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Synthesis of two new Nickel and Copper-Nickel vanadates used for propane oxidative dehydrogenation

Síntesis de dos nuevos vanadatos de Níquel y Cobre-Níquel usados en la deshidrogenación oxidativa de propano

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Abstract:

Two new vanadates have been successfully synthesized by the hydrothermal and coprecipitation methods. Both vanadates were calcined at 600 °C and the resulting catalysts were tested on reaction of oxidative dehydrogenation of propane. The catalysts were characterized by x-ray diffraction, atomic absorption, thermogravimetric analysis, and differential temperature analysis. The reaction was carried out in the temperature range of 350-500 °C. A conversion of propane of 10.6 % and a selectivity towards propene of 29.9 % at 400 °C were obtained with nickel vanadate; a conversion of 1.9 % and a selectivity of 56.9 % were reached at the same temperature with the nickel copper vanadate.

---------- *Keywords:* Oxidative dehydrogenation, nickel vanadate, copper-nickel vanadate, propane, propene

Resumen

Se probaron dos nuevos vanadatos en la deshidrogenación oxidativa de propano. Los catalizadores fueron sintetizados por el método hidrotérmico y de coprecipitación, la caracterización se llevó a cabo por medio de difracción de rayos X, absorción atómica, análisis termogravimétrico y análisis térmico diferencial. La reacción se realizó en un rango de temperatura de 350-500 °C. Con el vanadato de níquel se obtuvo una conversión de propano de 10.6 %

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y una selectividad hacia propeno del 29.9 % a 400 °C y con el vanadato de cobre y níquel se alcanzó a la misma temperatura una conversión de 1.9 % y una selectividad del 56.9 %.

---------- *Palabras Clave:* Deshidrogenación oxidativa, vanadato de niquel, vanadato de cobre-niquel, propano, propeno

Introduction

In recent years, the study of Oxidative Dehydrogenation (ODH) of alkanes has gained importance due to the high demand for light alkenes in plastic industries, and because of the way it may be used with natural gas in order to enhance its content in light alkanes. The ODH is an alternative route for the production of alkenes such as propene, since coke production does not occur, and there is no equilibrium limitation [1].

The highest yields achieved in the oxidative dehydrogenation of propane have been given with zinc and magnesium vanadates [2], K/Mo catalysts supported on mixed oxides of silicon and titanium [3], oxides of alkaline earth metals [4, 5] and an Ni(Co)MoO_4 trimetallic catalyst [6], among others. However, these catalysts yields do not exceed 24 %. Different factors make a catalyst useful in the oxidative dehydrogenation reaction, such as the nature of active oxygen species, the redox, and the acidic properties [1].

The magnesium vanadates are among the catalysts which have improved performance in these reactions [1-7]. The catalytic experiments made with these catalysts suggest that the high activity may be related to the easy removal of vanadates surface oxygen groups [8-11]; consequently, vanadium is found in many formulations of catalysts for oxidative dehydrogenation.

Different vanadium-based catalysts have been tested, either in bulk or supported form, mixed with calcium, nickel ,and copper, such as: V-Ca-O [12] with a conversion of 5 % and a selectivity of 48 %; hydroxyapatite calcium replaced with vanadium [13], reaching a conversion of 17.2 % and a selectivity of 52.4 % at 450 ºC; calcium magnesium vanadates [9], with conversion of 12.5 % and selectivity of 39.3 % at 450 ºC; copper magnesium vanadates [10], with a conversion of 9.3 % and a selectivity of 32.9 % at 450 ºC; and finally, nickel vanadates [14] with a conversion of 19.45 % and a selectivity of 49.9 % at 425 °C.

In this work, two new nickel and copper-nickel vanadates were synthesized by the hydrothermal and coprecipitation methods, this latter allows saving energy in the process of synthesis compared with other methods used in previous work [9-18] for similar materials. The characterization of and their catalytic activity in the oxidative dehydrogenation of propane has been reported.

Experimental

Preparation of catalysts

The precursors were first synthesized by the hydrothermal and coprecipitation methods [15], then calcined at 600 °C for 3 hours at 5 °C/min to obtain the final catalyst. In the hydrothermal synthesis, the solutions are mixed and the mixture is heated in lined-autoclave at a fixed temperature and autogen pressure. In the coprecipitation method, the mixture is kept at room temperature for a fixed time. Each precursor was prepared from individual solutions of vanadium, NH_4VO_3 (Merck 99 %), to which copper, $CuCl_2$-$2H_2O$ (Merck 99 %), and/or nickel, $NiCl_2$-$6H_2O$ (Merck 98 %), solutions were added. The precipitating agent used was NH_4OH (Merck 28-30 %) and the heating temperature for the hydrothermal method was 100 °C, as shown in table 1. The crystallization time varied between 72 and 96 hours. The solids precursors were called *NiV* and *CuNiV*. Calcined precursors (final catalysts) were labelled by adding the calcination temperature to each one of them (*NiV600* and *CuNiV600*).

