

VANADIUM OXIDES SUPPORTED ON PRECURSORS TYPE HYDROTALCITE: INFLUENCE OF THE ACID-BASE PROPERTIES ON THE OXIDATION OF ISOPROPANOL

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Abstract. Vanadium oxide supported on precursors type hydrotalcite was investigated in the oxidation of isopropanol. Hydrotalcites with different $y = \text{Mg}/\text{Al}$ ratios were synthesized by coprecipitation method of nitrates of the respective cations and K_2CO_3 as precipitant. The decomposition of these hydrotalcite precursors at 450°C yields homogeneous Mg_yAlO_x mixed oxides that contain the Al^{+3} cations totally incorporated into the MgO framework. The materials were characterized by chemical analysis, BET superficial area, X-ray diffraction, temperature-programmed reduction (TPR) and by isopropanol decomposition, a probe molecule to evaluate the acid-base properties. The results of TPR showed that the reducibility of V^{+5} decreases with the increase of magnesium loading in catalysts. The X-ray diffraction patterns of Al-rich hydrotalcite precursors showed the presence of crystalline phases of brucite and gibbsite. The chemical composition, the texture, the properties acid-base of the active sites and also the Mg/Al ratio influence strongly in the formation of the products in the oxidation of isopropanol. The Al-rich catalysts were much more active than the Mg-rich ones, converting isopropanol mainly to propylene.

Keywords: mixed oxides, hydrotalcites; isopropanol; V-Mg-Al catalysts.

1. Introduction

Hydrotalcite-type clays, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, and many other related minerals are basic solids with high surface areas (Miyata, 1983). Synthetic hydrotalcite-like layered double hidroxides (LDHs) compounds are mixed metal hydroxides with general formula $[\text{M}_{1-x}^{+2}\text{M}_x^{+3}(\text{OH})_2][\text{A}^{-m}]_{x/m} \cdot n\text{H}_2\text{O}$ where M^{+2} and M^{+3} represent divalent and trivalent cations in the octahedral sites within the hydroxyl layers, x is equal to the ratio of $\text{M}^{+3}/(\text{M}^{+2} + \text{M}^{+3})$ with a value varying in the range of 0.17-0.50, and A^{-m} is an exchangeable interlayer anion. LDHs have attracted much attention in recent years as catalyst precursors and catalyst support due to the ability of these materials to accommodate a large variety of divalent and trivalent cations, and formation of well-dispersed mixed oxides upon controlled thermal decomposition (Cavani et al., 1991). The catalytic properties of the hydrotalcite-derived mixed oxides largely depend on the activation procedure (Tichit et al. 1997).

Catalysts containing vanadium as the main component are among the extensively investigated for oxidative dehydrogenation (ODH) processes (Mamedov et al., 1995). In particular, much attention has been given to V-Mg-O mixed system, which proved as one of the most active and selective in the ODH of short-chain paraffins to corresponding olefins (López Nieto et al., 1999). Vanadate-intercalated LDHs have a possible application as precursors to catalysts for the selective oxidation of short chain paraffins (Dula et al., 2002).

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The transformation of isopropanol is a widely used test reaction for characterizing both the acidic and basic properties of solids (Deepak et al. 2002). The isopropanol decomposition on solid catalysts occurs through two pathways: the dehydration, which is generally catalyzed by the acidic sites or both acidic and basic sites and the dehydrogenation, which is catalyzed by basic sites.

In the present work, Mg-Al hydrotalcite precursors with different Mg/Al molar ratios were synthesized by coprecipitation method. The influence of interlayer-doping with vanadium on the catalytic properties of mixed oxide phases obtained upon calcinations of corresponding LDHs precursors were investigated for isopropanol decomposition, a molecule probes to evaluate the properties acid-basic of the catalyst. The samples were also characterized by chemical analysis, BET surface area, temperature-programmed reduction (TPR) and X-ray diffraction (XRD).

