

Influence of Vanadium Oxidation States on the Performance of V-Mg-Al Mixed-Oxide Catalysts for the Oxidative Dehydrogenation of Propane

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Abstract. V-Mg-Al mixed-oxide catalysts for oxidative dehydrogenation of propane were prepared by thermal decomposition of Mg-Al-layered double hydroxides with vanadium interlayer doping. The obtained catalysts were tested for the oxidative dehydrogenation of propane, obtaining good results in catalytic activity (conversion 16.55 % and selectivity 99.97 %). Results indicated that catalytic performance of these materials depends on how vanadium is integrated in the layered structure, which is determined by the Mg/Al ratio. Vanadium interlayer doping modifies the oxidation state of vanadium and consequently catalytic properties. Surface properties were studied by X-ray photoelectron spectroscopic and diffuse reflectance, UV-visible spectroscopy, and temperature programmed reduction (TPR). The analyses provided information about the oxidation state, before and after the reaction. From these results, it is suggested that selectivity to propylene and catalytic activity depend mainly on vanadium oxidation state.

Keywords: V-Mg-Al mixed-oxide, vanadium oxidation XPS, Diffuse reflectance UV-visible spectroscopy, Oxidative Dehydrogenation of propane.

Resumen. Se prepararon mezclas de óxidos de V-Mg-Al como catalizadores en la reacción de deshidrogenación oxidativa de propano. Los catalizadores se obtuvieron a partir de la descomposición térmica de hidróxidos Mg-Al de doble capa y modificados con vanadio en la intercapa. El comportamiento catalítico depende de la manera de incorporación del vanadio dentro de la estructura, la cual está definida por la relación Mg/Al. Los resultados obtenidos muestran que la relación Mg/Al determina la forma de incorporación y el estado de oxidación del vanadio en la estructura. Las propiedades superficiales se estudiaron por medio de espectroscopia fotoelectrónica de rayos X, espectroscopia UV-visible y temperatura programada de reducción. La información obtenida de estos análisis permitió establecer los estados de oxidación del vanadio antes y después de la reacción química. De acuerdo con estos resultados, se sugiere que la selectividad hacia propeno depende del estado de oxidación del vanadio en el catalizador.

Palabras clave: Óxidos de V-Mg-Al, oxidación del vanadio, XPS, reflectancia difusa, espectroscopia UV-visible, deshidrogenación oxidativa de propano.

Introduction

Over the last years, the increasing propene demand has impulsed the necessity for alternative ways to produce propene or propene-rich mixtures. Catalytic oxidative dehydrogenation of propane is an optional way to produce propene [1,2].

Most catalysts described in the literature are based on vanadium oxides as the active component [3,4]. In particular, vanadium-magnesium mixed oxide (VMgO) catalysts have been reported to exhibit a promising propene yield [5,6].

V/Al₂O₃ catalytic systems also have been studied, producing good results [7-9]. The acidic/basic nature, as well as the redox character, are the most important factors affecting the performance of selective oxidation catalysts [10]. Current investigation is focused on the examination of oxidation and reduction processes that take place on the catalyst surface [11]. Highly dispersed V⁵⁺ in a tetrahedral environment has been proposed as the selective site, however, the nature of active and selective sites and some other characteristics of catalysts (acid-base, redox, promoters, etc.) could have a significant effect as well. Thus, it has been suggested that the acid-base character of catalysts could influence the selectivity-determining step, which is probably related to the adsorption/desorption of olefin intermediates and reaction products [12].

The formal valence state of vanadium in different vanadium-based systems varies between V⁵⁺ (V₂O₅, VOPO₄, magnesium vanadate, VO₄, tetrahedral and VO₆ octahedral on MgO, hydrotalcites, sepiolite and Al₂O₃), V⁴⁺ (vanadyl pyrophosphate, solid solutions of MoO₃ in V₂O₅), and the V³⁺ and V⁴⁺ mixture in vanadium antimonite [13].

It has been indicated that the appearance and relative proportions of different phases in Mg-V-O or Al-V-O systems depend to a large extent on the method of catalyst preparation [14]. This prompted in some cases to employ synthetic procedures used for the preparation of layered double hydroxides to obtain precursors of potentially active mixed-oxide systems. Layered double hydroxides, known also as hydrotalcites or anionic clays, consist of brucite {Mg(OH)₂}-like layers with part of the divalent cations substituted by trivalent ones. For this reason, the layers acquire excess positive charge, compensated by the incorporation of hydrated anions in the interlayer space.

