Oxidative dehydrogenation of propane with cobalt, tungsten and molybdenum based materials

ABSTRACT: Oxidative dehydrogenation of propane is a reliable alternative for olefins production. This paper presents the results obtained on oxidative dehydrogenation of propane by using two materials based on cobalt, tungsten, and molybdenum. The materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), temperature programmed reduction (TPR), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The CoMo\(\phi\)y material was calcined at 623 K, transforming itself to \(\beta\)-CoMoO\(_4\) phase (CoMo\(\phi\)y623), the same phase is observed when the material is calcined at 873 K (CoMo\(\phi\)y873). CoMo\(\phi\)y623 showed the best performance in oxidative dehydrogenation of propane, a yield to propene of 3.4% was obtained at 623 K using a space velocity of 100 mL g\(^{-1}\) min\(^{-1}\). CoWs\(\phi\)y was calcined at 673 K, a low crystallinity wolframite was obtained. This material has a high selectivity to propene and low yield. CoMo\(\phi\)y873 has a selectivity and conversion within the range of the results reported in the literature. This is a prospective catalyst for the oxidative dehydrogenation of propane; it was stable for 24 h of continuous operation at 773 K.

RESUMEN: La deshidrogenación oxidativa de propano es una alternativa interesante para la obtención de olefinas. En este trabajo se presentan los resultados obtenidos en la deshidrogenación oxidativa de propano utilizando dos materiales a partir de cobalto, tungsteno y molibdeno. Los materiales fueron caracterizados utilizando Difracción de Rayos X (XRD), espectroscopía infrarroja con transformada de Fourier (FTIR), análisis termogravimétrico (TGA) y análisis térmico diferencial (DTA). El material CoMo\(\phi\)y al ser calcinado a 623 K se transforma en la fase \(\beta\)-CoMoO\(_4\) (CoMo\(\phi\)623), la misma fase es observada cuando el material es calcinado a 873 K (CoMo\(\phi\)873). CoMo\(\phi\)623 mostró el mejor rendimiento en la oxidación de deshidrogenación de propeno, un rendimiento de 3.4% se obtuvo a 623 K usando una velocidad de 100 mL g\(^{-1}\) min\(^{-1}\). CoWs\(\phi\)y fue calcinado a 673 K, un wolframita de baja cristalinidad fue obtenida. Este material tiene una alta selectividad para propeno y menores rendimientos. CoMo\(\phi\)y873 presenta una buena actividad y selectividad, comparable con otros materiales reportados en la literatura, y su potencial como catalizador en la deshidrogenación oxidativa de propano se hace más evidente con la prueba que muestra ser estable durante 24 h de operación continua a 773 K.
1. Introduction

Alkenes or olefins are traditionally obtained in oil refineries, either from natural gas through extraction processes, or by fluidized bed naphtha catalytic steam cracking. However, due to the constant growth in consumption of olefins and derivatives in the world market, these methods are insufficient. Thus, different synthesis paths to light olefins (C2-C4) production have been studied [1]. The dehydrogenation process offers the possibility to obtain olefins, and it requires high temperatures (>873 K). This condition can generate problems due to thermal cracking side reactions and fast and continuous coke formation; it can imply a total loss of the catalytic activity due to irreversible deactivation or a regeneration step of the catalyst [2].

To overcome the disadvantages of the alkane dehydrogenation process, several alternatives have been proposed, such as the development of catalysts with a higher selectivity and resistance to deactivation or coupling the dehydrogenation reaction (endothermic) with methane oxidation (highly exothermic), to provide the heat required for the dehydrogenation and shift the balance towards alkenes [3]. Nevertheless, the alternative that has aroused more interest is the oxidative dehydrogenation, using oxygen in the reaction mixture to generate olefins, without side or consecutive reactions. In the oxidative dehydrogenation, thermodynamic limitations are overcome, allowing milder operating conditions and avoiding the need for continuous catalyst regeneration. However, the main difficulty is to avoid the consecutive oxidation to carbon oxides from the light alkane, implying the need for the development of materials with high selectivity [4].

Transition metal oxides are recognized as the best catalysts for oxidative dehydrogenation. Molybdenum, vanadium and cobalt oxides show catalytic activity from 473 K [5]. Vanadium pentoxide is the most studied system. It does not present catalytic activity as a bulk material; the selectivity to propene obtained with supported V2O5 systems is between 60 and 80% and conversions about 1-15% [6–9]. The performance of niobium compounds is similar to that observed with vanadium compounds [10, 11].

Molybdenum compounds have shown low catalytic activity; nevertheless, different molybdates, such as NiMoO4, have higher conversions than those obtained with vanadium-based materials, with a lower selectivity [12–14]. Additionally, transition metal mixed oxides of Mo, V, Fe, Co, Ce, Mn, Te have been studied before, and they have shown a good catalytic activity in oxidative dehydrogenation [15–17].