Table 1 Synthesis conditions of the precursors

Material	*Gel molar composition*	*T, [°C]*	*t, [h]*
NiV	$NiCl_2 : NH_4VO_3 : 0.75NH_4OH: 172\ H_2O$	100	72
CuNiV	$NiCl_2: CuCl_2: 2NH_4VO_3 : 1.5NH_4OH: 341\ H_2O$	100	96

Characterization of the catalysts

The chemical composition of V, Cu and Ni of the two new materials was determined by atomic absorption on a Unicam Solaar. The identification of crystalline phases was carried out through the diffractograms obtained in a Rigaku Miniflex apparatus with radiation Cuk_α (λ = 1.5418 Å) operated at 40 kV and 30 mA and with the aid of the PDF-2 diffraction database (Powder Diffraction File). The thermogravimetric analysis (TGA) was performed in a TA Instruments Hi-Res TGA 2920 and the differential thermal analysis (DTA) was performed on a TA Instruments DSC 2920, both in a temperature range from 30 to 800 °C, 10 °C/min, under air atmosphere .

Indexing of the unit cell

The x-ray data for indexing were obtained in a Bruker diffractometer, equipped with a graphite monochromator, using radiation Cuk_α (λ = 1,5406 Å) operated at 40 kV and 40 mA, with a scan of 10 to 60° in 2θ, a step of 0.02°/step and a time per step of 5 seconds. The pattern decomposition was carried out using WINPLOT; the peaks found were analyzed using the CRYSFIRE, ITO, and TREOR algorithms. The refinement of the cell and the determination of the space group were performed with CHEKCELL.

Catalytic tests

The oxidative dehydrogenation of propane was carried out in a quartz reactor (i.d 5 millimeters, length 400 millimeters) at atmospheric pressure in a temperature range between 350-500 °C and a space velocity of 100 ml g^{-1} min^{-1}, using 0.2 grams of catalyst. The feed that contained 29 % propane and 71 % air, corresponding to a molar ratio of propane/air = 2. The reaction products were analyzed on-line by gas chromatography on Shimadzu GC-9A with thermal conductivity detector, using a 5A molecular sieve and Porapak Q columns.

Results and discussion

Characterization of catalysts

Precursors and materials obtained from calcinations were identified by x-ray diffraction. The diffractograms as a function of calcination temperature are shown in figure 1, and the identification of the crystalline phases present in the catalyst (the precursor calcined at 600 ºC) and the precursor are shown in table 2.

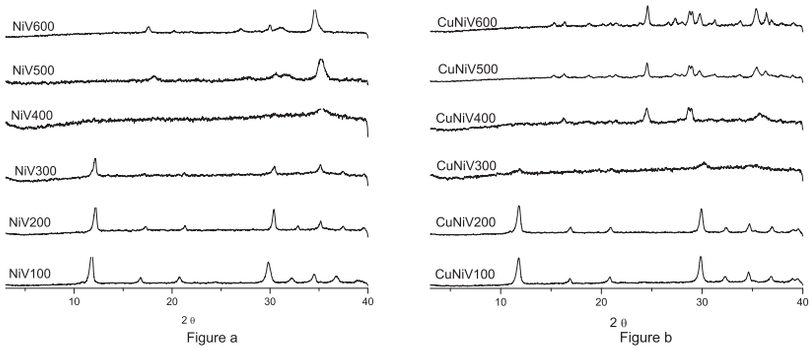

Figure 1 Diffractograms of a: *NiV*, b: *CuNiV* at different calcination temperatures

Table 2 Material identification

Material	*Crystalline phase*	*PDF*
NiV	Φ_z	New phase
NiV600	$Ni_3V_2O_8$	74-1485
CuNiV	Φ_z	New phase
CuNiV600	$Cu_3V_2O_8$ y $Ni_3V_2O_8$	74-1503 y 74-1485

The nickel and nickel-copper vanadates could not be found in the database consulted, which suggests a development of two possible new materials; however the XRD pattern is similar to fz, which has been obtained for other crystalline vanadate phases, but combined with zinc or copper [16-19]. The nickel catalyst (calcined precursor) was identified as $Ni_3V_2O_8$, and the nickel and copper ones as a mixture of $Cu_3V_2O_8$ and $Ni_3V_2O_8$.