Their general formula is given as {M(II)_{1-x}M(III)_x(OH)₂}A_{x/n}ⁿ⁻ · mH₂O, where M(II) and M(III) are the layer forming cations and Aⁿ⁻ is the interlayer anion. Due to the homogeneous distribution of M(II) and M(III) in the layered double hydroxides framework and the layered structure, during thermal decomposition these materials yield mixed oxides of both cations with unique surface and catalytic properties [15-18].

The aim of this paper is to determine the influence of different vanadium oxidation states V-Mg-Al mixed-oxide catalysts, on the performance of propane oxidative dehydrogenation. To achieve this, Mg-Al-layered double hydroxides were prepared with vanadium interlayer doping, and by varying Mg/Al ratio different valence state of vanadium were obtained,

Results and Discussion

X-ray photoelectron spectroscopy (XPS). Figure 1 shows the spectra of the hydrotalcites modified with vanadates before catalytic activity. Each spectrum exhibits two peaks that are characteristic of structure of vanadium ($2p_{3/2}$, $2p_{1/2}$), corresponding to a spin orbital with specific binding energies. The spectra of sample M2AV-27.3 with Mg/Al = 2 has one peak at 514.9 eV, corresponding to $V2p_{3/2}$, and another at 522.5 eV, corresponding to $V2p_{1/2}$. These values represent V_2O_4 species with a V^{4+} oxidation state. In samples M3AV-26.2 and M3AV-22.5 (Mg/Al = 3), one peak is at 516.4 eV, corresponding to $V2p_{3/2}$, and the other one at 523.5 eV, corresponding to $V2p_{1/2}$. The latter is characteristic of V_2O_5 species with a V^{5+} oxidation state. Finally, sample M4AV-25.1 (Mg/Al = 4) exhibits a peak at 516.5 eV, corresponding to $V2p_{3/2}$, (V^{5+} oxidation state) and a second one at 512.4 eV, reported for free V [19].

Thus, the structure and oxidation state depend on Mg/Al ratio of the synthesized hydrotalcites.

Figure 2 shows the XPS spectra of the synthesized hydrotalcites after the catalytic tests. The spectrum of the samples shows two characteristic peaks of the of vanadium structure ($2p_{3/2}$, $2p_{1/2}$), corresponding to spin orbital with binding energies located between 515.3 and 522.8 eV for all catalysts. These values of BE represent V_2O_3 species with a V^{3+} oxidation state.

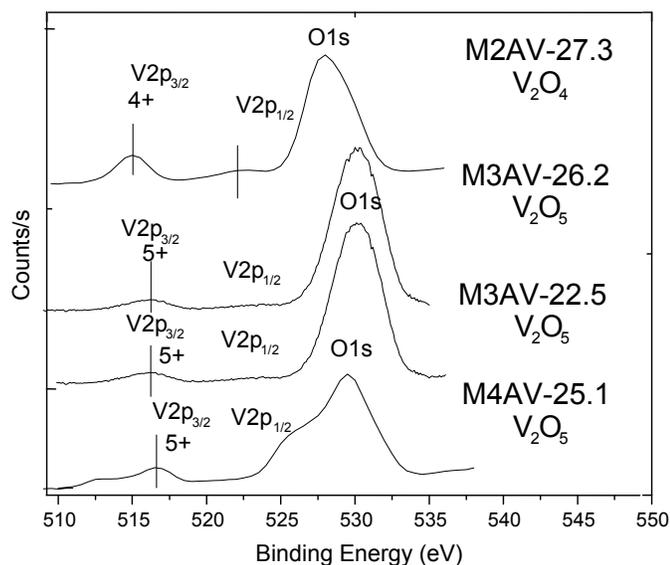


Fig. 1. XPS spectra of catalysts M2AV-27.3, M3AV-26.2, M3AV-22.5 and M4AV-25.1 before catalytic activity.

H_2 -TPR studies were carried out in order to clarify the vanadium oxidation states. As it can be seen in Figure 3, temperature programmed reduction profiles of all analyzed catalysts show a reduction peak around 808 K, related to consumption of H_2 , attributed to the change of V^{5+} to V^{4+} as the first step in the reduction of vanadium pentoxide as it has been reported [17].

By this way, H_2 -TPR results support the assignation of vanadium states using XPS spectroscopy.

