

Partial Oxidation of Ethanol Using $\text{VO}_x/\text{SBA-15}$ and $\text{VO}_x/\text{Fumed Silica}$ Catalysts in a Bench-scale Stainless Steel Reactor

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Abstract

Two $\text{VO}_x/\text{SBA-15}$ catalysts and three VO_x/SiO_2 -fumed silica, with 5, 10 and 1, 5, 10 %wt. vanadium content respectively, were tested in a stainless steel continuous flow reactor for the partial oxidation of ethanol. The catalysts were tested at 150 – 300 °C. Products were analyzed by GC-FID, GC-OFID and GC-MS. The aim was exploring the problematics which could be found when more industrial close conditions are used. The total conversion of ethanol and selectivity to acetaldehyde were different than the expected ones. For VO_x/SiO_2 -fumed silica, the total conversion was higher with a lower selectivity to acetaldehyde compared to $\text{VO}_x/\text{SBA-15}$ catalysts.

Keywords

ethanol, oxidation, acetaldehyde, vanadium, stainless steel

1 Introduction

Vanadium-based catalysts have been used and studied for the partial oxidation or oxidative dehydrogenation reactions [1-5]. Moreover, the oxidation of ethanol to acetaldehyde is being investigated with the aim of replacing the conventional processes based on hazardous agents such as chromate or permanganate [5, 6]. Besides, the dispersion and nature of the vanadium over the adequate support is an important issue to obtain a high catalytic activity [2, 7, 8].

With the aim of decreasing the use of fossil carbon sources, the green production of chemicals is one of the most important targets in the academic sphere and industry. Thus, platform chemicals from biomass have attracted attention in the recent years. Ethanol (bio ethanol) is one of the most important platform chemicals. And, as a result of the legislation-driven increase in demand for biofuels, the production of bioethanol has significantly increased [9] over the past years resulting in a drop in its price and increased availability. As published by the Renewable Fuels Association, the production of fuel ethanol in USA was approximately 23,700 and 55,700 billion of liters in 2007 and 2015 respectively [10] indicating a huge increment in its production. Acetaldehyde is an important intermediate used for the production of various bulk chemicals, including acetic acid, acetic anhydride, ethyl acetate, per acetic acid, butanol, 2ethylhexanol, pentaerythritol, chlorinated acetaldehydes, glyoxal, alkyl amines, pyridens and others [11]. The Wacker process was developed in late 1950s for the ethylene oxidation to acetaldehyde. Nevertheless, the need of using corrosive resistant materials together with expensive titanium reactor tubing or the need of purification of waste air and treatment of wastewater which are highly toxic and show antimicrobial activity encourage the research through the partial oxidation of ethanol to acetaldehyde which could be a more environmentally-friendly process. And, the acetaldehyde production via the oxidative dehydrogenation (ODH) of bio-ethanol could be a promising alternative to the Wacker process [12].

SBA-15 materials are being used mainly for other purposes different than the partial oxidation of ethanol. However, some works were published such as the research from Gayoung Lee

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et al. [13] who used these type of materials for the oxidation of ethanol with the aim of producing hydrogen gas. Guoan Du et al. [2] used vanadium grafted SBA-15 for the oxidation of methanol and Li et al. [14] used Ni/SBA-15 for the steam reforming of ethanol. Also, Mattos et al. [15] and Sun et al. [16] published works in which informed about the dependence of the ethanol catalytic transformations on acidity of the catalyst and reducibility of the metal. One work about the ethanol partial oxidation using different metal oxides including vanadium supported SBA-15 was published [17]. Several SiO₂ based catalysts with some vanadium content were characterized in a previous published work [18] with the aim of studying the variety of vanadium present on their surface and its acting in the partial oxidation of ethanol using a glass micro-scale reactor. In our case, due to the low activity of this type of materials compared to others such as VO_x/TiO₂ [17] these mesoporous catalysts were selected and tested with the aim of studying the possible problematics concerning to the use of a metal bench-scale stainless steel reactor for the partial oxidation of ethanol using high temperatures (250–300 °C). Thus, this information can be useful for the industry interested in the use of heterogeneous catalysis for the production of acetaldehyde from the ethanol.