Tungsten-based materials have not been extensively studied in this particular reaction. Mo-W and V-W mixed oxides supported on alumina or silica have been studied providing good selectivity results but not good conversion [18, 19]. Different catalytic systems for oxidative dehydrogenation of propane based on Co and Ni molybdates or tungstates have been tested; these systems showed a good selectivity and a promising propene yield [20, 21].

In this work, bulk materials in Co-Mo and Co-W systems have been synthesized, which are promising as catalytic precursors in oxidative dehydrogenation of propane. The conditions for a good catalytic performance were found, taking into account parameters such as selectivity, conversion, and stability.

2. Experimental

2.1. Catalysts preparation

Bimetallic precursors were prepared using a co-precipitation method and were denominated CoMoFy and CoWsFy. The synthesis was carried out by preparing solutions of the metal salts, which were mixed and homogenized during the required time to form the gel. The salts used were Co(NO3)2·6H2O (Merk), (NH4)2MoO4·4H2O (Merk) and WO3 (Aldrich); tungsten oxide was dissolved with NH4OH, the NH4OH was also used as the precipitating agent. Next, the precipitating agent was added to the mixture, which was allowed to crystallize for 4 h at 353 K. In the end, the solids were recovered by filtration. Table 1 shows the molar gel composition of the precursor materials. The precursors were dried in a convection oven at 373 K. The final catalyst was obtained from calcination of the precursors at the temperatures that were chosen based on the thermal behavior shown below. Calcination temperature was defined at 673 K for CoWsFy and at 623 K for CoMoFy.

Table 1 Molar gel composition for the synthesized precursors

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Gel molar composition</th>
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<tbody>
<tr>
<td>CoMoFy</td>
<td>MoO3:3Co(NO3)2:3NH4OH:186H2O</td>
</tr>
<tr>
<td>CoWsFy</td>
<td>WO3:3Co(NO3)2:3.8NH4OH:190H2O</td>
</tr>
</tbody>
</table>

Hereafter, the precursors or fresh materials are denominated CoMoFy and CoWsFy. The catalysts were denominated with the name of the precursor plus the calcination temperature: CoMoFy623 and CoWsFy673.

2.2. Materials characterization

X-Ray diffraction was carried out in a Miniflex model Rigaku equipment with Cu source (λ = 1,5418 Å) operated at 40 kV and 30 mA for values between 5 and 40° and with scanning rate 2° min⁻¹. The thermal stability of the materials was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA was carried out in TA Instruments Hi-Res TGA 2920 in a temperature range between 303 K and 1073 K, at a 10 K min⁻¹ heating rate, under inert atmosphere [N₂] and DTA was carried-out on a TA Instruments DSC 2920 model using the same conditions as in TGA. Additionally, fourier transform infrared (FTIR) spectra were obtained with a Perkin Elmer Spectrum One equipment. The samples were prepared as wafers containing ~1 wt% sample in KBr. Moreover, the temperature-programmed reduction (TPR) analyses was performed in a Zeton Altamira AMI-70; in this case, the pre-treatment was carried-out by heating the sample [50mg] from room temperature to 573 K under argon atmosphere, and the
catalyst reduction took place under a 30 mL min\(^{-1}\) flow of H\(_2\) (10 vol %)/Ar mixture, raising the temperature from room temperature to 1273 K at 10 K min\(^{-1}\).

### 2.3. Catalytic tests

Oxidative dehydrogenation of propane was performed in a quartz reactor, using a propane to oxygen molar ratio of 2:1 in the reactant mixture. Temperatures in the range 473-873 K were used, 0.4 g of catalyst and a space velocity of 50 mL g\(^{-1}\) min\(^{-1}\) (298 K and 1 atm) were used. For the catalyst that showed the best performance, different space velocities were tested. During each reaction, the effluent of the reactor was analyzed in a Shimadzu GC-9A gas chromatograph equipped with TCD detector and Molecular Sieve 5A and Porapack Q columns. Calculations of conversion, selectivity, and yield of the reaction for each catalyst were carried out. The main products were propene, CO\(_2\) and CO, and some traces of CH\(_4\) and C\(_2\)H\(_4\).

### 3. Results and discussion

#### 3.1. Characterization

**X-ray diffraction (XRD)**

![XRD patterns](image)

**Figure 1** XRD patterns for A: (1) CoMo\(\phi\)y, (2) CoMo\(\phi\)y calcined at 623K, (3) CoMo\(\phi\)y calcined at 873K, (4) \(\beta\)-CoMoO\(_4\) pattern. B: (1) CoWs\(\phi\)y, (2) CoWs\(\phi\)y calcined at 673K, (3) CoWO\(_4\) pattern.