Diffuse reflectance UV-vis spectra of the samples, before and after of catalytic activity, are presented in Figures 5 and 6, respectively. The intensity of the absorption edge decreases at lower average V oxidation states because the ligand-to-metal charge transfer becomes more difficult at lower cation valences where the lowest unoccupied states are partially filled and thus require electron transfer to a lower energy state [18]. From figure 4, it can be observed that M2AV-27.3 catalyst exhibits

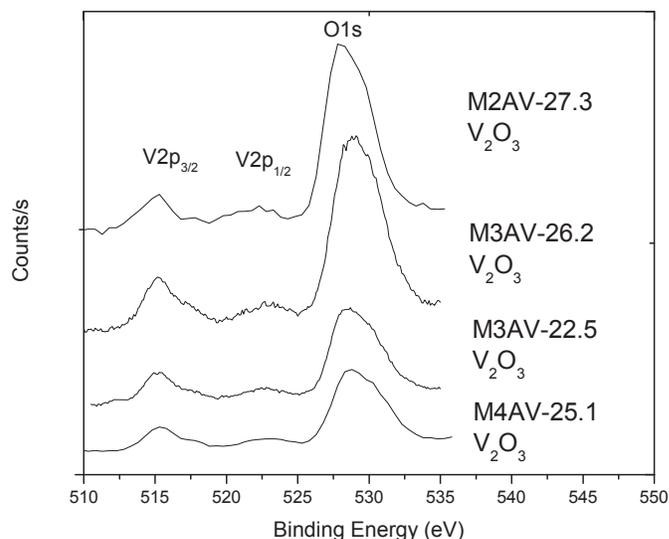


Fig. 2. XPS spectra of catalysts M2AV-27.3, M3AV-26.2, M3AV-22.5 and M4AV-25.1 after catalytic activity.

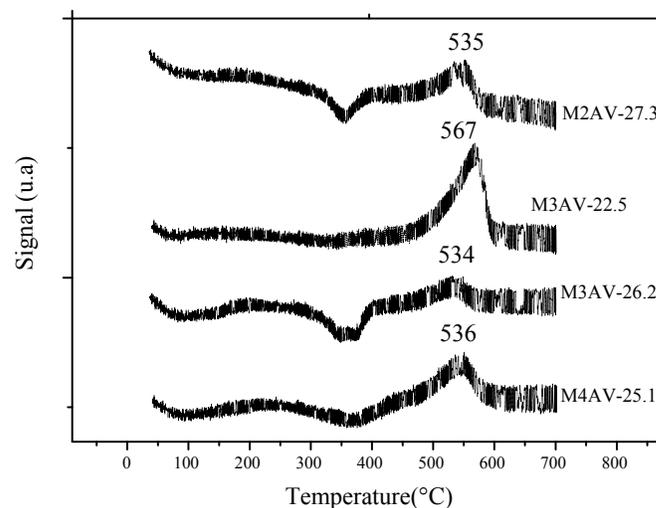


Fig. 3. TPR spectra of catalysts M2AV-27.3, M3AV-26.2, M3AV-22.5 and M4AV-25.1

a band at 3.6 eV, corresponding to V^{4+} , for M3AV-26.2 and M3AV-22.5 catalysts there is band at 4.3 eV, corresponding to V^{5+} , and finally for M4AV-25.1 the band is located at 3.6 eV, corresponding to V^{4+} and V^{5+} [18-21].

Figure 5 Shows that for the samples the band is located at 4.1 eV, corresponding to V^{3+} .

Catalytic activity studies

The catalysts obtained after calcination at 700 °C were tested for oxidative dehydrogenation of propane in a 673-813 K temperature range.

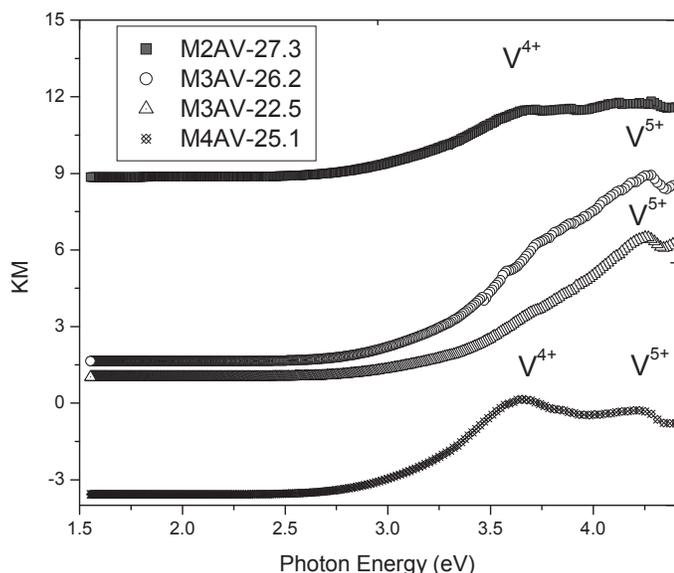


Fig. 4. UV-vis spectra of catalysts before oxidative dehydrogenation of propane.

