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Optimization of V_2O_5–MgO/TiO_2 catalyst for the oxidative dehydrogenation of propane effect of magnesia loading and preparation procedure

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The effect of magnesia loading and preparation procedure of vanadia on titania catalysts on the physico-chemical characteristics and the performance in propane oxidative dehydrogenation were investigated. A series of magnesia promoted vanadia catalyst (5 wt% V_2O_5) with varying amounts of MgO (1.9–10 wt%) were synthesized by synchronous and sequential deposition on titania support. The catalysts were characterized using several techniques (BET, XRD, H_2–TPR and NH_3–TPD). Both MgO loading and preparation procedure affect the catalyst surface properties and the behavior in the oxidative dehydrogenation of propane. Magnesia addition results in drastic increase in propene selectivity, while the effect on activity is negative. The activity is inversely related with the magnesia loading. Deposition of V_2O_5 on previously prepared MgO/TiO_2 presents a beneficial effect in the activity of the sample. The role of acidity and reducibility is explored. There is no correlation between reducibility and activity of the catalysts, whereas the acidity seems to influence the catalytic performance. Catalyst containing 5 wt% V_2O_5 and 1.9 wt% MgO prepared by sequential deposition of V_2O_5 on already doped with MgO titania exhibits the most interesting results.

KEY WORDS: oxidative dehydrogenation; propane, vanadia catalyst; magnesia modifier; sequential and synchronous deposition; acidity; reducibility.

1. Introduction

The accelerating global demand for light olefins leads to an indi cation for the development of new processes, which would overcome the disadvantages of the processes used nowadays. Steam cracking and fluid catalytic cracking of heavy petroleum fractions, the two established processes for propene production suffer from low propene selectivity and high separation cost. Propane catalytic dehydrogenation even though more selective than the established processes experiences thermodynamic limitations, high-energy consumption, side pyrolysis reactions and coke deposition in the system. Dehydrogenation of propane in the presence of oxygen presents a feasible option. However, industrialization of this process has not yet been considered, in that the most appropriate catalytic system has not been found. This catalyst should activate the alkane, maximize the production of the desired olefin and in parallel suppress the oxidation of both the reactive alkane and the produced olefin to carbon oxides. Most of the catalytic systems for the oxidative dehydrogenation of propane described in literature are based on transition metal oxides with vanadia as the protagonist metal oxide [1–3]. The catalytic behavior of vanadia is influenced by the dispersion of the vanadium species on the surface. A number of studies deal with the effect of support and preparation method for vanadia-supported catalysts [4–8]. V_2O_5 supported on TiO_2 is a well-established catalyst used in many industrial processes, such as selective reduction of NO_x with ammonia, the production of maleic anhydride, the selective oxidation and ammoxidation of hydrocarbons, etc., [1,9].

In order to improve the catalytic behavior of vanadia–titania system various additives have been examined and the most common ones are oxides of potassium, phosphorous, tungsten and niobium [6–12]. The role of additives is significant since they can modify the surface vanadium oxide structure and the physico-chemical characteristics, such as acid-base and redox properties [13]. Deo and Wachs studied various additives in order to understand the influence in the structure-reactivity relationship. They came to the conclusion that there are non-interacting additives (WO_3, SiO_2, Nb_2O_5) that do not significantly affect the structure of the surface vanadium oxide, whereas, the interacting ones (P_2O_5, K_2O) exhibit a pronounced effect on the structure and the reactivity of surface vanadia oxide [11].

V_2O_5 on TiO_2 is a very active catalyst in the oxidative dehydrogenation of propane; however, the selectivity to desired product is relatively low. In a previous study we studied the effect of MgO addition (10 wt%) to the

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catalytic properties of 5 wt% V_2O_5 on TiO_2 in propane oxidative dehydrogenation [14]. We found that Mg addition results in a significant increase in propene selectivity. The selectivity to propene is almost doubled at isoconversion. The promoting effect of the magnesia refers only to the selectivity. On the other hand the presence of the relatively high proportion of MgO disfavors the activity.

In an effort to optimize the performance of magnesia promoted 5 wt% V_2O_5/TiO_2 catalytic system, we report here the catalytic results obtained with samples containing different MgO loadings and prepared by different deposition sequence. Furthermore, the physico-chemical characteristics of the catalyst are explored aiming to correlate them with the catalytic behavior in oxidative dehydrogenation of propane.

2. Experimental

2.1. Catalyst preparation

The support used in all preparations was TiO_2 supplied by Norton with specific surface area 50.8 m^2/g. Prior to impregnation, the support was crushed and sieved to a particle size of 106–180 μm. Catalysts were prepared by the wet impregnation method, using as precursor for V_2O_5 and MgO the reagents NH_4VO_3 (Merck) and $Mg(NO_3)_2$ (J.T. Baker), respectively. Oxalic acid (Riedel-de Haen) was added to the solutions (NH_4VO_3/oxalic acid = 1/2 molar) to ensure dissolution of ammonium metavanadate precursor.

Catalysts with different magnesia loading were prepared by synchronous impregnation of V and Mg precursors. The percentage of V_2O_5 was kept constant and equal to 5 wt%, which corresponds to theoretical monolayer coverage (7–8 VOX/nm^2) [15]. MgO content varied from 1.9 to 10 wt%, corresponding to V/Mg atomic ratio from 1.16 to 0.22, respectively. After impregnation the samples were dried overnight at 120 °C and calcined at 600 °C for 6 h in synthetic air. Catalysts prepared using synchronous wet impregnation are denoted as [*x*V*y*Mg]–Ti, where *x* and *y* are the percentages of V_2O_5 and MgO, respectively. The unpromoted catalyst (5 wt% V_2O_5 on TiO_2) was calcined at 480 °C for 4 h while part of the sample was calcined at 600 °C for 4 h only for comparison.