1. Experimental

The hydrotalcite-type precursors were prepared by continuous coprecipitation at constant pH and temperature. This method comprises the simultaneous addition of an aqueous solution of the magnesium ($Mg(NO_3)_2 \cdot 6H_2O$) and aluminum ($Al(NO_3)_3 \cdot 9H_2O$) with theoretical Mg/Al atomic ratios in the range of 0.5-1.0 and K_2CO_3 (1.5 M) as precipitant in the continuous stirred reactor (150 mL) under vigorous stirring, at a pH constant of 10 and at temperature of 55^0C . After addition of reagents, the gel obtained was aged at 40^0C for 18 h under mild stirring. The material was cooled to room temperature, filtered and washed with a large amount of deionized water until a pH of 7 for complete removal of K^+ , and dried at 90^0C for 12 h. A series of vanadium-containing catalysts with V_2O_5 loadings of 17wt.% were prepared by a single impregnation of the LDHs precursors dry with aqueous solution containing ammonium metavanadate (Merck) at a temperature of 70^0C . Then, the solids were dried at 90^0C for 18 h and calcined at 450^0C for 4 h. Samples are labeled as V/MgyAl, where y is Mg/Al atomic ratios equal to 0.5, 0.89 and 1.0.

The elemental composition of the samples was determined by atomic absorption spectroscopy (AAS). The samples were digested with a mixture acid of HNO_3 and HF. The measurements were carried out by standard addition solution method by using a Perkin-Elmer Analyst equipment.

BET surface areas were measured by using a Quantachrome NOVA 1000 instrument by adsorption of nitrogen at -196^0C on 150 mg of sample previously degassed at 200^0C under high vacuum atmosphere for 2 h.

XRD diffraction patterns were obtained with a SEISERT Isodebyflex 1001 diffractometer operated at 40 kV and 30 mA by using Ni-filtered $CuK\alpha$ radiation ($\lambda = 0.15418$ nm). The samples in powder form were analyzed without previous treatment after deposition on a quartz sample holder. The identification of crystalline phases was made by using references from the ASTM files.

Temperature-programmed reduction (TPR) results were obtained in a Quantachrome Chembet-3000 apparatus loaded with 25 mg of catalyst. The samples were first treated in helium at temperature of 150^0C for 1 h. The

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samples were cooled to room temperature and were subsequently contacted with an H₂/N₂ mixture (H₂/N₂ molar ratio of 0.15 and a total flow of 40 mL/min) and heated, at a rate of 10⁰C/min, to a final temperature of 900⁰C.

The catalytic test of decomposition of isopropanol was realized in a fixed bed quartz tubular reactor (i.d. 10 mm, length 400 mm) operated at atmospheric pressure and temperature in the range of 170-290⁰C. The reactor was equipped with a coaxial thermocouple for catalytic bed temperature profiling. The isopropanol (99.7%, Merck) was injected in the piping of feeding of gases flowing of the reactor with aid of a pump Thermo Separation Product Spectra P100, in the flow rate of 0.05 cm³/min and diluted in a mixture of He and O₂ (molar ratio of 3/1) in the flow rate of 74 cm³/min. Reactants and reaction products were analyzed by on-line gas chromatography (VARIAN 3350), equipped with a thermal conductivity detector (TCD). A Carbowax 20 M on Chromosorb W column was used for separation of products. The catalyst mass was 100 mg, particle size 0.5-0.85 mm and the time contact was 2.4 g.h/mol_{isop}. The conversion was calculated from the reaction product on the basis of the carbon balance: the total molar amount of carbon in the effluent was assumed to be equal to the molar amount of carbon in the isopropanol fed to the reactor.

2. Results and discussion

The chemical composition of and BET specific surface areas (Sg) of the catalysts are shown in Table 1 for V/Mg_yAl catalysts.

Table 1. Chemical composition and BET specific surface areas for the samples studied

Sample	Chemical analysis by AAS					Sg (m ² .g ⁻¹)
	R* (nominal)	R* (molar)	Mg (wt%)	Al (wt%)	V ₂ O ₅ (wt%)	
V/Mg _{1.0} Al	0.50	0.43	15.6	11.7	18.1	99
V/Mg _{0.89} Al	0.53	0.54	11.8	13.8	15.6	105
V/Mg _{0.50} Al	0.67	0.66	8.20	15.6	16.3	128

(*) R = Al/(Mg+Al)

Elemental chemical analysis data for Mg and Al were similar to those expected from the initial concentrations of the solutions used during synthesis, suggesting complete precipitation of Mg and Al salts during synthesis. The potassium content in all the mixed oxides was below 0.1 wt%, which confirms that potassium ions were effectively removed by washing of the precipitated precursors. The vanadium in all the catalysts was close to the nominal value. The BET specific surface area varies in depending of the V₂O₅ content.

