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# A bifunctional catalyst based on Nb and V oxides over alumina: oxidative cleavage of crude glycerol to green formic acid

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Abstract: A bimetallic vanadium and niobium oxide catalyst using alumina as support was developed for the conversion of crude glycerol from biodiesel production into formic acid. The high dispersion of the active oxides phase combined with the presence of acid and redox active centers resulted in a high glycerol conversion (> 90% during 25 h) with a good selectivity to formic acid (~55%). This process is the first example of a heterogeneous liquid-phase process for the conversion of crude glycerol to formic acid, which is an important chemical intermediate currently derived from petroleum feedstock.

## 1.Introduction

The production of renewable fuels has received attention from governments, policy makers and the industrial sector worldwide. Among these non-fossil fuels, biodiesel has been one of the most promising options. Global biodiesel production has been growing in recent years. In 2016 more than 30.8 million m<sup>3</sup> (Mm<sup>3</sup>) were produced, 7.5% more than in 2015. The main producing countries in 2016 were the United States (5.5 Mm<sup>3</sup>), Brazil (3.8 Mm<sup>3</sup>) and the countries of the European Union produced 10.7 Mm<sup>3</sup>. It is estimated that in the future, biodiesel production will grow by around 4.5% annually, reaching 41 Mm<sup>3</sup> in 2022.1 In Brazil, due to its large agricultural sector and government subsidies, biodiesel is regarded as a means to make the fuel sector sustainable. A drawback of biodiesel production is the co-generation of a large amount (~ 10% by weight) of crude glycerine with little commercial value. Accordingly, a larger number of catalytic conversion steps have been explored to add value to this by-product of biodiesel production.<sup>2-3</sup> Among those, the use of catalysts with acidic and oxidizing properties such as metal oxides, alumina-silica or noble metals have been considered.<sup>3</sup> Glycerol dehydration is performed in the presence of solid acid catalysts in water, producing products such as acrolein and 2-hydroxy propanone.<sup>3</sup> Another route is the conversion of glycerol to C1 products such as formic acid (FA).<sup>4</sup> Recently, FA has been proposed as a suitable hydrogen

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<sup>†</sup> Corresponding author – E-mail: <u>oliveira.hds.82@gmail.com</u> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x and CO<sub>2</sub>.<sup>5</sup> The cleavage of the C-C bond of glycerol to FA can be achieved by homogeneous Pd(II) catalysis with H<sub>2</sub>O<sub>2</sub>.<sup>6</sup> Continuous flow in a fixed bed reactor present industrial viability to yield FA from crude glycerol, which may help to make production of this chemical intermediate more environmentally benign. Some works have shown good results to yield solketal, glyceric acid and tartronic acid from glycerol. <sup>7,8</sup> Many types of catalysts are being investigated for the efficient conversion glycerol to products with higher added value. Most reactions involve chemistry-grade glycerol, which does not guarantee that the catalytic effect would be the same when the crude glycerol is employed. Crude oil contains about 10 wt% water. Some examples of crude oil conversion are catalytic reforming and dehydration to produce acrolein.9-12 Concerning dehydration, there are several works employing the acidic properties of niobium-based catalysts.13-15 The concept of combining niobium and vanadium to promote dehydration and oxidation in a one-pot reaction has also been discussed.<sup>16-20</sup> There is limited work on the liquid phase one-pot conversion of crude glycerol to formic acid.

storage compound, because it can be easily decomposed to H<sub>2</sub>

Vanadium oxides are potential catalysts for liquid-phase oxidation.<sup>21</sup> For instance, vanadium oxide supported on Nb<sub>2</sub>O<sub>5</sub> presents increased catalytic activity in methanol oxidation to formaldehyde compared with Nb<sub>2</sub>O<sub>5</sub>.<sup>22</sup> Nb<sub>2</sub>O<sub>5</sub> itself has also been used as a catalyst for dehydration, oxidation, epoxidation, transesterification and acetalization reactions.<sup>10-18</sup> In some cases, increased catalyst longevity and suppressed coke formation have been associated with niobium oxides.<sup>13-14</sup> Supporting vanadium and niobium oxides on a support like alumina will modify their properties and, sometimes, this also results in different structure-performance relations, resulting in synergy.<sup>23-25</sup>

