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\textsubscript{ϕ} material was calcined at 623 K, transforming itself to \(\beta\)-CoMoO\textsubscript{4} phase (CoMo\textsubscript{ϕ}623), the same phase is observed when the material is calcined at 873 K (CoMo\textsubscript{ϕ}873). CoMo\textsubscript{ϕ}623 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\textsuperscript{-1} min\textsuperscript{-1}. CoWs\textsubscript{ϕ} was calcined at 673 K, obtaining a low crystallinity wolframite. This material has a high selectivity to propene and low yield. CoMo\textsubscript{ϕ}873 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 CoMo\textsubscript{ϕ} material fue calcinado a 623 K, transformándose a la fase \(\beta\)-CoMoO\textsubscript{4} (CoMo\textsubscript{ϕ}623), la misma fase se observa cuando el material es calcinado a 873 K (CoMo\textsubscript{ϕ}873). CoMo\textsubscript{ϕ}623 mostró el mejor rendimiento en la deshidrogenación oxidativa de propano, un rendimiento a propeno de 3.4% se obtuvo a 623 K usando una velocidad de 100 mL g\textsuperscript{-1} min\textsuperscript{-1}. CoWs\textsubscript{ϕ} fue calcinado a 673 K, obteniendo una fase wolframita de baja cristalinidad. Este material muestra una alta selectividad a propeno y un bajo rendimiento. CoMo\textsubscript{ϕ}873 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 exothermal), 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 total 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 CoMo₇y and CoWs₇y. 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]₃MoO₄·4H₂O (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 CoWs₇y and at 623 K for CoMo₇y.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Gel molar composition</th>
</tr>
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<tbody>
<tr>
<td>CoMo₇y</td>
<td>MoO₃·Co(NO₃)₂·3 NH₄OH·186 H₂O</td>
</tr>
<tr>
<td>CoWs₇y</td>
<td>WO₃·3NH₄OH·190 H₂O</td>
</tr>
</tbody>
</table>

Table 1 Molar gel composition for the synthesized precursors

Hereafter, the precursors or fresh materials are denominated CoMo₇y and CoWs₇y. The catalysts were denominated with the name of the precursor plus the calcination temperature: CoMo₇y623 and CoWs₇y673.

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 H₂ (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, CO₂, and CO, and some traces of CH₄ and C₂H₄.

3. Results and discussion

3.1. Characterization

X-ray diffraction (XRD)

Thermal analysis (TA)

For CoMoϕ, Figure 2(a), a weight loss of 11.9% is observed between 373 K and 623 K, which corresponds to two exothermic events related to the evolution of volatile species from the lamellar solid, crystallization water and ammonia, the latter present in the structure as balance cation. In contrast, with CoWsϕ (Figure 2(b)), an apparent single event between 373 K and 673 K is observed, with a weight loss of 5.6%. However, a shoulder is observed at 570 K, the main event at 608 K is assigned to the evolution of crystallization water, and the shoulder is related to a lower amount of ammonium cation present in the CoWsϕ structure. The highest temperatures at which materials no longer present thermal events are 623 K for CoMoϕ and 673 K for CoWsϕ. For this reason, these temperatures were set as calcination temperatures to obtain the final catalysts.

Temperature programmed reduction (TPR)

The TPR profiles for the calcined materials are presented in Figure 3. For CoMoϕ, consistency with the reduction temperatures reported by Brito and Barbosa [25] for β-CoMoO₄ were observed. It was established that a reduction to lower valence oxidized states takes place, generating
equimolar mixtures of CoMoO₄ and CoMoO₃ 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 CoWᵦ₆₇₃ 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].

In CoWᵦ₆₇₃ 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 octahedral coordination. Meanwhile, the band at 873 cm⁻¹ is related to symmetric vibration, and the bands at 784, 725 and 570 cm⁻¹ are related to the asymmetric wolframite-type oxide vibrations, where the tungsten has octahedral coordination [28, 29]. For CoWᵦ₆₇₃, 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 WO₆ 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 CoMoᵦ₆₂₃ has a measurable catalytic activity from 523 K and CoWᵦ₆₇₃ 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 CoMoᵦ₆₂₃, with 18.5% conversion at 623 K, while CoWᵦ₆₇₃ 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 CoMoᵦ₆₂₃ tends to be stable at temperatures above 573 K, with a value close to 27%.
Figure 5 (A) Propane conversion and (B) selectivity to propene as a function of the temperature with a space velocity of 50 mL g\(^{-1}\) min\(^{-1}\). CoMo\(\phi\)\(y\)\(_{623}\) (■), CoWs\(\phi\)\(y\)\(_{673}\) (○).

In order to explore CoMo\(\phi\)\(y\)\(_{623}\) 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 CoMo\(\phi\)\(y\), 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 CoMo\(\phi\)\(y\) was calcined at a higher temperature (873 K) and denominated CoMo\(\phi\)\(y\)\(_{873}\). The XRD pattern for CoMo\(\phi\)\(y\)\(_{873}\), Figure 1(a), did not show any significant changes in the structure, and it also corresponds to \(\beta\)-CoMoO\(_4\).

Figure 6 Dependence on conversion (■), yield to propene (▲) and selectivity to propene (○) with space velocity for CoMo\(\phi\)\(y\)\(_{623}\) at 623 K.

Conversion and selectivity values obtained with CoMo\(\phi\)\(y\)\(_{623}\) and CoMo\(\phi\)\(y\)\(_{873}\), at 100 mL g\(^{-1}\) min\(^{-1}\) space velocity to different temperatures, are shown in Table 2. At the same temperature, CoMo\(\phi\)\(y\)\(_{873}\) 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 CoMo\(\phi\)\(y\)\(_{873}\) with higher temperature is due to the expected increase in conversion with temperature.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Selectivity to propene</th>
<th>Conversion</th>
<th>Yield</th>
<th>Selectivity to propene</th>
<th>Conversion</th>
<th>Yield</th>
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Table 2 Catalytic activity of CoMo\(\phi\)\(y\)\(_{623}\) and CoMo\(\phi\)\(y\)\(_{873}\)
Catalytic stability of CoMoϕy873 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%.

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−) 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 CoMoϕy. After calcination of the CoMoϕy, the β-CoMoO4 (CoMoϕy623 and CoMoϕy873) phase was obtained. For the cobalt-tungsten precursor material denominated CoWsϕy is a mixture of scheelite-type oxides and wolframite-type oxide according with the FTIR and DRX results. A low crystalline wolframite-type material (CoWsϕy673) is obtained after calcination.

The best catalytic activity, based on selectivity to propene and conversion, was observed for CoMoϕy623. 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

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6. References

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