The compositions of metals in the new precursors were analyzed and the amount of nickel was 33.1 % for *NiV* and 14.81 % for the *CuNiV*, the copper amount for the latter was 14.94 %. As demonstrated by XRD, the two new materials have the same structure of phase fz, whose general formula for zinc vanadate is $Zn_3(OH)_2V_2O_7 \cdot 2H_2O$ [15]. In our case, this formula should be maintained, but the divalent metal will not be Zn but Ni and/or Cu. Taking into account the proposed theoretical formula $M_{3-x}(OH)_2V_2O_{7-x} \cdot nH_2O$, where M: Ni or a mixture of Cu and Ni and n the number of hydration water molecules) for a fy phase and the chemical analysis, the following formulas $Ni_{2.2}(OH)_2V_2O_{6.2} \cdot 1.1H_2O$ for *NiV*, and $Ni_{0.63}Cu_{0.59}(OH)_2V_2O_{5.22} \cdot 0.9H_2O$ for *CuNiV* were established.

These formulas agree quite well with experimentally obtained results, because the theoretical percentages of Ni and H_2O in *NiV* is 33.6 % and 9.8 %, respectively (9.8 %, experimental of H_2O); for *CuNiV* the theoretical percentages of Ni and Cu are respectively 15.7 % and 15.8 % and H_2O is 9.9 % (9.9 %, experimental of H_2O).

Thermograms of the precursors (Figure 2) show a weight loss up to 100 °C, which is associated with humidity in the material.

Figure 2a shows a weight loss of 5.2 % accompanied by an endothermic event between 100-250 °C, which is due to desorption of hydration water. There is an endothermic event with a weight loss of 4.61 %, associated to the OH^- present in the structure between 250 and 500 °C; the percentage of theoretical mass loss is equal to that found experimentally, with a value of 9.8 %, which provides the following thermal decomposition reaction:

$$Ni_{2.2}V_2O_{6.2}(OH)_{2.2} \cdot (H_2O)_{1.2} \rightarrow 2.3H_2O \uparrow + Ni_{2.2}V_2O_{7.3} \quad (1)$$

Figure 2b shows two endothermic events, first at 200-250 °C, where weight loss is 8 %, associated with the desorption of hydration water, and the second in a range at 250-400 °C, accompanied by a weight loss of 4 %, assigned to the release of water from the structure hydroxyl. The theoretical total weight loss was 9.9 %, which was equal to experimentally obtained. The following thermal decomposition reactions were proposed:

$$Ni_{0.63}Cu_{0.59}(OH)_2V_2O_{5.22}(H_2O)_{0.9} \rightarrow 1.9H_2O\uparrow + 0.5Ni_{1.26}V_2O_{6.26} + 0.5Cu_{1.18}V_2O_{6.18} \quad (2)$$

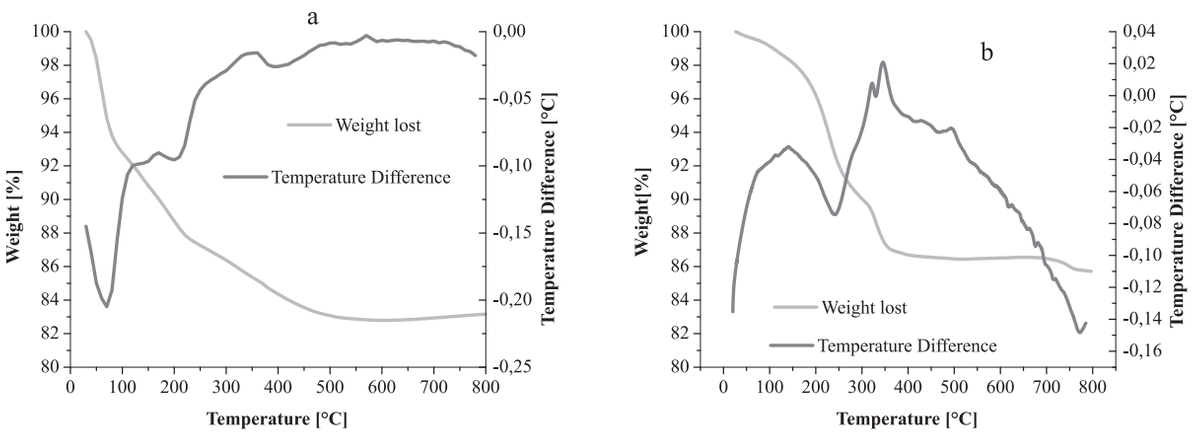

Figure 2 TGA and DTA of the precursors, a: *NiV*, b: *CuNiV*. Exo up

The decomposition reactions for the *NiV* and *CuNiV* precursors show that the mixed oxides formed after calcination are not exactly the same to those found with the identification by XRD, since they are not stoichiometric.