Herein, we report on the continuous liquid-phase conversion of crude glycerol to formic acid. Niobium and vanadium oxides were impregnated on an alumina support. The properties of the catalyst were characterized by X ray

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diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy,  $N_2$  adsorption/desorption at -196 °C,  $NH_3$  temperature-programmed desorption, temperature-programmed reduction and oxidation ( $H_2$ -TPR) and ( $O_2$ -TPO).

## 2.Experimental

#### 2.1 Catalyst preparation

A commercial Y-alumina obtained from boehmite supplied by Sasol North America was used as the support. Prior to use, the support was calcined at 550°C for 5 h and labelled as Al<sub>2</sub>O<sub>3</sub>. Catalysts were prepared by wet impregnation. An amount of 0.395 g (1.56 mmol) VOSO<sub>4</sub>.5H<sub>2</sub>O was dissolved in 3.0 mL demineralized water and added to a suspension of alumina (3.0 g in 6.0 mL demineralized water). The suspension was stirred and heated to 70°C until dry. The resulting sample is designated V/Al<sub>2</sub>O<sub>3</sub>. The bimetallic catalyst VNb/Al<sub>2</sub>O<sub>3</sub> was prepared by dissolving the same amount of VOSO<sub>4</sub>.5H<sub>2</sub>O and 0.090 g (0.23 mmol) NH<sub>4</sub>NbO(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) in 2.5 mL of demineralized water). The procedure was the same as for the V/Al<sub>2</sub>O<sub>3</sub> catalyst. Finally, these catalyst precursors were calcined in air at 500°C for 5 h after heating to this temperature at 10°C/min.

#### 2.2 Catalyst characterization

Powder X-ray diffraction (XRD) measurements were carried out using CuK radiation in the 20 range 10–70° in a RIGAKU D-MAX 2200 X-ray diffractometer. Textural characterization was carried out by recording nitrogen adsorption-desorption isotherms at - 196°C in an Autosorb IQ2 Quantachrome system. Prior to measurement, the samples were degassed at 200°C for 8 h prior to analysis. The total pore volume was estimated from the amount of nitrogen adsorbed at  $P/P_0 = 0.95$ . The pore size distribution was calculated based on NLDFT method. Raman spectroscopy analysis were performed in backscattering mode using a Horiba Jobin-Yvon LabRAM HR spectrometer, with excitation at 632.8 nm from a helium-neon ion laser. The system included 1800 grooves mm<sup>-1</sup> diffraction gratings, a Peltiercooled CCD detector, and a confocal Olympus microscope (50X objective lens). NH<sub>3</sub>-TPD measurements were carried out in an ASAP 2910 Chemisorption (Micromeritics) equipped with a TCD detector. For this purpose, 0.05 g of catalyst was pre-treated by heating up to 400°C at 10 °C min<sup>-1</sup> during 2h in a He flow of 50 mL min<sup>-1</sup>, and then the sample was exposed to 5 vol% NH<sub>3</sub>-He (50 mL min<sup>-1</sup>) for 40 min at 60°C. Afterwards, the NH<sub>3</sub> desorption profiles were collected by heating at a rate of 6°C min<sup>-1</sup> to 900°C. Temperature-programmed reduction and oxidation (H<sub>2</sub>-TPR) and (O<sub>2</sub>-TPO) were performed in a fixed bed quartz reactor with a Quantachrome ChemBet 3000 analyzer. The reduction of the samples was carried out using  $H_2/N_2$  (5 vol.%) as reductant (flow rate = 80 cm<sup>3</sup> min<sup>-1</sup>) A 200 mg of the samples placed in the reactor were activated in a flow of synthetic air at 400 °C at a rate of 10 °C min<sup>-1</sup>. After sample was cooled to RT in helium, then, it was heated at a rate of 10 °C min<sup>-1</sup> to 1000 °C under the reducing feed. After the reduction experiment ( $H_2$ -TPR) the sample was cooled to 40 °C in helium.  $O_2$ /He (3 vol.%) mixture was used as oxidant (flow rate = 60 cm<sup>3</sup>