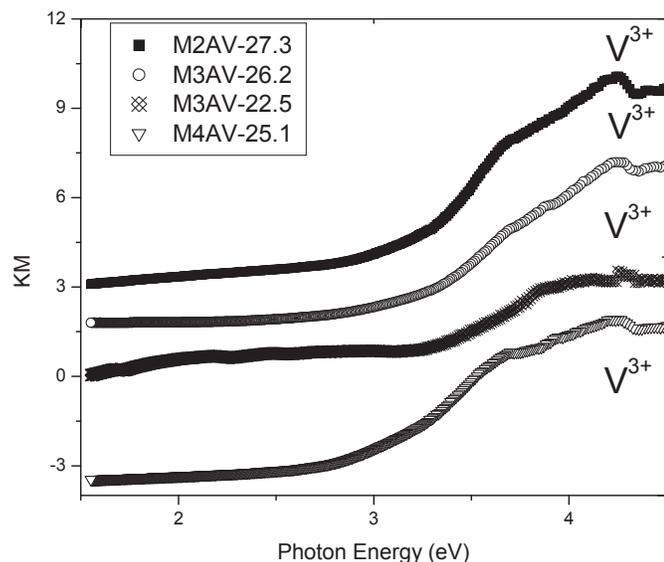


Fig. 5. UV-vis spectra of catalysts after oxidative dehydrogenation of propane.

Figs. 6 and 7 show the effect of reaction temperature on propane conversion and selectivity, respectively. The highest propane conversion and selectivity to propene at 693 K was achieved by M3AV-26.2 catalyst with Mg/Al = 3 and vanadium concentration of 26.2 % (Conversion 21 % and Selectivity 99.97 %). Nevertheless, good results were also produced by M3AV-22.5 catalyst with Mg/Al = 3 and vanadium concentration of 22.5 %, (Conversion 16.6 % and Selectivity 99.6 %) between 713 and 813 K.

XPS spectra provide insight on the structure and oxidation state in the catalysts surface, which was identified to depend on Mg/Al ratio. Diffuse reflectance UV-vis analyses confirm XPS results on the oxidation state of vanadium. This is useful for establishing the relationship between catalyst activity and structure.

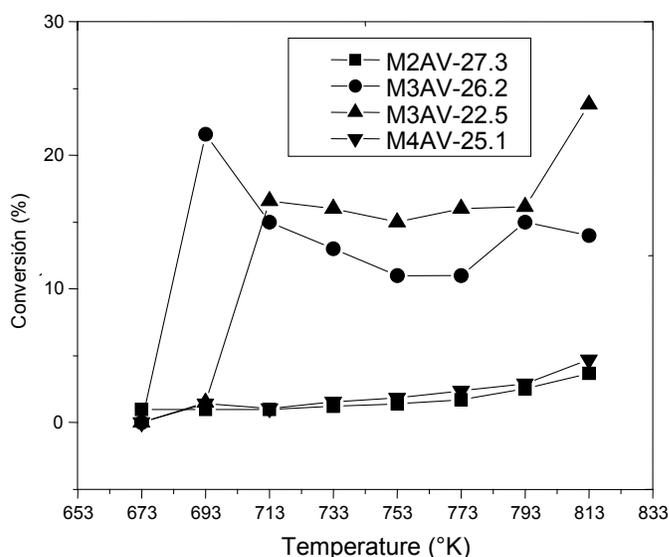


Fig. 6. Propane conversion as function of reaction temperature

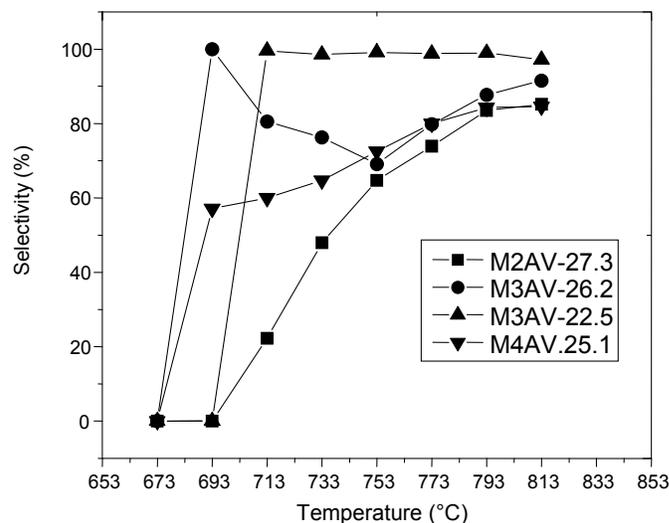


Fig. 7. Propane selectivity to propene as function of reaction temperature

M3AV-26.2 and M3AV-22.5 catalysts provided much higher performances during the oxidative dehydrogenation of propane, particularly the selectivity to propene (99.97 %), which is probably caused by the V_2O_5 structure.