To investigate the effect of oxide deposition sequence on the physico-chemical characteristics, the 5 wt% V_2O_5 on TiO_2 promoted with 10 wt% MgO sample was prepared by synchronous and sequential deposition. Sequential deposition took place in two different ways. The first step was the introduction of MgO on TiO_2 followed by intermediate drying and calcination at 600 °C for 3 h in air. In a next step V_2O_5 was deposited on MgO–TiO_2 and the sample was dried overnight and finally calcined at 480 °C for 3 h in air. Catalysts prepared by this route are symbolized as *x*V–*y*Mg–Ti, where *x* and *y* are the percentages of V_2O_5 and MgO, respectively. The second path included the reverse procedure of depositing the oxides and the catalysts naming changes to *y*Mg–*x*V–Ti.

$MgTiO_3$ ilmenite crystalline phase was synthesized by using equimolar mixture of MgO and TiO_2 powders with an excess of 2% mol MgO. The mixture was calcined at 900 °C for 2 h, then grinded and calcined at 500 °C for 1 h and finally sintered at 1300 °C for 2 h. The preparation procedure followed for ilmenite was based on literature data [16,17]. The characteristics of all prepared catalytic samples are presented in table 1.

2.2. Catalyst characterization

The surface area of the samples was measured by N_2 adsorption at 77 K by means of the multipoint BET analysis method, using an Autosorb-1 Quantachrome flow apparatus. Samples were dehydrated in vacuum at 250 °C overnight before surface area measurements.

Powder XRD patterns were obtained at room temperature using Cu (Kα) radiation at a Siemens D500 diffractometer.

Temperature programmed reduction (TPR) with H_2 and temperature programmed desorption (TPD) of NH_3 were carried out in a home-made gas flow system equipped with a quadrupole mass analyzer (Omnistar, Balzer). Catalyst sample (0.2 g) was placed in the U-tube reactor and pretreated in flowing He for 0.5 h at 500 °C followed by cooling at room temperature. In TPR measurements, the inlet total flow (5% H_2 in He) was 50 cm^3 /min and the temperature increased linearly at a rate of 15 °C/min from 30 to 700 °C. The main (m/z) fragments registered were $H_2 = 2$, $H_2O = 18$ and He = 4.

Ammonia (5% NH_3 in He) with total flow of 50 cm^3/min was adsorbed at 50 °C for 1 h followed by 2 h flushing under flowing He to remove weakly held ammonia. Desorption of adsorbed species was monitored from 50 °C to 700 °C using a ramp rate of 15 °C/min. The main fragments recorded were $NH_3 = 17$ and 15, $H_2O = 18$, He = 4, NO = 30, $N_2 = 28$, $N_2O = 44$. Quantitative analysis of ammonia adsorbed was based on fragment m/e = 15.

Table 1
Characteristic properties of the catalysts

Catalysts	Wet impregation sequence of V and Mg oxides	MgO, wt%	Ratio V/Mg atomic	SSA, m^2/g	Crystal size, nm
5V–Ti	–	–	–	43.0	31.8
[5V1.9Mg]–Ti	synchronous	1.9	1.16	20.2	44.2
[5V3.6Mg]–Ti	synchronous	3.6	0.60	28.5	40.4
[5V10Mg]–Ti	synchronous	10	0.22	38.7	33.8
5V–10Mg–Ti	sequential	10	0.22	30.1	34.9
10Mg–5V–Ti	sequential	10	0.22	24.4	40.9

2.3. Catalytic experiments

The catalytic experiments were conducted in a conventional flow system. The reactor used was a fixed bed quartz reactor (I.D. 9 mm) equipped with coaxial thermocouple for catalyst temperature monitoring. The catalyst loaded was mixed with equal amounts of quartz particles of the same size to avoid hot spots in the catalytic bed. The catalyst was pretreated in oxygen flow at 500 °C for 0.5 h. The composition of the reacting mixture used was $C_3H_8/O_2/He = 5/5/90$. Two series of experiments were performed. In the first series, the performance of the samples was examined as a function of reaction temperature ranging from 350 °C up to 550 °C using the same catalyst weight ($W = 0.1$ g) and total flow rate ($F = 100$ cm^3/min). In the second series, the temperature was kept constant at 500 °C W/F ratio was varied from 0.002 to 0.09 g.s.cm^{-3}. Products were analyzed on line using a Varian 3700 chromatograph equipped with a TC Detector. Two columns in a series-bypass configuration were used in the analysis:a Porapak Q and an MS 5A. The reaction products were mainly C_3H_6, CO_2, CO and H_2O. The amount of oxygenates other than CO_x was negligible at the reactor exit. The selectivity of the products was calculated on carbon basis. The conversion of propane in the empty reactor, under the conditions (temperature, flow) used, was lower than 2%, confirming the absence of reactions in the gas phase.

3. Results and discussion

3.1. Surface area and XRD

Table 1 presents the characteristic properties of the samples. The catalysts exhibit significantly different surface areas. Addition of MgO to the 5V–Ti catalyst results in significant decrease of the specific surface area, which is inversely proportional to the amount of MgO added. The higher calcination temperature (600 °C) of the magnesia promoted catalysts could account for the decrease in the surface area. However, the differences appear are more severe among the magnesia containing catalysts, indicating different extent of structural modifications induced by magnesia. The drastic reduction of the surface area in sample [5V1.9Mg]–Ti compared to that of the samples with higher amount of magnesia could be attributed to changes in titania crystal size and possible beginning of crystallographic transformation of anatase during calcination. Crystal sizes of titania as calculated from X-ray diffractograms, using the Scherrer formula, show a slight but definite tendency to decrease with increasing MgO content (table 1).