mL<sup>-1</sup>) in the temperature-programmed oxidant  $(IPrQ)_{a}$  The oxidation of the materials was performed from 40% 2000 Cat a rate of 10 °C min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha spectrometer, equipped with a monochromatic smallspot X- ray source and a 180° double focusing hemispherical analyser with a 128-channel detector. Spectra were obtained using an aluminium anode (Al  $K\alpha$  = 1486.6 eV) operating at 72 W and a spot size of 400  $\mu m.$  Survey scans were measured at constant pass energy of 200 eV and region scans at 50 eV. The background pressure was  $2 \times 10^{-9}$  mbar and during measurement,  $3 \times 10^{-7}$  mbar Argon, because of the charge compensation of the dual beam source. Data analysis was performed using Casa XPS software. The binding energy was corrected for surface charging by taking the C 1s peak of carbon as a reference at 284.5 eV. Thermogravimetric analysis was performed on a Shimadzu-TGA50H thermos-balance at 800°C in air atmosphere and flow of 100 mL min<sup>-1</sup>, with a heating rate of 10°C min<sup>-1</sup>.

#### 2.3 Catalytic activity

A crude glycerol (by-product of biodiesel production) donated by Petrobras Biofuels previous neutralized was used in neutral pH. The characterization of crude glycerol was performed before reactions using gas chromatograph coupled with mass spectrometer (GC-MS) and thermogravimetric (TG) analysis. Measurements for thermal analysis were performed on a Shimadzu Thermobalance-TGA50H equipment at 800 °C in air atmosphere and 50 ml min<sup>-1</sup> flow, with a heating rate of 10 °C min<sup>-1</sup>. The feeding consisted of a mixture of 1/1 (v/v) of residual glycerol and hydrogen peroxide (50%, v/v) with a continuous flow of 0.50 mL min<sup>-1</sup>. The catalytic reactions were run in a stainless-steel reactor (60 x 1.5 cm), filled with 600 mg catalyst at WHSV =  $0.5 h^{-1}$  and 200°C. Glycerol and reaction products were analysed by GC-MS using an Agilent HP-5MS column (length 30 m, diameter 250 µm and film thickness 0.25 µm 5 % poly(methylphenylsiloxane).

# 3.Results and discussion

The materials were characterized by XRD as shown in Figure 1. The XRD pattern is similar in three materials with the most presence of crystalline phase ( $\gamma$ –Al<sub>2</sub>O<sub>3</sub>, PDF card 10-0425) as highlighted (#) in Figure 1. Samples calcined of V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub> showed no reflections of vanadium oxides, niobium oxides or mixtures. These results indicate that the mentioned oxides are amorphous or with very small sizes, within the detection limits of XRD, i.e. small particles (< 4 nm) cannot generate X-ray diffraction pattern.<sup>26</sup> As we can see the intensities of reflections were reduced, may suggest overlapping surface by small amount of vanadium oxide or niobium oxide due to impregnation method.

XPS was used to study the chemical composition of the surface of the two samples. The V 2p XPS spectra (ESI, Fig. S1) contain a feature at 517.0 eV which can be related to  $V^{5+}$ .

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Figure 1. XRD patterns of samples  $Al_2O_3$ ,  $V/Al_2O_3$  and  $VNb/Al_2O_3$ .

Accordingly, we suggest that both V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub> might contain V<sub>2</sub>O<sub>5</sub> phase. The peak observed at 207.2 eV in the Nb 3d XPS spectrum of VNb/Al<sub>2</sub>O<sub>3</sub> can be assigned to Nb<sup>5+</sup> species.<sup>30,31</sup> From a quantitative fitting analysis, we can infer that the atomic V/Al ratios are 0.23 and 0.25 for the V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub> samples, respectively. This result indicates that the vanadium is equally well dispersed on the support surface of both catalysts. For the mixed VNb/Al<sub>2</sub>O<sub>3</sub> sample, a Nb/Al atomic ratio of 0.05 shows a lower dispersion than for V.