**Figure 2** Thermal analysis for (A) CoMo\(\phi\)y, (B) CoWs\(\phi\)y. Solid lines represent the thermogravimetric analysis (TGA), dash lines represent the differential thermal analysis (DTA).

**Temperature programmed reduction (TPR)**

The TPR profiles for the calcined materials are presented in Figure 3. For CoMo\(\phi\)y623 consistency with the reduction temperatures reported by Brito and Barbosa [25] for \(\beta\)-CoMoO\(_4\) were observed. It was established that a reduction to lower valence oxidized states takes place, generating
equimolar mixtures of Co$_2$Mo$_3$O$_8$ and Co$_2$MoO$_4$ species, followed by a high-temperature reduction to the metals; these events take place at 807 K and 1113 K respectively. Additionally, a shoulder at 973 K is observed, which can be attributed to the reduction of an amorphous phase impurity obtained when calcination of the lamellar precursor took place. This amorphous phase was not observed by X-ray diffraction.

For CoWs$\phi$y673 the reduction events are observed from 673 K upwards, with two peaks at 1073 K, and 1123 K. Complete reduction of the material is achieved at temperatures near 1173 K. This profile is common for tungsten oxide catalysts, which present reduction at temperatures higher than 1073 K [26].

**Figure 3** TPR profiles for CoMo$\phi$y623 and CoWs$\phi$y673 by reduction with 10% H$_2$/Ar mixture, from room temperature to 1273 K at 10 K min$^{-1}$

**Fourier transform infrared spectroscopy (FT-IR)**

Infrared spectra were obtained for the precursors and the calcined materials (Figure 4). For CoMo$\phi$, bands at 928 and 620 cm$^{-1}$ are associated with symmetric O-Mo-O stretching vibrations; the bands at 865, 806, 751 and 475 cm$^{-1}$ correspond to asymmetric O-Mo-O stretching. All the bands correspond to characteristic vibration modes MoO$_4^{2-}$ tetrahedra. For CoMo$\phi$y623, bands at 943, 841, 784, 704 and 418 cm$^{-1}$ are observed, which correspond to the vibration bands of β-CoMoO$_4$ structure [27]. This confirms the XRD results, cf. Figure 1(b).

In CoWs$\phi$ spectra, bands at 915, 813 and 418 cm$^{-1}$ are observed, which agree with the vibration bands observed for scheelite-type oxides, where tungsten is in tetrahedral coordination. Meanwhile, the band at 878 cm$^{-1}$ is related to symmetric vibration, and the bands at 750, 682, 647, 570 and 525 cm$^{-1}$ are related to the asymmetric wolframite-type oxide vibrations, where the tungsten has octahedral coordination [28, 29]. For CoWs$\phi$y673, there is a good agreement with the reported information for wolframite [30], indicating octahedral coordination of cobalt and tungsten. The band at 873 cm$^{-1}$ is related with WO$_6^{6-}$ octahedra symmetrical stretching, while the bands at 784, 725 and 570 cm$^{-1}$ are related with asymmetric stretching of the same group; the band at 460 cm$^{-1}$ corresponds to the bending of it. The deformation of the spectra is caused by the low crystallinity of the solid observed in the XRD pattern, Figure 1(b).

**Catalytic tests**

Figure 5(a) shows that CoMo$\phi$y623 has a measurable catalytic activity from 523 K and CoWs$\phi$y673 from 573 K. The propane conversions are relatively high (Figure 5(a)), taking into account the low temperatures at which catalytic activity was evaluated. The catalyst that presented the best performance, regarding conversion, was CoMo$\phi$y623, with 18.5% conversion at 623 K, while CoWs$\phi$y673 reached conversions smaller than 10% even at 673 K. However, selectivity (Figure 5(b)) at 623 K presents an inverse behavior to that observed with the conversion. Selectivity to propene for CoMo$\phi$y623 tends to be stable at temperatures above 573 K, with a value close to 27%.
In order to explore CoMoϕ623 as a catalyst, the reaction temperature was fixed at 623 K, and the space velocity was tested between 50 and 150 mL g⁻¹ min⁻¹. The results are shown in Figure 6. A high space velocity could avoid a total occupancy of the active sites available in the catalyst. Therefore, the conversion could be low. Lower space velocity implies longer contact time; this can increase the conversion and the side reactions. For CoMoϕy, the best yield at 623 K was obtained at a space velocity of 100 mL g⁻¹ min⁻¹. Then, higher temperatures were used to increase the conversion. For this purpose, the precursor material CoMoϕy was calcined at a higher temperature (873 K) and denominated CoMoϕy873. The XRD pattern for CoMoϕy873, Figure 1a, did not show any significant changes in the structure, and it also corresponds to β-CoMoO₄.