According to literature, the crystal transition from anatase to rutile starts at 600 °C for pure TiO_2 and rutilization can be accelerated by the presence of promoters and metal oxides at the surface of titania anatase. Vanadium catalyzes this phase transformation, which occurs at much lower temperatures. This transformation of anatase to rutile results in an increase to the apparent crystal size, thus decreasing the surface area [18,19].

The samples with the same composition 5 wt% V_2O_5-10 wt% MgO but prepared via different deposition sequence show significantly different surface areas. Synchronous deposition of V and Mg keeps the surface area high while sequential results in drastic decrease. Changes in titania crystal size are also observed between these samples indicating different degree of starting rutilisation of the titania.

TiO_2 anatase diffraction lines were present in all XRD patterns (figure 1). No other crystal configuration of the titania support (rutile or brookite) was detected. Furthermore, the absence of V_2O_5 peaks in the diffractograms confirmed the fine dispersion of vanadia species on the catalytic surface. MgO peaks were absent, even when theoretical monolayer coverage of magnesia was exceeded (MgO loading higher than 3.6 wt%). Theoretical surface coverage is estimated at 14.77 Mg atoms/nm^2 [20]. This can be attributed to the good dispersion of magnesia and/or high interaction of magnesia with titania forming the $MgTiO_3$ crystalline phase. Indeed, characteristic peaks of $MgTiO_3$ are

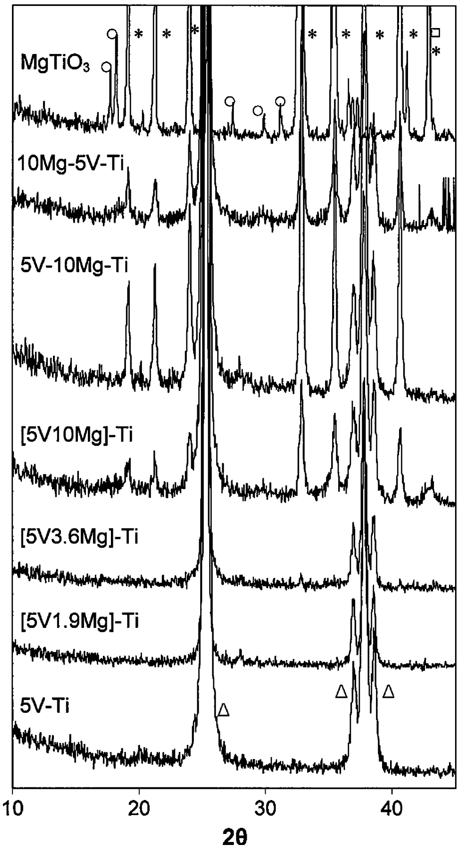

Figure 1. X-ray diffraction patterns of vanadia catalysts, (Δ) TiO_2, (∗) $MgTiO_3$, (○) $MgTi_2O_5$, (□) MgO.

present in the samples with high magnesia loading (10 wt%). The effect of deposition sequence to the extent of Mg and Ti interaction is clearly depicted by the different intensity of the $MgTiO_3$ diffraction lines (figure 1). The intensity of $MgTiO_3$ diffraction lines is considerably higher for the sample 5V–10Mg–Ti where MgO is deposited first on bare titania.

Taking into account the difference in the electronegativity between V (1.63), Ti (1.54) and Mg (1.31), MgO should had formed bonds and furthermore crystalline mixed phases with V than with Ti. However, according to XRD patterns $MgTiO_3$ is formed. This could be attributed to sulfur impurities (S electronegativity 2.58) of the titania support which attract Mg electrons and subserve the formation of the mixed Mg–Ti crystalline phase. It is worthy to note that crystalline TiO_2 is in excess in the preparation mixture compared to V_2O_5, rendering the reaction between TiO_2 and MgO more probable. On the other hand, the formation of mixed V–Mg phases cannot be excluded but in very small amounts lower than the XRD detection limit.

The effort to prepare the $MgTiO_3$ resulted in the successive formation of the geikelite (ilmenite) phase, which dominates, whereas MgO and $MgTi_2O_5$, also exist, but in small amounts (figure 1).

3.2. Temperature programmed reduction

Temperature programmed reduction with hydrogen (H_2-TPR) is a useful technique to probe the reducibility of catalysts and is of great importance, since there are reports claiming about a correlation between reducibility and catalytic activity in oxidative dehydrogenation of propane [2,21].

In general, the addition of alkali or alkaline earth metals to vanadia catalysts hinders the reduction [6,13,22]. Actually, in our samples, MgO addition results in a significant increase of the maximum temperature for H_2 uptake in the TPR measurements compared to V_2O_5/TiO_2 catalyst (figure 2). This change in the ease of vanadium reduction can be attributed to the different vanadia dispersion and stronger vanadia interaction with magnesia and titania [23]. It is worth noting that both the percentage of MgO and the sequence of deposition affect the ease of vanadia reduction.