Figures 1, 2 and 3 show the XDR patterns of the precursors dried at 90⁰C and catalyst calcined at 450⁰C with different molar composition, defined as R = Al/(Mg+Al). XDR patterns for precursors Mg-Al dried at 90⁰C, as shown in Figure 1, showed that all samples contained a phase crystalline type hydrotalcite. The precursors with R = 0.53 and R = 0.63, were identified the phases gibbsite (Al(OH)₃) and brucite (Mg(OH)₂). The intensity of these phases increases with amount of aluminum in the precursor. The experimental values of the intensities of the

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peaks were compared with the theoretical values obtained in the files (ASTM). The variation in the intensity of the peaks of the hydrotalcite is related with the lattice parameter a . The parameter a values decreased linearly (following a Vegar's law) with Al content increase starting from $R = 0.5$ ($a = 3.08\text{\AA}$), $R = 0.53$ ($a = 3.06\text{\AA}$) and $R = 0.67$ ($a = 3.04\text{\AA}$). This variation of parameter a value was attributed to the substitution of the cations Mg^{+2} with larger ionic radius for the cations Al^{+3} of smaller ionic radius in the structure of the hydrotalcite. Díez et al. (2003) reported the same phases and they found that the value of the lattice parameter reduces when the amount of Al in the precursor increases from $R = 0.10$ ($a = 3.132\text{\AA}$) to $R = 0.67$ ($a = 3.020\text{\AA}$).

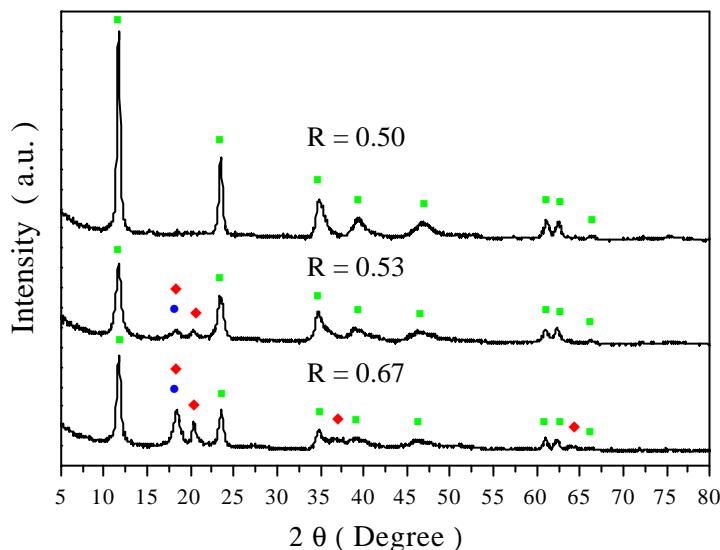


Fig. 1. XDR patterns of precursors dried at 90°C (■) hydrotalcite, (◆) gibbsite and (●) brucite.

Figure 2 illustrates the XDR patterns of the three precursors dried to 90°C that were impregnated with ammonium metavanadate.

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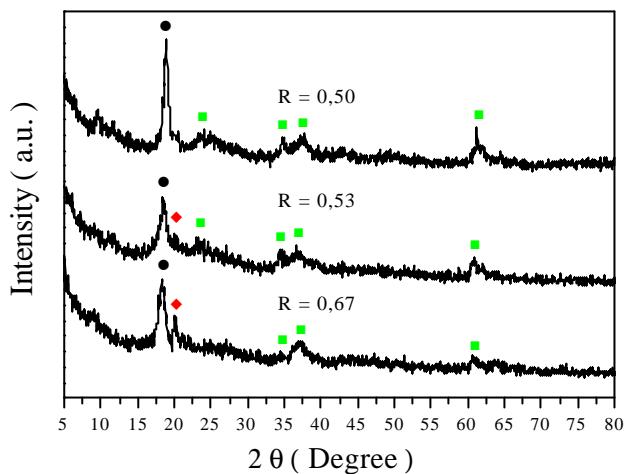


Fig. 2. XDR patterns of V-LDHs precursors (■) hydrotalcite, (◆) gibbsite and (●) peak no identified.