The Raman spectra for the vanadium and niobium oxides supported in the alumina catalysts are shown in Figure 2. Although the XRD pattern was very similar for three samples (Al<sub>2</sub>O<sub>3</sub>, V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub>), the Raman spectra are distinct and allow us to evidence the presence of niobium and vanadium oxides on the surface of the alumina. Alumina does not present vibrational modes evident in the region from 500 to 1100 cm<sup>-1</sup>, which facilitates the detection of vibrational modes related to oxides (V and Nb) supported on the surface.<sup>27</sup> The samples supported with vanadium and niobium exhibited a broadband in 982, a more intense band at 865 cm<sup>-1</sup> and other weaker bands in 932, 901, 804, 791 and 768 cm<sup>-1</sup>. On the other hand, for the sample supported with vanadium, were evidenced by two bands, in approximately 982 and 932 cm<sup>-1</sup>. Thus, the weakest bands in the region from 750 cm<sup>-1</sup> to 810 cm<sup>-1</sup> observed in the spectrum of the  $VNb/Al_2O_3$  could be attributed to the Nb-O bonds in slighted distorted NbOx species and Nb-O-Nb angle deformations present on bulk Nb<sub>2</sub>O<sub>5</sub>. The bands at 982 cm<sup>-1</sup> and 933 cm<sup>-1</sup> present in both spectra (V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub>) could be assigned to a stretching mode of terminal bond V=O, and V-O-V and V-O bonds.<sup>27-29</sup>

The presence of a hysteresis loop confirms the presence of mesopores as observed in the  $N_2$  adsorption/desorption isotherms (do not shown here). It is interesting to note that the presence V and Nb active phases provoke a hysteresis increase, indicating that interparticle pores have been created with the



Figure 2. Raman patterns of samples V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub>.

impregnation process. In general, the catalysts showed pore distribution in the range of 20-50 Å. The VNb/Al<sub>2</sub>O<sub>3</sub> showed a narrow distribution, which can improve the selectivity of catalytic conversion of glycerol in the mesopores. Physical property data are shown in Table 1.

**Table 1.** BET specific area, the total pore volume and acid sites amounts of the catalysts.

Catalyst <sup>[a]</sup>	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1 [a]</sup>	V <sub>P</sub> /cm <sup>3</sup> g <sup>-1[b]</sup>	Acid sites/mmol NH <sub>3</sub> .g <sup>-1 [c]</sup>
Al <sub>2</sub> O <sub>3</sub>	243	0.29	1.30
V/Al <sub>2</sub> O <sub>3</sub>	152	0.31	0.75
VNb/Al <sub>2</sub> O <sub>3</sub>	212	0.36	0.89

[a]=S<sub>BET</sub> surface specific area; [b]=  $V_P$  total pore volume (P/P<sub>0</sub> 0.95)).

Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed in order to assess the surface acidity (Table 1). As expected, the alumina support itself displays a high acidity. However, the material containing niobium oxide also showed good acidity, probably due to the presence of Nb<sub>2</sub>O<sub>5</sub>, which is known to exhibit this property.<sup>17,18</sup> These data suggest that the bimetallic catalyst containing V and Nb dispersed on alumina has the potential to act in reactions that require some acidity. Figure 3 report the desorption studies at the programmed ammonia temperature (NH<sub>3</sub>-TPD). It can be seen that the catalysts show similar profile of ammonia desorption before  $(V/Al_2O_3)$  and after the addition of niobium  $(VNb/Al_2O_3)$ . However, the catalyst with Nb exhibits higher ammonia desorption throughout the entire temperature range. This characteristic should influence its catalytic activity, since in the presence of hydrogen peroxide, niobium compounds promote the formation of peroxo groups (Nb-O-O) by the reaction with part of these observed acidic groups.