2 Experimental

The materials were synthesized and characterized (and tested in a micro-scale glass reactor for the partial oxidation of ethanol) in a previous work [18] according to described methods [18–23].

Fumed silica (Aldrich) was used as support and the SBA-15 mesoporous silica chosen as the second support was prepared by procedure reported by Zukul et al. [21]. Vanadium oxo-complexes were included by wet impregnation procedure by appropriate amount of ethanol/H₂O solution of vanadyl acetylacetonate (Aldrich). The impregnated samples were dried at 120 °C in air overnight and then calcined at 600 °C for 8 h in dry air flow [18].

The characterizations were exposed in the published work by Čičmanec et al. [18]. The chemical composition of the investigated samples was determined by X-ray. The particle morphology of starting silicas as well as modified samples was evaluated by scanning electron microscopy images. Adsorption isotherms of nitrogen at 77 K were measured using an ASAP 2020 instrument. The UV–vis diffuse reflectance spectra of dehydrated diluted samples were measured using. The spectra were recorded in the wavelength range 190–850 nm. All Raman spectra were measured under dehydrated conditions. Raman spectrometer equipped with CCD detection. Spectra were excited by Smart Excitation Laser (Thermo Scientific) with a laser wavelength of 780 nm. The redox behavior of VO_x surface species was investigated by the temperature programmed reduction by hydrogen (H₂-TPR) The changes of hydrogen concentration were monitored by the TCD detector [18].

Two VO_x/SBA-15 materials, V(5%)/SBA-15 and V(10%)/SBA-15 containing 5 and 10 wt.% of vanadium content respectively, and three VO_x/SiO₂ fumed silica (V(1%)/SiO₂, V(5%)/SiO₂ and V(10%)/SiO₂ containing 1, 5 and 10 wt.% of vanadium content respectively, were tested. Four additional tests were carried out using SBA-15, fumed silica materials without vanadium content and two blank tests (with and without SiC as filler in the reactor) respectively.

All catalysts were tested with the aim of determining their activity and selectivity in the oxidation (oxidative dehydrogenation, ODH) of ethanol using a bench-scale stainless steel reactor. The two blank tests were carried out using the same conditions than for the normal tests. The procedure for introducing the catalyst and SiC was described by J. M. Hidalgo et al. [17]. A continuous flow reactor (stainless steel 316) with length of 1000 mm was used. The reaction was carried out with 1 g of catalyst. The catalysts were prepared in pellets form with 0.5 mm of diameter. The catalyst bed had a length of 301 mm and was located in the central part of the reactor. The catalyst and silicon carbide (0.5 mm particles) were mixed thoroughly (20 ml SiC + 1 g of catalyst) and loaded into the reactor. Finally, the remaining free volume of the reactor was filled with silicon carbide. Air flow, used for the catalytic reaction, was fed directly (activation 1 h at 400°C; 5 °C min⁻¹ from room temp.) or mixed with feedstock before entering the reactor. All catalysts were tested at 150, 200, 250 and 300°C using 5 Nl h⁻¹ air flow, 1 bar of pressure and 5 g h⁻¹ of ethanol. The products were collected at time on stream (TOS) TOS = 2 h in two collectors, the first one cooled by water to room temperature and the second one cooled to 0 °C. Each two collected liquid samples were mixed to one sample and analyzed using a GC-FID “Agilent 7890A” and GC-OFID “Agilent-Wasson-ECE Instrumentation”. Gaseous products were analyzed by the method “Refinery Gas Analysis” RGA (Agilent Technologies) with a GC 7890A Agilent (USA). The products were identified by using by using standard reference compounds along with GC–MS analyses using Thermo Scientific ITQ 1100 unit.