An intense peak was observed in the three samples at $2\theta = 18.32^\circ$ ($R = 0.50$), $2\theta = 18.47^\circ$ ($R = 0.53$) and $2\theta = 18.89^\circ$ ($R = 0.67$). Other less intense peaks correspond to the phase gibbsite ($2\theta \approx 20^\circ$) and Mg-Al hydrotalcite ($2\theta \approx 24^\circ, 35^\circ, 39^\circ$ and 61°), respectively. No peaks due to V_2O_5 crystalline are seen in all samples. Bhattacharyya et al. (1995) prepared oligovanadate-pillared hydrotalcite-type materials. The solid obtained with pH in the range of 7.0-8.5 showed in XDR a structure hydrotalcite-type with a more intense peak at $2\theta \approx 18.5^\circ$. They attributed that the species oligovanadate of the precursor was $V_4O_{12}^{4-}$ anions presents in the interlayer of the structure of the hydrotalcite. Dinka et al. (1998) considered that the d_{001} spacing value of the decavanadate ($V_{10}O_{28}^{6-}$) intercalated LDHs was 9.9 Å. Other authors (Dula et al., 2002), introduced anions decavanadate into the interlayer space of the precursor Mg-Al with hydrotalcite structure. They found a peak corresponding to α -Mg₂V₂O₇ magnesium pyrovanadate phase at $2\theta \approx 18^\circ$ (ASTM 39-816) in the sample calcined to 550°C. In our results obtained by DRX, the peak in the samples at $2\theta \approx 18.3^\circ, 18.5^\circ$ and 18.9° (Figure 2) can correspond to the anions $V_4O_{12}^{4-}$ present in the interlayer of the precursor with hydrotalcite structure $Mg_4Al_2(OH)_{12}(V_4O_{12})_{0.5}$ (Bhattacharyya et al., 1995).

The XDR patterns of the vanadium-containing LDHs, calcined at 450°C, are presented in Figure 3. The presence of peaks was observed at $2\theta \approx 35^\circ, 43^\circ$ and 63° that correspond the MgO phase in the three samples and a small peak at $2\theta \approx 65^\circ$ attributed the MgAl₂O₄ phase for the catalyst with $R = 0.67$. No peaks due to V_2O_5 crystalline are seen in all catalyst samples.

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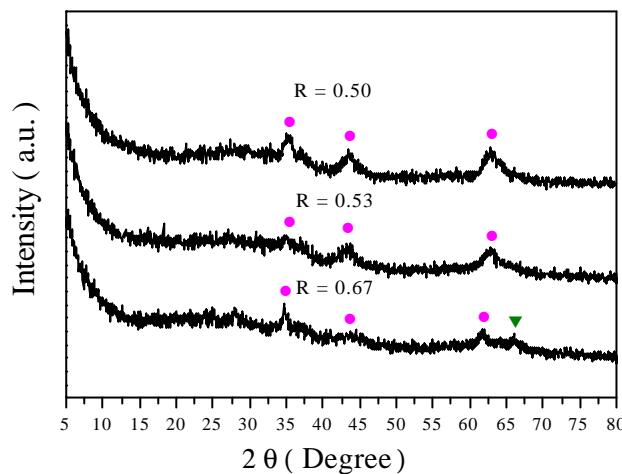


Fig. 3. XDR patterns of V-LDHs precursors calcined at 450°C, (●) MgO and (▼) MgAl₂O₄.

The TPR profiles of V₂O₅ bulk and catalysts are presented in Figure 4. The TPR profile pure V₂O₅ shows two major peaks at 663°C and 696°C and one minor reduction peak at 836°C. The peaks correspond to reduction of V⁴⁺³³ (first step), V⁴⁺ (second step) and V³⁺ (third step). The same profile of TPR was obtained by Koranne et al (1994) using the V₂O₅ bulk.

The Figure 4-b to 4-d shows the profiles of TPR of the catalysts V/Mg_yAl. The presence of a single reduction peak in the catalysts V/Mg_yAl is due to reduction of V⁵⁺ to V⁴⁺ species. The results also showed that the maximum temperature of reduction of the vanadium increases with the increase of the amount of magnesium in the catalyst starting from R = 0.67 (568°C), R = 0.53 (608°C) and R = 0.50 (614°C). This increase in the maximum temperature of reduction can be attributed the formation of a larger amount of MgO phase in the catalyst, which decreases the reducibility of the vanadium species.