As shown in table 2, the catalyst with low magnesia loading, [5V1.9Mg]–Ti, exhibit higher reduction temperatures than the catalyst with 5 times higher magnesia loading [5V10Mg]–Ti (compare 591 °C with 567 °C respectively). One would expect the opposite effect, since it is often reported that increase of additive loading results in an increase of T_{max} [24,25]. The titania crystal rearrangement (rutilisation) which seems to proceed with higher rates in the samples [5V1.9Mg]–Ti and [5V3.6Mg]–Ti is probably one of the reasons for the higher reduction temperatures. To prove that vanadia on rutile is less reducible than vanadia on anatase we prepared a sample containing 5 wt% V_2O_5 on titania, calcined at higher temperature (600 °C), where titania starts to transform from anatase to rutile. The temperature of maximum H_2 consumption of this sample was 100 °C higher than that of the 5VTi sample (calcined at 480 °C). Similar increase of the temperature of maximum H_2 consumption with increasing titania calcination temperature has also been reported [26].

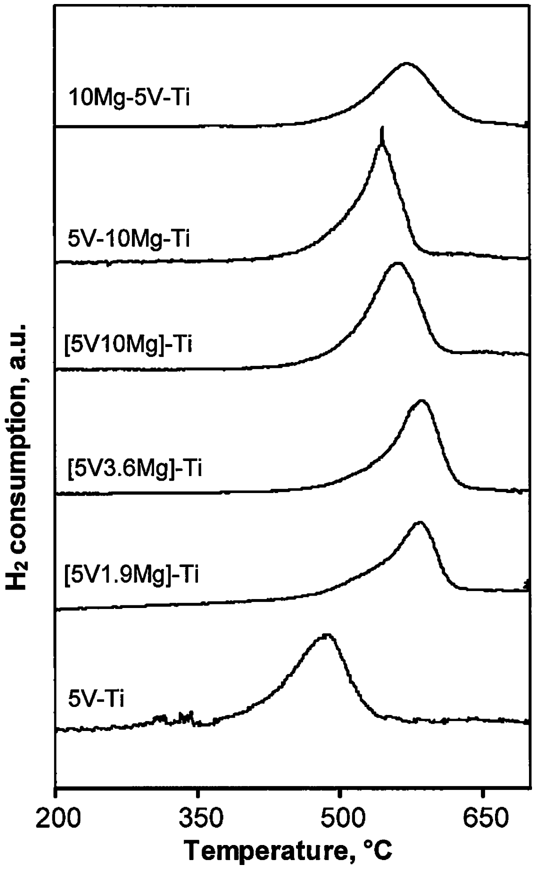

Figure 2. H_2-Temperature programmed reduction profiles of Mg containing vanadia catalysts.

The sequence that the V and Mg oxides are deposited on TiO_2 surface does not have a significant influence on the temperature of maximum hydrogen reduction (table 2). In particular, it seems that the accessibility of reducible sites is affected to a modest degree by the

Table 2
Reducibility and acidity of the catalysts

Catalyst	TPR H_2, T_{max}, °C	Acid sites, μmol NH_3 ads./g cat.		
		Total	Weak	Medium
5V–Ti	490	0.70	0.50	0.20
[5V1.9Mg]–Ti	591	0.39	0.20	0.19
[5V3.6Mg]–Ti	593	0.30	0.07	0.23
[5V10Mg]–Ti	567	0.25	0.06	0.19
5V–10Mg–Ti	550	0.37	0.19	0.18
10Mg 5V–Ti	576	0.29	0.10	0.19

sequence of the V and Mg deposition. Reduction of vanadia species is easier on the sample where vanadia was introduced on doped titania with magnesia (5V–10Mg–Ti).

3.3. Temperature programmed desorption of ammonia

Besides reducibility, the acidity of the catalyst plays a significant role in the oxidative dehydrogenation of alkanes. Temperature programmed desorption of ammonia is a common technique for testing the acidity of catalysts.

The profiles of ammonia desorbed as a function of temperature are compiled in figure 3. The dominating signal of N containing compounds was that of NH_3. The signals corresponding to N_2, NO, NO_2 and N_2O were less than 1%. The amount of NH_3 desorbed per gram of catalyst is presented in table 2. Desorption of NH_3 in Mg promoted catalysts appears as a broad asymmetric peak extended up to 400 °C implying the presence of more than one acidic sites. The non-promoted 5V–Ti catalyst presents a narrower desorption peak.

Addition of basic MgO leads as expected to a drastic decrease in acidity, which is proportional to the magnesia content for the samples prepared by synchronous deposition (table 2). Vanadia on rutile is claimed to be less acidic than vanadia on anatase [27]. To check if the decrease in acidity is also due to the beginning of rutilization of titania crystals, the sample with 5 wt% V_2O_5 supported on titania rutile was tested under the same conditions. NH_3-TPD testing of this sample (not shown) presented similar quantities of desorbed ammonia with the vanadia catalyst supported on titania anatase, confirming that the decrease in total acidity is exclusively due to magnesia addition.

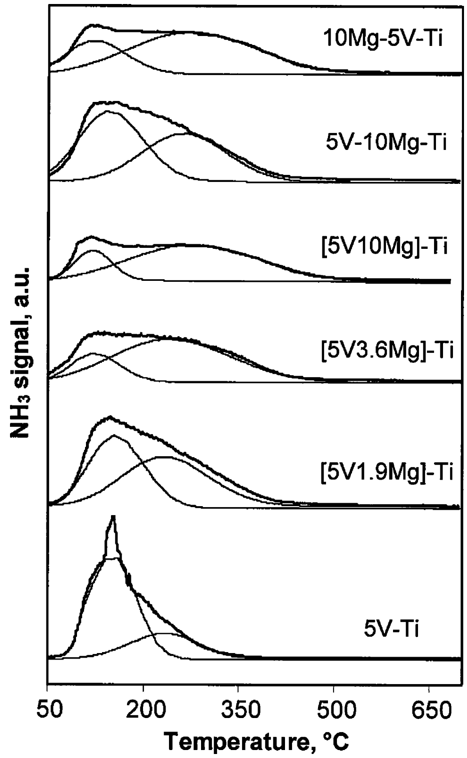

Figure 3. NH_3-Temperature programmed desorption profiles of Mg containing vanadia catalysts.