3 Results and Discussion

As written in the experimental part, a set of SBA-15 and fumed silica supported vanadium catalysts was carried out. In all cases, the reaction conditions were: 1 g of catalyst; 5 g l⁻¹ of ethanol 96 %vol.; 5 Nl h⁻¹ air; T = 150, 200, 250, 300 °C.

In all cases, the CO, CO₂, and ethylene contents, in the products, were lower than 1 wt.% at T < 300 °C, .

For the two blank experiments (Fig. 1), with and without SiC, almost the same results were found (conversion and selectivities). In that cases, the conversion was higher when higher temperature was used. The conversions were lower than 10 % up to 250 °C. Up to 200 °C, the conversion was lower than 5 %wt. At 200 and 225 °C the conversion was 1.1 % and 3.1 % respectively with a main selectivity to acetaldehyde and acetic acid (51.6, 73.1 and

39.8, 23.7 % respectively). The conversion was higher at 250 °C ($X_t = 9\%$; Acetaldehyde = 66.4 %; acetic acid = 29.7 %). At 300 °C, the conversion resulted to be much higher (with similar selectivities) than the obtained at lower temperatures and the selectivity to acetaldehyde was 50-75 %wt. So, a high activity was found when a catalyst without vanadium was used. Thus, some possible activity due to the stainless steel walls of the reactor could be also involved in the reaction. Comparing these results with the published ones by P. Čičmanec and col. [18] (in which a glass micro-scale reactor and the same catalysts were used) we can find that blank reaction in that case presented practically no conversions so in this case, the non-inert activity of the reactor was confirmed especially at higher temperatures (more than 250 °C). Although the catalysts used were the same than the used by P. Čičmanec and col. [18], the reaction conditions, in general, including the type of reactor, were different. So, taking in account the results of the blank tests (Fig. 1), only a relative comparison between the activities of the different used catalysts using this concrete reactor system (stainless steel one) could be done at temperatures higher than 250 °C. Thus, in the case of pretending a low conversion generated by the metal walls of the reactor, the temperatures higher than 250 °C should be avoided.

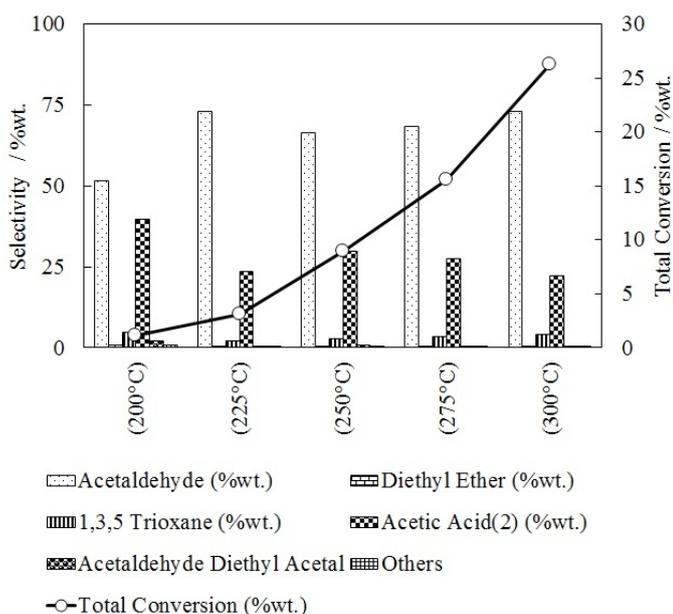


Fig. 1 Total conversion and product selectivities for the partial oxidation of ethanol (%wt.) without catalyst or SiC (empty reactor). The reaction was carried out at $T = 200, 225, 250, 275, 300\text{ }^{\circ}\text{C}$; $5\text{ g of EtOH h}^{-1}$ feed flow; 5 NI h^{-1} air flow; 1 bar of pressure.

Tests using SBA-15 and fumed silica catalysts (Fig. 2) presented high selectivity to acetaldehyde being the acetaldehyde diethyl acetal the main secondary product. Surely, the production of acetaldehyde diethyl acetal was due to the presence of acid sites which facilitated the reaction of acetaldehyde with ethanol forming this product [17, 24]. In all cases, the selectivity to acetaldehyde was higher than 65 %.