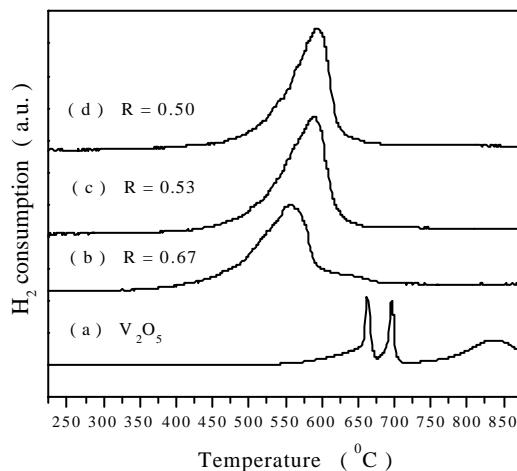


Fig. 4. Results of TPR profiles of (a) V₂O₅ bulk, (b) V/Mg_{0.5}Al, (c) V/Mg_{0.89}Al and (d) V/Mg_{0.10}Al.

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The results of catalytic tests for the reaction of decomposition of the isopropanol at 270°C, 280°C and 290°C over catalysts are listed in Table 2. The catalytic results were calculated, respectively, in terms of the consumed amount of isopropanol for area, for time (mol. m⁻². min⁻¹) and for the rate of formation of the products (RFP). To avoid the reduction of V⁺⁵ species in the catalyst, oxygen was mixed with the isopropanol.

Table 2. Results of catalytic tests for the reaction of decomposition of the isopropanol over various catalysts

Catalysts	RFP (mol. m ⁻² . min ⁻¹)					
	Propylene			Acetone		
	270°C	280°C	290°C	270°C	280°C	290°C
V/Mg _{1.0} Al	0.01	0.18	0.40	0.30	0.29	0.21
V/Mg _{0.89} Al	0.09	0.29	0.38	0.26	0.23	0.21
V/Mg _{0.50} Al	0.38	0.40	0.41	0.12	0.11	0.09

The activity for the isopropanol conversion showed that the propylene formation increases with the rise of temperature and it is favored by the decrease of magnesium in the catalyst. On the other hand, the formation of acetone decreases with the rise of temperature and with the increase of magnesium content in the catalyst. The formation of diisopropyl ether was below 0.5% in all the catalytic tests.

The Figure 5 shows the results of the catalytic test of the V/Mg_{0.5}Al catalyst in the reaction of decomposition of the isopropanol the versus the reaction of temperature. The conversion of the isopropanol increases with the rise of temperature and reaches a maximum in the temperature of 290°C. The propylene formation is favored starting from the temperature of 240°C, however, the formation of acetone is disfavored starting from this temperature. In works mentioned previously (Wang et al. 1999), the increase of the temperature favors the propylene formation through the dehydration of the isopropanol.

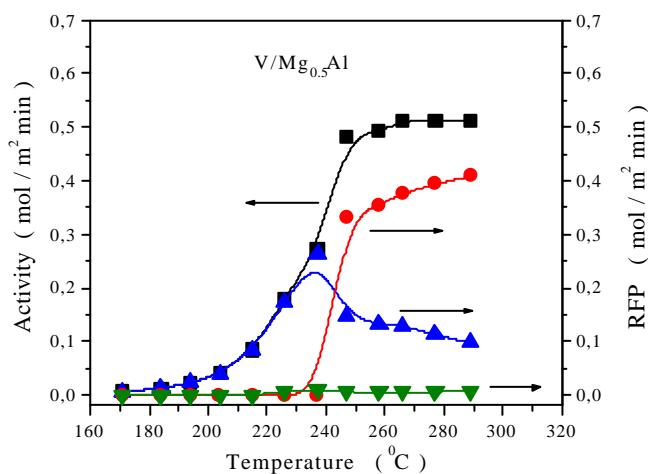


Fig. 5. Catalytic test of the V/Mg_{0.5}Al catalyst in the reaction of decomposition of the isopropanol. Isopropanol (■) and propilen (●).