Based on the thermal behavior of precursors, it was decided to calcine them at 600 °C, temperature at which there is no further loss of mass or phase change.

Indexing

The precise determination of the positions of the peaks in the X-ray pattern was carried out using the WINPLOT program. Obtained reflexions were used as input for the CRYSFIRE program. To find the best cell for the *NiCuV*, the reflections were tested in the CHEKCELL program. The hexagonal cell was initially tested, but two lines were not indexed. Orthorhombic cells were indexed, but their figure of merit was very low. With cells in the triclinic system, all reflections were not indexed. The best solution was the monoclinic cell, with a figure of merit 14 and I20 of 20. In the case of *NiV* material, a similar procedure of *CuNiV* was followed. The data given for CRYSFIRE were analyzed and checked with the CHEKCELL program. One of the selected results showed a figure of merit of 20, but the found cell parameters were divided by 2, because the unit cell showed a very large volume (V = 1298 Å^3) if these values are compared with the phase ϕz. However, this first analysis did not work, since not all lines were indexed, then, the cells reported by Zhang [19] and Hoyos [17], who worked with similar materials, were tested. The first assay was not good. Finally, the cell was refined and inscribed in the hexagonal system.

The refinement of the cell and the space group determination were carried out with CHECKCELL. Tables 3 and 4 show the crystallographic data of new materials.

Table 3. Crystallographic data of nickel and copper vanadate, phase Φ_z

Composition: $Ni_{0.63}Cu_{0.59}(OH)_2V_2O_{5.22}(H_2O)_{0.9}$
System: Monoclinic λ= 1.5406 Å
Cell parameters a =15.1657Å b =5.4771Å c = 5.1194Å b = 109.29
Space group : P21n

h	k	l	2θ observed	2θ calculated
2	0	0	12.3754	12.3567
-1	0	1	17.3143	17.3085
1	0	1	21.2831	21.2431
4	0	0	24.8692	24.86
2	1	1	30.2742	30.2557
0	2	0	32.6992	32.6732
-2	0	2	34.9987	35.0286
-1	2	1	37.2284	37.2047
-3	2	1	39.3921	39.3927
-6	1	1	39.8021	39.725
5	0	1	41.6502	41.6061
2	0	2	43.3041	43.2638
-2	2	2	48.6476	48.6521
-4	2	2	50.46	50.4715
-8	1	1	50.962	50.9775
4	0	2	52.0752	52.1658
-2	3	1	53.6495	53.6552
2	2	2	55.2598	55.2519
1	0	3	59.8246	59.8153
-7	1	3	62.7981	62.792
-6	3	0	64.1709	64.1843
-7	3	1	67.0608	67.1268
-1	4	1	71.2454	71.2299
1	4	1	72.6041	72.596

Table 4 Crystallographic data of nickel vanadate, phase Φ_z

Composition: $Ni_{2.2}V_2O_{6.2}(OH)_2 \cdot (H_2O)_{1.1}$
System: Hexagonal λ = 1.5406 Å
Cell parameters: a =10.1988 Å c =14.3759 Å
Space group : P-3c1

h	k	l	2θ observed	2θ calculated
0	0	2	14.3003	14.30
1	1	0	20.2054	20.21
1	1	2	24.8427	24.84
0	0	4	28.8288	28.82
1	2	1	31.9967	31.93
1	1	4	35.4469	35.46
0	3	2	38.3264	38.33
2	2	0	41.0679	41.08
2	2	1	41.7240	41.75
2	2	2	43.6993	43.71
0	3	4	46.2505	46.25
2	2	3	46.8285	46.83
1	1	6	48.7312	48.72
2	2	4	50.9520	50.95
1	4	0	55.2827	55.30
2	2	5	55.9356	55.93
0	3	6	57.5333	57.55
0	0	8	59.7332	59.71
2	2	6	61.6378	61.63
1	4	4	63.5571	63.56
3	3	4	71.2206	71.20
2	2	8	75.0259	75.03
1	2	9	76.7262	76.75

Catalytic Activity

The catalytic behaviour of the vanadates in the reaction of oxidative dehydrogenation of propane was studied; the products were propylene and CO_2. Table 5 shows the variation of conversion and selectivity with temperature for the catalysts. It can be seen that as the temperature increases so does the conversion, but the selectivity decreases dramatically, it could be a consequence the temperature favors the kinetics of CO2 yields. With the *NiV* catalyst was not possible to test above 400 °C due to the inability to control the inflow, possibly for excessive coke deposition and subsequent plugging of output of the reactor.