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Figure 3.  $NH_3$ -TPD analysis of  $Al_2O_3$ ,  $V/Al_2O_3$  and  $VNb/Al_2O_3$ .

These species are known to be highly oxidizing which should explain the presence of products from reactions in acid and oxidant sites.<sup>32</sup>

Fig. 4-A shows the TPR profiles of the V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub> catalysts. A sharp reduction peak at near 624 °C is observed for V/Al<sub>2</sub>O<sub>3</sub>, that is associated to the layers of vanadium oxide over alumina, in agreement with the literature.<sup>33</sup> The peak observed for VNb/Al<sub>2</sub>O<sub>3</sub> had a slight displacement to a lower temperature (603 °C) and this can favour the reduction process of vanadium oxide. Thus, the presence of a small amount of niobium oxide over surface favours the reduction of the material. This fact leads to an improvement of the reactivity of the catalyst surface, since redox processes are vital for the reaction. Fig.4-B shows representative profiles of  $O_2$ -TPO of V/Al<sub>2</sub>O<sub>3</sub> and VNb/Al<sub>2</sub>O<sub>3</sub>. It is remarkable the increase of the oxidation peaks occurring between 150 and 700 °C for the niobium-containing catalyst. The TPO analysis shows that the VNb/Al<sub>2</sub>O<sub>3</sub> has major ability to suffer oxidation compared to  $V/AI_2O_3$ . It is reported in literature that the niobium presence can favour the oxygen storage capacity in some oxide materials.<sup>33, 34</sup> The presence of niobium oxide over  $V/AI_2O_3$  catalyst may favour the oxidation process at low temperature, that is interesting for redox processes. This result suggests a strong interaction between niobium and vanadium oxides over alumina, which is a desired property for glycerol conversion.

The kinetic study of the residual glycerol conversion system employing the continuous flow with catalyst in a fixed bed at catalyst, favoring the product obtained from the oxidative 200°C is shown in Figure 5. In general, the catalysts exhibit high conversion of the substrate even on only the pure support.

This result must be due to the acidity of alumina, which should promote the dehydration glycerol products formation. In fact, the only products observed were predominantly compounds related to glycerol condensation, i.e., cyclic ethers with five and six rings.<sup>35</sup>



**Figure 4.** Profiles of temperature-programmed of  $V/Al_2O_3$  and  $VNb/Al_2O_3$  catalysts: (A) H<sub>2</sub>-TPR; (B) O<sub>2</sub>-TPO.

On the other hand, reactions using the materials containing vanadium (V/Al<sub>2</sub>O<sub>3</sub>) and especially after the incorporation of niobium (VNb/Al<sub>2</sub>O<sub>3</sub>), showed relatively high amount of formic acid (FA). This compound is of great interest to the petrochemical industry as it acts as a platform molecule to obtain polymeric compounds.<sup>35,36</sup>

The distribution of products observed for the catalyst after the addition of vanadium indicates a high formation of formic acid at the first reaction times. In the longer reaction time the increase of dioxanes, 4-hydroxymethyl-1,3-dioxolano (DIOXO) and 5-hydroxy-1,3 dioxane (DIOXA) are observed (Fig. 6A). This result indicates that the oxidative capacity of the catalyst is lost during the reaction time, possibly caused by the inability of vanadium oxide to activate hydrogen peroxide for a long time. This can occur due to the deposition of by-products (coke formation) on the sites containing the reactive species of vanadium, reducing its catalytic activity.

It is known that reactions in the presence of catalysts having acidic properties promotes the formation of polymeric compounds and coke formation may even occur for.<sup>14</sup>

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**Figure 5.** Crude glycerol conversion in continuous flow with catalysts.