Acidity also changes among the samples containing the same amount of MgO and V_2O_5, but prepared via different procedure. Sequential deposition of V and Mg oxides leads to higher acidity than synchronous deposition. In particular, the catalyst 5V–10Mg–Ti, in which V_2O_5 was deposited on already doped with MgO titania, exhibits the highest acidity.

The experimental curves of ammonia desorption were analyzed by a mathematical program (ORIGIN 50) and deconvoluted into three individual desorption peaks of Gaussian function with maximum in the range 130–250, 260–400 and 450–550 °C, corresponding to ammonia chemisorbed on weak, medium and strong acid sites respectively.

The amount of strong acid sites is almost negligible in all catalysts, whereas the attention is drawn to the distribution of weak and medium acid sites. More precisely, the amount of medium acid sites remains almost constant, indicating that the presence of Mg does not affect these sites. On the other hand the addition of the alkaline earth metal oxide decreases drastically the amount of weak acid sites (table 2). The same behavior was observed in the chromia/alumina catalytic system promoted with potassium studied by Rombi *et al.* [28]. The acid site strength distribution was greatly influenced by the amount of the promoter. They observed that the less acidic sample, the sample with the highest potassium loading, shows lower amount of weak acid sites.

The addition of the same amount of MgO with the different sequence affects also the distribution of weak and medium sites (table 2). It is confirmed again that the number of the medium sites is almost unaffected, while weak sites are subjected to changes. Deposition of V on already prepared MgO–TiO_2 (5V–10Mg–Ti sample) exhibits the highest total acidity among these samples and the highest number of weak acid sites. The strong interaction of Mg with Ti, which is also depicted by the higher intensity of $MgTiO_3$ peaks in X-ray diffractograms (figure 1), implies less effect on V and consequently on weak sites. It is worthy to note that NH_3-TPD of the prepared $MgTiO_3$ ilmenite phase showed negligible adsorption of ammonia (not shown).

Deconvolution of ammonia peaks is not only a mathematical analysis, giving information about the physical meaning of the sites, but in this case can illuminate the nature of the acid sites. The strength of the acid sites can be correlated to their nature considering that on the surface of monolayer catalyst there are two types of vanadia tetrahedral species capable to adsorb NH_3 [26]. The first type without

OH-groups serves as Lewis acid sites, and the second one, that coordinates OH-groups, serves as Brønsted acid sites. It is also stated that ammonia adsorbed on Brønsted acid sites desorbs easier than Lewis coordinated ammonia during temperature programmed desorption [26,29]. Thus, the first deconvolution peak could be ascribed to Brønsted acid sites and the second to Lewis acid sites. Strong acid sites, although not present in the samples under study, can be related to strongly bound ammonia on the catalytic surface, leading at high temperatures to decomposition products [30].

The presence of both Lewis and Brønsted acid sites in vanadia–titania system has been stated in our previous study [14]. However, the differences observed between the previous and the present study may be attributed to the different probe molecules and the experimental conditions used. The existence of Brønsted acidity is proved to be related to the presence of water [31]. The high vacuum used during the activation of the sample before IR measurements in our previous study probably resulted in the extensive removal of weak-OH groups. Additionally, taking into account the selection criterion for probe molecules suggested by Lercher and coworkers, the size of the molecule plays significant role [32]. The molecule of ammonia has smaller size than the molecule of pyridine and it could be that in the present case more acid sites can be reached.

According to the above correlation between the strength and the nature of the acid sites, addition of MgO results in a decrease of Brønsted (weak) acid sites, whereas the Lewis (medium) acid sites are almost unaffected. The higher the magnesia loading, the higher is the decrease to the Brønsted acid sites. Furthermore, Brønsted acidity is also influenced by the sequence of oxides deposition. Grzybowska *et al.* observed similar decrease in Brønsted acidity when potassium oxide was introduced in vanadia–titania system [33].

3.4. Catalytic results

3.4.1. Effect of Mg loading

Our recent studies in oxidative dehydrogenation of propane over vanadia on titania catalyst showed that incorporation of Mg in the vanadia catalyst while beneficial for the selectivity, had a detrimental effect on the conversion [14]. The activity of vanadia catalysts promoted with different amounts of MgO (1.9–10 wt%) as a function of temperature is shown in figure 4. The data of the unpromoted vanadia catalyst are also included. It is observed that the percentage of MgO in the catalyst (higher V/Mg atomic ratio) is inversely related with the activity. At 400 °C, the sample with 1.9 wt% MgO shows 70% less propane conversion than the unpromoted 5VTi. The decrease is much more severe with the sample containing 10 wt% MgO. The activity expressed as mole of propane converted per second and m^2 of the catalyst presents the same trend.