Table 5 Performance of catalysts at different temperatures. Space velocity 100 ml×g^{-1}×min, molar ration of propane/air = 2 and 0.2 grams of catalysts

Catalysts	Conversion [%]		Selectivity [%]		Temperature
	Propane	Oxygen	Propene	CO_2	[°C]
CuNiV					
	0.7	3.7	65.6	34.4	350
	1.9	12.4	56.9	43.1	400
	3.6	35.5	11.3	88.7	450
	9	72.3	10.5	89.5	500
NiV					
	4.4	43.4	53.7	46.3	350
	10.6	97.1	29.9	70.1	400

It can be noticed that the best performance is achieved with the *NiV*, with a conversion of propane of 10.6 % and selectivity to propene of 29.9 %. However, the catalyst most selective to propene was the nickel and copper trimetallic catalyst. Since *NiV600* catalyst showed the best results, other experiments were conducted at different space velocities, 100, 200 and 400 ml g^{-1} min^{-1}, in order to observe its effect on the reaction. It was decided to work at 350 °C, because at this temperature was obtained the highest selectivity.

From figure 3 it can observed that when the space velocity increases, the conversion of propane decreases and the selectivity to propene increases, as expected, because at high space velocity there is less contact time and therefore there is less possibility to occur side reactions how the CO_2 production. There is also a decrease in catalytic activity due to the short time that the propane molecule is in contact with the catalyst.

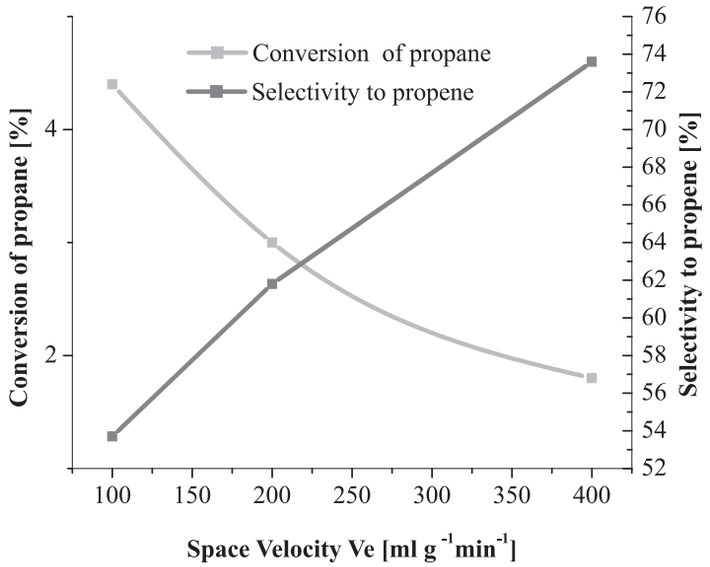

Figure 3 Conversion of propane and selectivity to propene at different space velocities for the *NiV600* at 350 °C and 0.2 g of catalyst

Conclusions

Two new materials ϕz type, comprised from vanadium-nickel and vanadium-nickel-copper, with the formula $Ni_{2.2}V_2O_{6.2}(OH)_2 \cdot (H_2O)_{1.1}$ and $(Ni_{0.52}Cu_{0.48})_{1.22}(OH)_2V_2O_{5.22} \cdot H_2O_{0.9}$, respectively, were synthesized by the hydrothermal and coprecipitation methods. These materials were calcined at 600 °C in order to obtain catalysts for the propane oxidative dehydrogenation reaction. The best performance was obtained with the *NiV600* (conversion of propane of 10.6 % and selectivity to propene of 29.9 % at 400 °C). The low conversion obtained with Cu catalyst could be attributed to low accessibility to the vanadium sites (the active site), occurred by masking with copper atoms.

The precursor materials identified as *NiV* and *CuNiV* showed a change in their composition and structure to be calcined; leading to formation of metastable phases, which are more dense than initial precursor, as are shown with the X-ray diffraction identification.

The catalyst (NiV600) showed good activity, but it is remarkable that the method of preparation of the precursor is much better than reported by Zhaorigetua et. al [14] for other Zn-V catalyst, in terms of saving energy.

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