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The transformation of isopropanol is frequently used as a test reaction to determine acid-base properties of oxide catalysts (Díez et al., 2003). The reaction can give with main products acetone, propylene and to a lesser extent, diisopropyl ether. The dehydration carried out in acid sites or concerted acid-base pair sites giving the propylene and diisopropyl ether, and the dehydrogenation to acetone occurring in basic sites. Ether formation must involve an inner-molecular coupling reaction. Many contradictory interpretations concerning the mechanism of isopropanol dehydration have been presented and isopropanol transformation cannot be a simple test of acidity (Haffad et al., 2001). On the other hand, the reaction of decomposition of the isopropanol cannot distinguish between the Lewis and Brönsted sites. The presence of species with redox properties, such as the vanadium in the catalysts synthesized in this work, can be important in the reaction of dehydration and dehydrogenation of the isopropanol. Unsupported V₂O₅ possess both Lewis and Brönsted surface acidity (Busca et. al., 1989). When vanadia is supported on metal oxide support, a decrease in the number of surface Lewis acid sites and an increase in the number of surface Brönsted acid sites has been detected (Datka et al., 1992). The diminution of Lewis acidity would be related with the coordination of the VO_x species on the metal oxide support and the increase in the Brönsted acidity is due to groups V-OH of the VO₄⁻² and V₂O₇H₂⁻² species on the support (Ferreira, et. al. 1999). In previous works, Aramendia et al. (1996) reported that the reaction of dehydratation of the isopropanol on MgO is related with the Brönsted acidity. Other authors (Díez et al., 2003) have reported that Al-rich Mg_yAlO_x samples ($R > 5$) convert isopropanol mainly to propylene via an E₂ mechanism occurring on dual Al⁺³-O⁻² sites. These Al-rich Mg_yAlO_x samples are mixed oxides that contain a separate quasi-amorphous Al₂O₃-like phase, which possess dual Al⁺³-O⁻² active sites that dehydrate isopropanol to propylene at high turnover rates. In this work, the results of DRX evidenced the presence of the gibbsite phase in the samples with $R = 0.53$ and 0.67 . In the calcined samples it was not possible to identify the Al₂O₃ phase, however the MgO phase was identified in all the samples and a small peak at $2\theta \approx 65^{\circ}$ was attributed to the MgAl₂O₄ phase in the catalyst with $R = 0.67$. In compensation, the increase of Al loading in the mixed oxides promotes a larger propylene formation due to the creation of new acid sites attributed the substitution of Mg⁺² by Al⁺³ in the matrix of the precursor. In all the samples the vanadium loadings varied between 16 to 18 wt% of V₂O₅. The presence of the vanadium on the mixed oxides favors the formation of acid sites (Lewis and Brönsted) that would be participating in the formation of the propylene in all the samples. Therefore, it is important to emphasize that the lack of information about the interaction of the vanadium in the structure of the hydrotalcite hindered a better interpretation of the results obtained in this study.

3. Conclusion

In this work, the synthesis of the precursors with different relationships molars $R = Al/(Mg+Al)$, for reaction of continuous coprecipitation, promoted the formation of hydrotalcite-like materials. The increase of the

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composition of the aluminum in the precursor in the range of $R = 0.53$ to 0.67 provided the formation of segregated phases of gibbsite and brucite in the structure of the hydrotalcite. The vanadium addition on hydrotalcite-type precursors might have incorporated $V_4O_{12}^{4-}$ anions in the interlayer space of the phase type brucite. The results of TPR showed that the growing increase of the Mg loadings in the catalyst promotes an increase in the maximum temperature of reduction of the vanadium species in the catalyst. This increase in the maximum temperature of reduction can be attributed to the formation of a larger amount of MgO phase in the catalyst, which decreases the reducibility of the vanadium species. In the catalytic tests for the reaction of decomposition of the isopropanol, the catalyst with larger concentration of magnesium produced more acetone. The largest activity in the formation of acetone in the $V/Mg_{1.0}Al$ catalyst is due to the presence of the magnesium (basic sites) in larger amount. In compensation, the catalyst with larger amount of aluminum ($V/Mg_{0.5}Al$) was more selective in the formation of the propylene for having a larger number of acid sites. The presence of the vanadium in the catalysts favors the formation of new acid sites in the catalyst and promotes a larger transformation of the isopropanol to propylene.

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