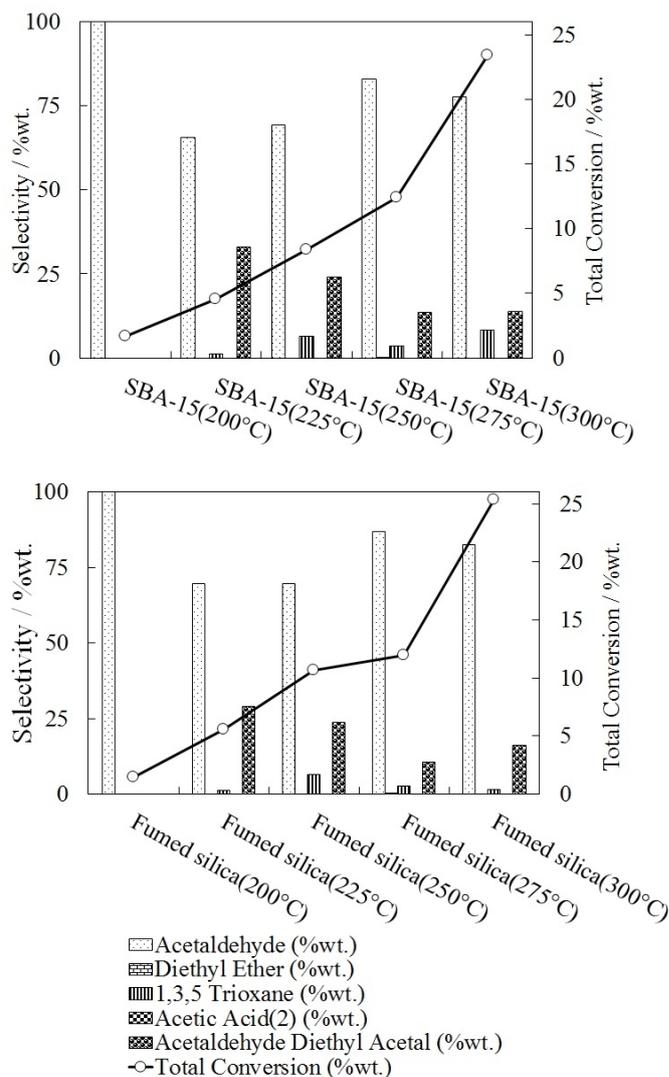


Fig. 2 Total conversion and product selectivities for the partial oxidation of ethanol (%wt.) with SBA-15 and fumed silica supports catalysts. The reaction was carried out at $T = 200, 225, 250, 275, 300\text{ }^{\circ}\text{C}$; $5\text{ g of EtOH h}^{-1}$ feed flow; 5 NI h^{-1} air flow; 1 bar of pressure; 1 g of catalyst without vanadium.

The total conversion was lower than 5 %wt. up to 250 °C. (except for catalyst V(5%)/SBA-15). In addition, for the tests using the catalysts V(1%)/SiO₂ and V(5%)/SiO₂, the selectivity to acetaldehyde was lower than the obtained selectivity for the blank test. Nevertheless, for all catalysts VO_x/SBA-15, the selectivity obtained was higher than 90 % and higher than the selectivity obtained for the blank test.

The V(1, 5 and 10%)/SiO₂ catalysts presented a low total ethanol conversion and low selectivity to acetaldehyde compared to the other vanadium supported VO_x/SBA-15 catalysts which also presented much higher selectivity to acetaldehyde. Nevertheless, the selectivity to acetaldehyde was improved when the temperature was 250 °C in all cases.