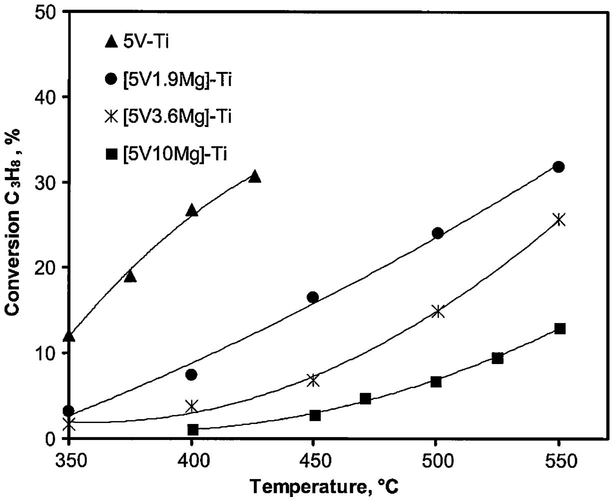

Figure 4. Propane conversion as a function of temperature for Mg containing vanadia catalysts prepared by synchronous deposition (W/F:0.06 g.s.cm^{-3}, $C_3H_8/O_2/He$:5/5/90).

Acidity has been proposed as one of the main factors that influence the activity [2] and present results are in line with this statement. The increase in activity parallels the increase in acidity as depicted in figure 5. Since weak sites are subjected to changes due to the presence of Mg, we suggest that the less the weak acid sites (Brønsted), the lower is the activity. Arena and coworkers studied the acid base properties of supported vanadia catalysts and they also claimed that the low surface reactivity of vanadia magnesia catalyst is attributed to the poor population of Brønsted acid sites [21].

In order to get a clear picture of the propene selectivity at various levels of conversion, runs were conducted at constant temperature (T = 500 °C) with various W/F. Selectivity to propene as a function of conversion for the MgO containing vanadia catalysts is illustrated in figure 6. Indeed, the addition of MgO

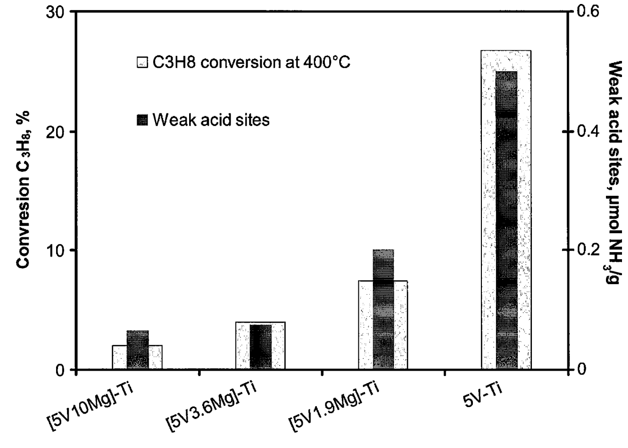

Figure 5. Relationship between weak acid sites and activity in propane ODH for Mg containing vanadia catalysts prepared by synchronous deposition.

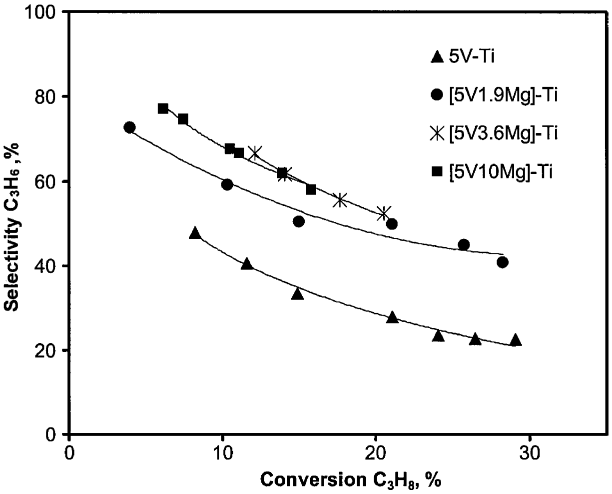

Figure 6. Selectivity to propene as a function of propane conversion at 500 °C Mg containing vanadia catalysts prepared by synchronous deposition (C_3H_8/O_2/He:5/5/90).

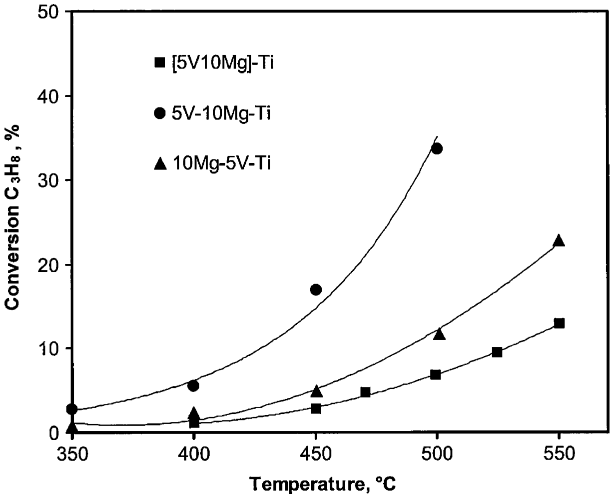

Figure 7. Propane conversion as a function of temperature for vanadia on titania catalysts containing 10 wt. % MgO prepared by synchronous and sequential deposition (W/F:0.06 g.s.cm^{-3}, C_3H_8/O2/He:5/5/90).

favors high selectivity of propene within the whole range of conversions tested. Compared to the unpromoted catalyst the increase in selectivity is almost doubled, though surprising that the boost in selectivity is almost unaffected by the magnesia concentration. It is stated in the literature that alkali or alkaline earth metal addition favors alkene desorption and prevents the overoxidation of propene to carbon oxides [13,34]. It is thus consequent to correlate the changes in acid base character, imposed by the Mg promoter, with selectivity. However, this change of acid base character cannot explain the similar selectivities obtained with the samples containing different magnesia loadings. Other structural properties of the samples may also control the selectivity of the desired product.

