were suggested and investigated. Several advances will be described and discussed in the following paragraphs.

### 3.1. Novel preparation techniques for new vanadium-based catalysts

The chemical/physical properties of catalysts are largely depending on the support, the synthesise methods, the pre-/post-treatment, etc. The most commonly used methods including the impregnation, deposition-precipitation, co-precipitation have been used everywhere and also widely applied in the laboratory scale [55], which will not be included herein. Specific synthesis strategies such as sol-gel method and other physical treatments will also lead to the transformation of composition phases, different location and exposure of active sites, synergistic effect between compositions, which are essential factors for the catalytic performances as confirmed by the previous work of the group [56–60]. Here in this part, we will mainly focus on several typical but specific synthesis methods that were introduced to vanadium-based catalysts.

#### 3.1.1. Hydrothermal process with ultrasonic pretreatment

Khalameida et al. [61] compared the specific methods including the mechanochemical treatment (MChT), hydrothermal treatment (HTT), microwave treatment (MWT) as well as ultrasonic treatment (UST), the SEM of which is as shown in Fig. 2. It can be seen that very specific morphology and porosity can be obtained by using these techniques. Ahmad et al. [62] successfully synthesized the  $\text{VO}_x$  nanotubes by using the ultrasonic technique. And it was revealed that with only 15 min ultrasonic treatment, the well-ordered layer-like structure and tube-like morphology with open ends could be achieved, which was impossible without the assistance of ultrasonic treatment.

As it is mentioned above, the most amazing effect by synthesizing vanadium-based catalysts with ultrasonic treatment is the possibility to modify the composition phase and porosity. Yang and co-workers studied the  $\text{Mo}_{1.00}\text{V}_{0.80}\text{O}_n$  and  $\text{Mo}_{1.00}\text{VaTe}_{0.17}\text{O}_n$  ( $n = 0.40\text{--}1.00$ ) catalysts with different Mo/V ratios by hydrothermal method after the ultrasonic pretreatment [63]. The as-synthesized samples were then carried out to catalyze the oxidation of propane. The fact was revealed that the vanadium content of each sample played a key role for the

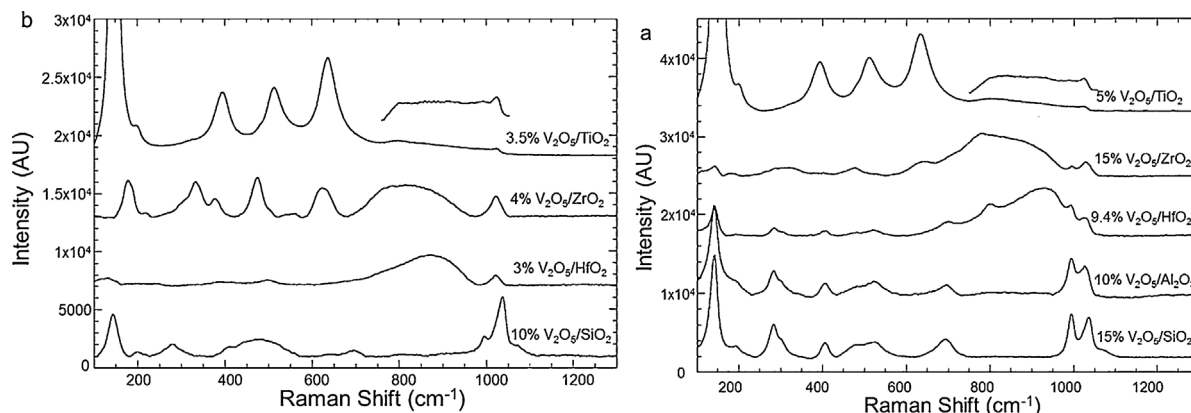


Fig. 1. Raman spectra of supported vanadium oxide catalysts with  $\text{VO}_x$  surface densities of (a) 3.9–7.7  $\text{VO}_x/\text{nm}^2$  and (b) 2.1–3.3  $\text{VO}_x/\text{nm}^2$  ( $\text{VO}_x$  weight loading;  $n_s = \text{VO}_x$  surface density in  $\text{VO}_x/\text{nm}^2$ ) [52].

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