The total conversion obtained at 300 °C was similar for the blank, V(1%)/SiO₂ and V(5%)/SiO₂ tests. The possible origin of the high activity found in the blank test could be due to the presence of iron oxide in the stainless steel which could

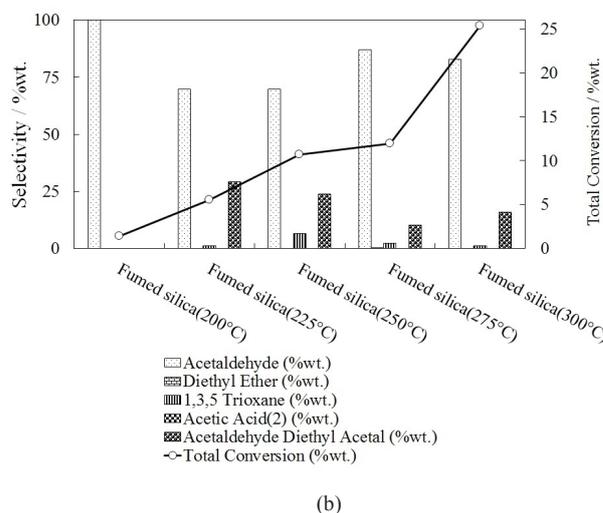
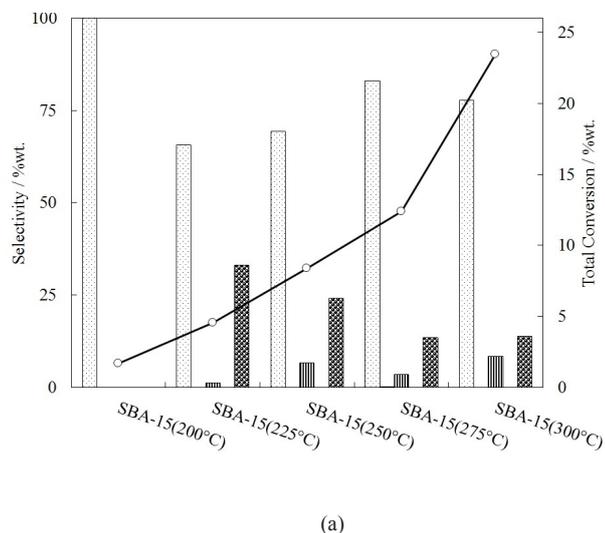


Fig. 3 Ethanol conversion (Xt; %wt.) and selectivities (%wt.) to acetaldehyde (AA), diethyl ether (DE), acetaldehyde diethyl acetal (ADA), 1,3,5 trioxane (Tr), acetic acid (AcA), ethylene, carbon oxides, C5+C6 hydrocarbons and others. The reaction was carried out at 300 °C; 5 g of EtOH h⁻¹ feed flow; 5 NI h⁻¹ air flow; 1 bar of pressure; 1 g of catalyst.

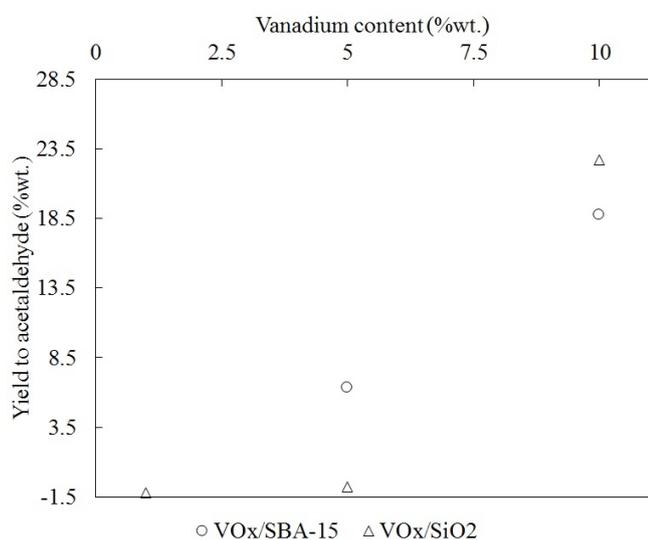


Fig. 4 Yield to acetaldehyde calculated according to the formula "CATALYST {[Total Conversion (%wt.)*Selectivity to Acetaldehyde (%wt.)]/100} - BLANK {[Total Conversion (%wt.)*Selectivity to Acetaldehyde (%wt.)]/100}". The reaction was carried out at 300 °C; 5 g of EtOH h⁻¹ feed flow; 5 NI h⁻¹ air flow; 1 bar of pressure; 1 g of catalyst.