3.4.2. *Effect of deposition sequence*

The order of Mg addition to the titania supported vanadia catalysts seems to be critical for the performance in the oxidative dehydrogenation of propane. The sequence of magnesia introduction affects mostly the activity of the catalysts and not the selectivity, which remains at the same levels. In figure 7, the conversion of propane is plotted versus reaction temperature for promoted vanadia catalysts with the same magnesia loading (10 wt%) but different oxide deposition sequence. It is clear that sequential deposition of V and Mg on titania leads to significantly higher activity than synchronous. The beneficial effect is more pronounced with the sample where V was deposited on Mg doped TiO_2. The high activity of the 5V–10Mg–Ti sample cannot be ascribed to the $MgTiO_3$ mixed phase, which is detected in increased amounts. Tests conducted with the prepared pure $MgTiO_3$ phase showed that the activity of this phase is nil at the reaction conditions used. The activity is in good correlation with the acidity and in particular with the amount of weak acid sites as clearly shown in figure 8. The propene selectivity at 500 °C obtained at various conversion levels is presented in figure 9. Similar selectivities are observed between the three catalytic samples. Present results suggest that selectivity to propene is not affected by the preparation procedure figures 10 and 11.

The superior performance of 5V–10Mg–Ti compared to that of 10Mg–5V–Ti catalyst could be due to higher vanadia dispersion on the surface. In case of magnesia deposited on previously prepared V–TiO_2, partial dissolution of vanadium oxide in the magnesia precursor solution might be possible and since vanadia is the active phase, this re-dispersion is undesirable. Similar results have been reported by Courcot and coworkers, for the vanadia–titania system promoted with potassium

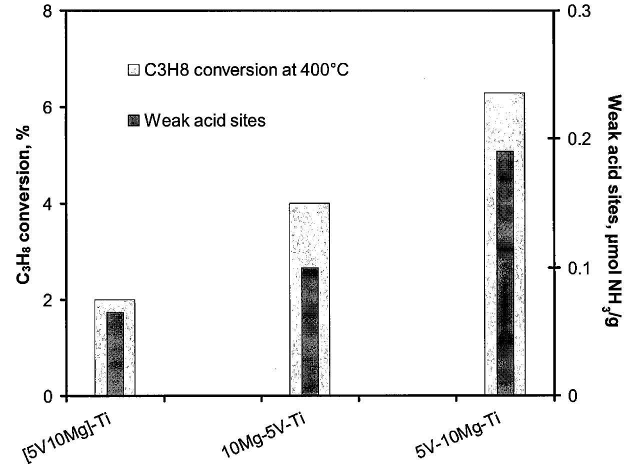

Figure 8. Relationship between weak acid sites and activity in propane ODH for vanadia on titania catalysts containing 10 wt. % MgO prepared by synchronous and sequential deposition.

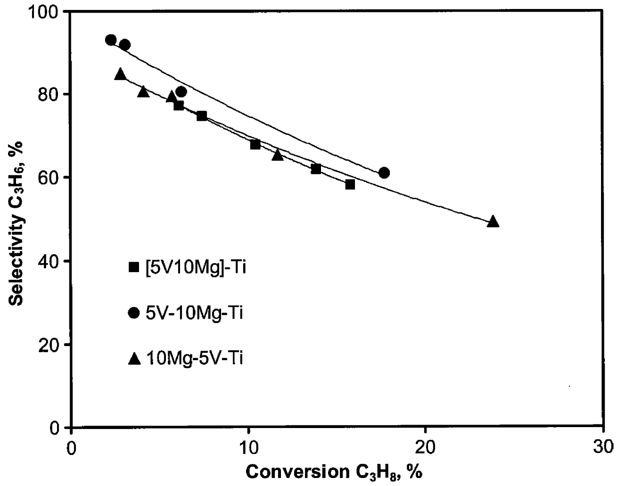

Figure 9. Selectivity to propene as a function of propane conversion at 500 °C for vanadia on titania catalysts containing 10%wt. MgO prepared by synchronous and sequential deposition ($C_3H_8/O_2/He$:5/5/90).

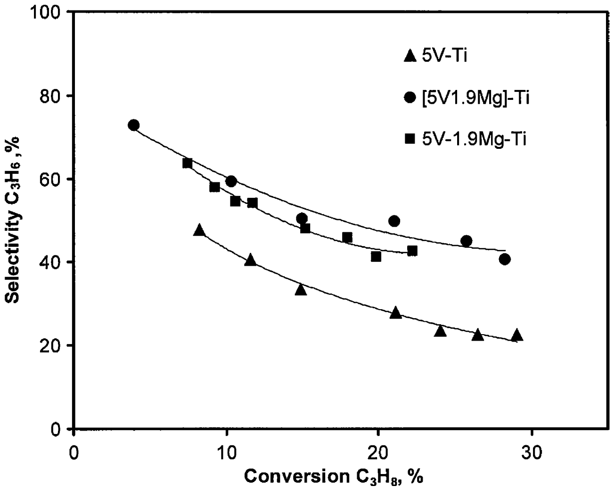

Figure 11. Selectivity to propene as a function of propane conversion at 500 °C for vanadia on titania catalysts containing 1.9 wt.% MgO prepared by synchronous and sequential deposition ($C_3H_8/O_2/He$:5/5/90).

[12]. When vanadia was deposited on titania doped with potassium, the activity in the oxidative dehydrogenation of propane was higher.

3.4.3. Optimum catalyst formulation

To take advantage of the main conclusions that (i) the presence of MgO on vanadia catalyst drastically increases the selectivity, (ii) the sequence of Mg introduction affects the activity and (iii) the decrease in activity due to Mg addition is much less in low loadings, we decided to continue working with vanadia catalyst promoted with 1.9 wt% Mg prepared by sequential introduction of MgO and V_2O_5 (in the order mentioned) on titania support.