However, after the addition of niobium (Fig. 6B) there is an increase in FA content and decrease of dioxanes. This profile indicates that the niobium oxide present on the surface of the alumina enhances the oxidative action of the cleavage of glycerol. Some authors reported that niobium compounds could act as reaction promoters, reducing the active phase deactivation.<sup>37</sup> These results are in agreement with those observed by NH<sub>3</sub>-TPD analysis, where it was evident

a greater possibility of peroxo groups formation, which are a strong oxidizing species when the niobium is present in the catalyst. 1-hydroxy-2-propanone (HPN), which is a product of glycerol dehydration probably due to acid sites from the alumina and niobium oxide surfaces was also observed. Recent work has also shown that niobium oxide might favor the formation of both sites, acid and oxidizing groups on its surface by the decomposition of hydrogen peroxide.<sup>38</sup>

As previously mentioned, crude glycerol was submitted by GC-MS (ESI, Fig S2) and TG analyses to identify level of purity and other possible substances present (ESI, Fig S3). TG analysis shows crude glycerol mass loss suggests the presence of approximately 19% water, 75% glycerol and the remaining 6% salts. From reaction point of view, there are several works of interest for producing new molecules from glycerol through catalysts with elements of the group five and six of periodic table. For example, Soriano et al.,<sup>39</sup> studied bimetallic catalysts employing catalysts based on W and V to promote simultaneous dehydration and oxidation to acrylic acid. The reactions were carried out in the gas phase with a low glycerol concentration. The present work presents a high conversion and selectivity by employing a high concentration of glycerol. In addition, residual glycerol from biodiesel production was used, which results in a greater difficulty for the action of the catalysts.

The catalyst developed in this present work presents bifunctional character as indicated by the observed products.





**Figure 6.** Products distribution of catalysts reaction with  $V/Al_2O_3$  (a) and  $VNb/Al_2O_3$  (b). (4-hydroxymethyl-1,3-dioxolano (DIOXO) and 5-hydroxy-1,3 dioxane (DIOXA).

We suggest that the sequence of by-products formation by oxidative cleavage of glycerol to small molecules takes place in a first step (oxidizing sites). In a second step, there is a driving force towards acetalization between non-converted glycerol and formaldehyde yielding 4-hydroxymethyl-1,3-dioxolano and 5-hydroxy-1,3 dioxane (over acid sites), according to Gonzalez-Arellano et al.<sup>40</sup> Thereby, the niobium catalyst, even at light loading on the support, showed better ability to increase the glycerol cleavage rate instead of the acetalization step, maintaining FA selectivity in 21 h of reaction in a liquid phase system. Reactions with glycerol from biodiesel production present extra difficulty for this substrate. The main difficulty is related to the relatively high amount of NaCl.

Fig. 7 shows the product distribution for the  $Al_2O_3$  support. Cyclic products such as 4-hydroxymethyl-1,3-dioxolane (DIOXO), 5-hydroxy-1,3 dioxane (DIOXA) and hydroxypropanone (HPN) were observed.

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**Figure 7.** Products distribution of Al<sub>2</sub>O<sub>3</sub> support.

It is possible to attribute the reaction activity to the high acidity of the alumina support, as verified by the  $NH_3$ -TPD, which is also demonstrated by other studies in the literature.<sup>40</sup> These results show that the use of only the support promotes the formation of a low amount of formic acid, indicating that the presence of Nb and V is essential for a good selectivity for the product of interest.

# Conclusions

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In summary, continuous flow reactions were performed using residual glycerine from biodiesel production using bifunctional catalysts containing vanadium and niobium oxide dispersed on alumina. XPS and XRD analyses indicated a high surface dispersion of the active phase, generating interparticle mesoporous pores. The synergic action of the catalysts has been proven by the types of products generated, contemplating molecules from reactions in acid sites and oxidizing groups. Formic acid was the product obtained with good selectivity (~55%) in the presence of Nb and V over alumina. Herein we showed, for the first time, the production of this important petrochemical feedstock using liquid-solid reaction with stability for several hours of continuous reaction.

# **Conflicts of interest**

There are no conflicts to declare.

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# **GRAPHICAL ABSTRACT**

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