act as catalyst [24-27]. Test using the V(1%)/SiO₂ catalyst presented similar selectivity to acetaldehyde and acetic acid compared to the blank test. Test using the V(5%)/SiO₂ solid presented the 1,3,5 trioxane as the second main product. So, in this case, the production of 1,3,5 trioxane was linked to the higher temperatures in accompaniment of a decrease in the production of acetic acid or acetaldehyde diethyl acetal. The highest total conversion of ethanol was found for the V(10%)/SiO₂ catalyst followed by V(10%)/SBA-15 which presented lower total conversion but a higher selectivity to acetaldehyde and acetic acid.

With the aim of comparing the catalyst activity between these solids, the moles of acetaldehyde produced per hour per moles of vanadium supported on SBA-15 or fumed silica were

Table 2 Moles of acetaldehyde produced per hour per moles of vanadium supported on SBA-15 or fumed silica at T = 150, 200, 250 and 300 °C.

Temp. (°C)	A mole	B (acetaldehyde) mole ⁻¹	C mole ⁻¹	D (vanadium) h ⁻¹	E h ⁻¹
150	0	5	14	4	0.1
200	2	2	6	12	0.7
250	13	14	40	32	4
300	52	44	189	180	23

A: V(5%)/SBA-15; B: V(10%)/SBA-15; C: V(1%)/SiO₂;

D: V(5%)/SiO₂; E: V(10%)/SiO₂

calculated (Table 2). Nevertheless, taking in account the high conversion found for the blank test, these results should be used only for the relative comparisons between each catalyst. The highest yield to acetaldehyde per vanadium moles were found for V(1 and 5%)/SiO₂ catalysts due to the extra contribution of the blank activity. Catalyst V(5%)/SBA-15 presented a higher yield to acetaldehyde at 300 °C compared to V(10%)/SBA-15 or V(10%)/SiO₂ (Fig. 3).

In addition, the yield to acetaldehyde (300 °C) was calculated (Fig. 4) taking as reference the acetaldehyde production during the blank test without catalyst. So the amount of acetaldehyde produced by each catalytic test was subtracted by the amount produced during the blank test. The highest yield was obtained for the catalysts with the highest vanadium content.

According to the publication by P. Čičmanec et al. [18], the main products, using a glass micro-scale reactor, were acetaldehyde and ethylene with yields >90 % to acetaldehyde. In addition, the catalyst with the lowest amount of monomeric species of vanadium oxide (catalysts with 1% of vanadium) on the surface of the support should presented the lowest yield to acetaldehyde (less oligomeric and bulk like species of vanadium oxide). However, when the metal bench-scale reactor was used,

due to the much more complex system used in a 316 stainless steel reactor (higher contact time and dimension of the reactor) the results were completely different than the expected [16] at temperatures higher than 250 °C, obtaining different products and lower selectivity to acetaldehyde. These results could be useful information for applied research for industry (big metal reactors). So, higher temperatures than 250 °C should be avoided in this type of reaction using metal reactors as showed in this concrete work to elude non-expected products.

4 Conclusions

Five VO_x/SBA-15 and VO_x/fumed silica catalysts, with 5, 10 and 1, 5, 10 %wt. vanadium content respectively, were tested in a stainless-steel bench-scale continuous flow reactor. The highest conversions were found for catalysts with the highest amount of vanadium. Test using V(10%)/SBA-15 presented the highest selectivity to acetaldehyde and test using V(10%)/SiO₂ catalyst presented the highest yield to acetaldehyde. Test using stainless-steel 316 bench-scale reactor presented different results than the expected, especially at temperatures higher than 250 °C due to the non-inert activity of the metal oxides present in the reactor.

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