The catalyst 5V–1.9Mg–Ti was characterized using the same techniques as the other samples and the results are presented in table 3. Compared to the other sample [5V1.9Mg]–Ti with the same composition but prepared by synchronous deposition of the oxides, the modified sample 5V–1.9Mg–Ti has higher surface area and significantly higher amount of acid sites. The difference in acidity is due to the increased number of the weak (Bronsted) acid sites while medium (Lewis) sites remain almost the same. It is confirmed that the depostion sequence affects the physico-chemical characteristics of the magnesia promoted vanadia catalysts.

The performance of this new catalyst was tested as a function of temperature and the results are presented together with that of the catalyst with the same composition, but prepare with synchronous V and Mg deposition and of the non-promoted catalyst. The deposition first of Mg and then of V on titania has a measurable effect on the conversion. While the decrease in activity with the [5V1.9Mg]–Ti sample is 70% compared to the non promoted one, it reduces to 35%

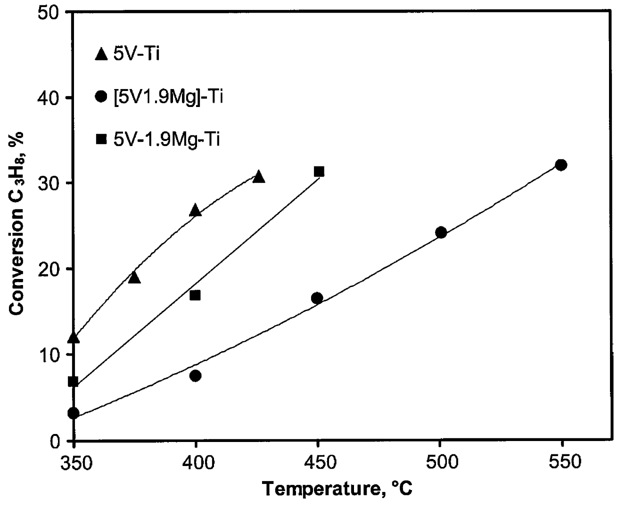

Figure 10. Propane conversion as a function of temperatute for vanadia on titania catalyst containing 1.9 wt.% MgO (W/F:0.06 g.s.cm^{-3}, $C_3H_8/O_2/He$:5/5/90).

Table 3
Physico-chemical characteristics of the 5 wt%. V_2O_5/TiO_2 catalyst promoted with 1.9 wt%. MgO

	5V–1.9Mg–Ti
Oxides deposition	sequential
% wt MgO	1.9
Atomic Ratio V/Mg	1.16
SSA, m^2 /g	41.3
Crystal size, nm	30.6
Crystalline phases	TiO_2
TPR H_2, Tmax, °C	580
TPD NH_3 (μmol NH_3/g cat.)	
Total acid sites	0.63
Weak acid sites	0.40
Medium acid sites	0.23

with the new sample (figure 10). The high selectivity to propene is sustained, verifying that the effect of the preparation sequence on the selectivity is almost negligible, as we see in figure 11.

According to our results, no relation between reducibility and catalytic activity was found, taking into account that the catalyst with the best catalytic performance (5V–1.9Mg–Ti) exhibits temperature of maximum H_2 consumption higher than that of catalysts with lower activity. It is well known that oxidative dehydrogenation reaction over transition metal oxide catalysts involves the redox cycle between V^{+5} and V^{+4} and consequently a good redox behavior might be favorable [35–37]. Present results suggest that other factors than reducibility control the catalytic behavior. It might be that the reoxidation of reduced vanadium sites plays an important role in the rate determining step and not the reduction [24].

It must be underlined that the 5 wt% vanadia on titania catalyst promoted with 1.9 wt% MgO prepared by sequential deposition of first MgO and then V_2O_5 on TiO_2 shows very promising results in propane oxidative dehydrogenation. It is worthy to report that the productivity in propene achieved at 500 °C amounts to 2 kg C_3H_6 per kg catalyst per h, one of the highest ever met in the open literature.

4. Conclusions

The physico-chemical properties and the catalytic performance in propane oxidative dehydrogenation of the vanadia on titania catalysts promoted with Mg are influenced by the amount of the promoter and the deposition sequence. Magnesia preferably reacts with the support forming $MgTiO_3$, especially when it is first deposited on the bare support, while vanadia remains in its amorphous state. The temperature at maximum hydrogen consumption is shifted to higher temperatures irrespective of the amount of the Mg added and the deposition sequence. Acidity as measured by NH_3-TPD is functioned by the Mg loading and the deposition sequence. More precisely the medium acid sites, ascribed to Lewis site, are not affected by the introduction of the alkaline earth metal compound while weak sites, ascribed to Brønsted sites, are greatly influenced.

Addition of magnesia in the vanadia on titania catalyst exhibits interesting results in the oxidative dehydrogenation of propane, especially in terms of selectivity to the desired product propene. The loss in activity caused by magnesia can be diminished with low loading. The sequence of depositing the oxides plays a significant role in catalytic activity. Neither the magnesia percentage, nor the sequence of oxide deposition affects the selectivity to propene, which remains high (80% higher than that of the undoped sample). There is a good correlation between catalytic activity and surface acidity. The amount of the weak acid sites, attributed to Brønsted acidity, parallels with the activity of the catalyst. The results obtained do not support any relation between reducibility and catalytic activity. The catalytic system 5 wt% V_2O_5 on previously prepared 1.9 wt% MgO/TiO_2 exhibits very promising results with very high productivity to propene.

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