Conversion and selectivity values obtained with CoMoϕ623 and CoMoϕy873, at 100 mLg⁻¹min⁻¹ space velocity to different temperatures, are shown in Table 2. At the same temperature, CoMoϕy873 provided a smaller yield, possibly because of the decrease in the catalyst surface area occurred by the calcination of the precursor at a higher temperature. At higher temperatures, a constant behavior is observed for the selectivity of this catalyst as a function of conversion, within the experimental error. Therefore, the increasing yield obtained with CoMoϕy873 with higher temperature is due to the expected increase in conversion with temperature.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>CoMoϕy623</th>
<th>CoMoϕy873</th>
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<tbody>
<tr>
<td></td>
<td>Selectivity to propene</td>
<td>Conversion</td>
</tr>
<tr>
<td>523</td>
<td>65.3</td>
<td>0.5</td>
</tr>
<tr>
<td>573</td>
<td>40.5</td>
<td>2.1</td>
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<tr>
<td>623</td>
<td>27.9</td>
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<tr>
<td>673</td>
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<td>723</td>
<td>34.0</td>
<td>25.0</td>
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<td>773</td>
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<td>823</td>
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<td>873</td>
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</table>
Catalytic stability of CoMo\(\phi\)y873 was tested at 773 K in continuous reaction for 24 h (see Figure 7) and no loss of catalytic activity was observed. The average conversion value was 20.6%.

The main product of the oxidative dehydrogenation of propane is propene; nevertheless, carbon oxides (CO and CO\(_2\)) are usually formed as by-products via propane and propene combustion. The propane combustion reaction occurs in parallel with ODH; this explains the inability to reach a 100% selectivity to propene [31]. A consecutive oxidation of propene as a function of the temperature can be explained regarding the bond dissociation energy (BDE). The BDE for the methylene hydrogen is 98 kcal mol\(^{-1}\) in propane and 88 kcal mol\(^{-1}\) in methyl hydrogen in propene [32]; therefore, the transformation of propene to carbon oxides is promoted at higher temperatures. To avoid the oxidation, the propene desorption should be a fast step in the reaction.

The ability of the metal ions to switch between oxidation states, the electronic conductivity of the material, the mobility of lattice oxygen, as well as, the type of oxygen present at the surface are just some of the factors that can affect the activity and selectivity of a catalyst [33]. Even though, a direct comparison of the catalytic activity between CoMo\(\phi\)y623 and CoWs\(\phi\)y673 cannot be made for the differences in the composition and structure. The reducibility can be correlated with the redox capacity of materials, which is necessary for the catalytic activity through a Mars-vans Krevelen mechanism. In our case, CoMo\(\phi\)y623 has a lower onset temperature for the reduction, as well as, the higher catalytic activity in the temperature range studied. The yields achieved with CoMo\(\phi\)y623 and CoMo\(\phi\)y873, at different temperatures, are comparable to the ones already reported in the literature; the best yield for cobalt-based materials is around 11% [34–36].

Moreover, the difference in the selectivity, Figure 5(b), value between cobalt molybdate and cobalt tungstate could be attributed to the cobalt, it lies in a high spin state in the tungstate, while it is in a low spin state in the molybdate. This is consistent with cobalt forming an inorganic radical (Co–O\(_{\cdot}\)) in the tungstate and not in the molybdate, a species highly active in attacking paraffins, improving the velocity of methylene hydrogen abstraction [37].

4. Conclusions

The synthesis method used is suitable to obtain precursors materials for the catalytic oxidative dehydrogenation of propane. The cobalt- molybdenum precursor material was identified as CoMo\(\phi\)y. After calcination of the CoMo\(\phi\)y, the \(\beta\)-CoMo\(_2\)O\(_4\) (CoMo\(\phi\)y623 and CoMo\(\phi\)y873) phase was obtained. For the cobalt-tungsten precursor material denominated CoWs\(\phi\)y is a mixture of scheelite-type oxides and wolframite-type oxide according with the FTIR and DRX results. A low crystalline wolframite-type material (CoWs\(\phi\)y673) is obtained after calcination.

The best catalytic activity, based on selectivity to propene and conversion, was observed for CoMo\(\phi\)y623. The good catalytic performance of this material was related to a low onset temperature in the hydrogen reduction profiles. This material was tested at higher temperatures, the selectivity was constant, and the conversion increased. This material is promising for the ODH of propane.

The cobalt-tungsten material is interesting because it exhibited a high selectivity, then it is recommended to study other reaction variables to increase the conversion.

5. Acknowledgments

We thank CODI of Universidad de Antioquia, Colciencias and CNPq for partial financial support.

6. References

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