The observed activity for these catalysts might be related to the reducibility of surface V^{5+} species.

Conclusions

In summary, the present study demonstrates that the combination of XPS and diffuse reflectance UV-vis spectroscopy provides important information on the oxidation states and active surface sites of catalyst used for the oxidative dehydrogenation of propane.

The acidic and basic nature, as well as the redox character, are the most important factors affecting the performance of selective oxidation catalysts.

The acid-base character of hydrotalcites modified with vanadates, containing Al and Mg and calcined at 973 K, determined the reducibility of vanadium species and consequently the activity of these catalysts.

Experimental

Catalysts preparation

Vanadium-magnesium-aluminum mixed-oxide catalysts (V-Mg-Al-O) (hydrotalcite) were prepared by coprecipitation. About 200 mL of decarbonated and deionized water were put in a one liter round-neck flask, filled with nitrogen, and stirred keeping temperature at about 30°C. An aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (sample Mg/Al = 2: $Mg^{2+} = 0.50$ mol/L, $Al^{3+} = 0.25$ mol/L); (sample Mg/Al = 3: $Mg^{2+} = 0.75$ mol/L, $Al^{3+} = 0.25$ mol/L); (sample Mg/Al = 4: $Mg^{2+} = 1.0$ mol/L, $Al^{3+} = 0.25$ mol/L) was added dropwise, keeping pH of the reacting mixture at 10 by dropwise addition of NaOH solution (2 mol/L). The resulting white slurry was stirred for 24 h. The obtained precipitate was filtered, washed with water and dried at 80 °C for 48 h.

Procedure of Anion Exchange (Pillars)

The exchange of NO_3^- to VO_3^- anions was performed by contacting the hydrotalcite with a solution of ammonium metavanadate. A first solution containing 60 g of hydrotalcite dispersed in 100 mL of deionized and decarbonated water, and a second one consisting of 2.4 g of NH_4VO_3 dissolved in 50 mL of water, were mixed and stirred at 333 K for 1 h. After filtration, the solids were washed and dried at 393 K for 24 h. The obtained solids were treated at 973 K for 6 h (samples: M2AV-27.3, M3AV-26.2, M3AV-22.5 and M3AV-25.1).

Characterization

The X-ray photoelectron spectroscopic (XPS) analyses were carried out with a ESCALAB 250 spectrometer using a monochromatic Al- $K\alpha$ X-ray source. Binding energy (BE) scale was referenced to the C 1s line peak at 284.8 eV, originated from adventitious carbon contamination, to account for charging effects [16].

The Temperature programmed reduction (TPR) analyses was carried out in a Micromeritics TPD/TPR 2900 apparatus consisting of a quartz U- reactor using 10% H_2 in argon and heating rate of 283 K/ min. The samples were pretreated in flowing N_2 (99.99%) at 723 K for 0.5 h and cooled in N_2 . During the reduction, samples were heated from 50 to 1173 K.

Diffuse reflectance UV-vis analyses, in the range of 2-6 eV, were performed employing a Perkin Elmer Lambda 900 spectrophotometer with a diffuse reflectance attachment, using MgO as reference. Spectra of catalysts were collected under ambient conditions and analyzed with the Kubelka-Munk treatments [17,18].

Catalytic Activity

Catalytic tests were carried out at atmospheric pressure in a fixed-bed tubular flow quartz reactor (internal diameter = 5 mm and operation length = 21 cm). A small amount (0.1g) of catalysts was loaded in the midsection of the reactor, and above the catalyst bed quartz granules were loaded to quench the possible homogeneous reactions. The reactor was pretreated at 573 K for 1 hour 30 min, passing continuously an oxygen-nitrogen mixture with molar composition of 1:3.762. After pretreatment, the reactor was heated from 573 to 673 K, a feed mixture composed of propane-oxygen (1:1) and oxygen-nitrogen (1:3.762) was passed through the reactor. Initiation of catalytic tests was carried out in the 673-813 K temperature range. Analysis of reactants and products was carried out with a Perkin Elmer Autosystem XL gas chromatograph.

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