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[V,Al]-MCM-22 catalyst in the oxidative dehydrogenation of propane

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Abstract

MCM-22 zeolite containing vanadium atoms either at structural or at ion-exchange positions was synthesized and tested in propane oxidative dehydrogenation (ODH) reaction in a fixed bed reactor, at temperatures between 340 and 560 °C. Acidity of these materials, as well as of similar materials that did not contain vanadium, was characterized by ammonia temperature programmed desorption (TPD-NH_3). Vanadoaluminosilicates contain a higher number of acid sites, which present higher acidity in relation to the aluminosilicates. They also presented better performances in propane ODH, as they lead to higher values of conversion without loss of selectivity. Ion-exchange with alkaline ions leads to a decrease in cracking reactions, which are caused by strong Brønsted acid sites.

Keywords: [V,Al]-MCM-22; Vanadoaluminosilicates; Oxidative dehydrogenation of propane

1. Introduction

Oxidative dehydrogenation (ODH) of propane is a promising alternative to the traditional dehydrogenation for the production of propene, as it uses exothermic reactions that operate at lower temperatures. The greatest obstacle for its application is the reaction of overoxidation of propene to CO_x that occurs in high conversions of alkanes and that significantly limits the reaction yield [1].

Catalysts that have shown higher ODH rates and propene selectivities are usually based on supported V or Mo oxides [2–7]. Those traditional catalysts have, in general, low superficial areas and thus, a low number of exposed catalytic sites. Zeolitic catalysts, as having high superficial areas (and thus, a higher density of catalytic sites) may, in principle, favour an increase in selectivity for propene at higher conversions, as the reactions occur inside the restricted space of the zeolitic channels and/or cavities.

Zeolite-based catalysts have been tested in ODH of light alkanes [8–11], but the structure and acid sites roles have not yet been fully understood. ZSM-5 zeolite and ALPO-5 materials having MFI and AFI structures, respectively, were tested in propane ODH. In both cases the catalytic activity as well as the selectivity to propene can be enhanced by isomorphous incorporation of V ions in the zeolite framework [8–11].

The aim of this paper is to study the behaviour of V-modified MCM-22 zeolite towards propane ODH. Two different methods of insertion of vanadium in the MWW structure were used, hydrothermal one-pot synthesis ([V,Al]-MCM-22), and ion-exchange of VO_2^+ cations (VO-[Al]-MCM-22). Spectroscopic characterization of the samples is already reported elsewhere [12].

2. Experimental

2.1. Synthesis

Synthesis gels of [Al]-MCM-22 were prepared according to Marques et al. [13] in the following composition:

$$1.0\,SiO_2 : 0.02\,Al_2O_3 : 0.20\,NaOH : 0.60\,HMI : 30\,H_2O$$

where HMI stands for hexamethyleneimine, the structure directing agent. Hydrothermal treatments were carried out under static conditions at 150 °C for 240 h.

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Synthesis gels of V-MCM-22 were prepared in the following composition:

$$1.0\,SiO_2 : 0.02\,Al_2O_3 : 0.03\,VOSO_4 : 0.30\,NaOH : 0.60\,HMI : 30\,H_2O$$

The synthesis procedure was also adapted from Marques et al. [13] introducing $VOSO_4$ as the vanadium source. For preparation of the gel, $VOSO_4$ has been added together with the aluminum source, $Al(NO_3)_3$, and the method for preparing [Al]-MCM-22 has been followed as described [13]. Hydrothermal treatments were carried out under static conditions at 150 °C for 192 h.

The structure directing agent of [Al]-MCM-22 and [V,Al]-MCM-22 was removed by heating under argon from room temperature to 500 °C at a heating rate of 1 °C min^{-1} and leaving at this temperature for 12 h under argon flow. Subsequently, the sample was heated up to 580 °C under argon and the sample was left at this temperature for 6 h under dry oxygen flow.

Calcined [Al]-MCM-22 sample were ion-exchanged with Na^+, K^+ or NH_4^+ (0.1 mol L^{-1} sodium nitrate, potassium nitrate or ammonium acetate solutions at a ratio of 10 mL of solution/gram of zeolite, stirring at 60 °C for 24 h), while calcined [V,Al]-MCM-22 samples were ion-exchanged with Na^+ or NH_4^+ following the same procedure as for [Al]-MCM-22. The exchanged samples were heated up to 500 °C under Ar flow, and once the temperature was reached, the gas was changed to oxygen and the sample left in this condition for 6 h. These samples were named Na-[Al]-MCM-22, K-[Al]-MCM-22, H-[Al]-MCM-22, Na-[V,Al]-MCM-22 and H-[V,Al]-MCM-22, respectively.

VO-[Al]-MCM-22 samples were made by ion-exchange of [Al]-MCM-22 with 0.1 mol L^{-1} $VOSO_4$ solution (at a ratio of 10 mL of solution/gram of zeolite, stirred at 60 °C for 24 h; pH 1.6 with concentrated H_2SO_4).

2.2. Catalyst characterization

2.2.1. Elemental analysis

Elements concentration was determined by solubilizing the samples by oxidizing alcaline fusion with lithium metaborate. The resulting material was dissolved and the elements were determined by atomic absorption with a Varian A-5 spectrophotometer, using a nitrous oxide/acetilene flame.

2.2.2. X-ray diffraction (XRD)

Data were collected for the as-synthesized and calcined samples as hand-pressed wafers on a Shimadzu XRD 6000 diffractometer at room temperature with CuK_α radiation, generated at 40 kV and 30 mA from 1.4 to 50° 2θ at a rate of 2° min^{-1} and slits of 0.5°, 0.5° and 0.3 mm for exit, reception and divergence, respectively.

2.2.3. Pore-structure analysis

Textural properties of the samples were determined on a Micromeritics ASAP 2000 instrument using N_2 at 77 K as adsorbate.

2.2.4. Temperature programmed ammonia desorption (NH_3 TPD)

NH_3 TPD was done by using a Micromeritics TPD/TPR 2900 analyser, equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer. Samples were satured with pure ammonia at 100 °C for 1 h and, after being purged with pure He for 2 h at room temperature, were heated until 700 °C at a 10 °C min^{-1} rate under He flow (25 cm^3 min^{-1}).

2.3. Catalytic activity measurements

Catalytic activity tests of propane oxidative dehydrogenation were carried out in a fixed bed quartz micro reactor operating under atmospheric pressure. The feed composition was 2.5% propane, 5% O_2, He balance (in volume). The contact time was fixed at 0.11 g h dm^{-3} and the reaction temperature ranged from 340 to 560 °C. Analysis of hydrocarbons was performed by an on-line Hewlett-Packard HP5890A (series II) gas chromatograph equipped with a Poraplot capillary column and a flame ionization detector (FID). Concentration of O_2, CO and CO_2 was measured by an on-line Hartmann & Braun URAS 10 E continuous analyser. Water produced by the reaction was retained by a $CaCl_2$ trap, in order to avoid condensation in the cold parts of the experimental apparatus.

3. Results and discussion

The elements concentration in the calcined and/or exchanged [Al]-MCM-22 and [V,Al]-MCM-22 samples, determined by element analysis, are reported in Table 1.

A comparison between XRD of [V,Al]-MCM-22, calcined [Al]-MCM-22 and VO-[Al]-MCM-22 can be observed in

Table 1
Composition of the samples, determined by elemental analysis and predominant type of vanadium species present in the samples

Sample	%V_2O_5 (m/m)	Type of V species	SiO_2/Al_2O_3	SiO_2/V_2O_5	Al/V	Na/Al	K/Al
H-[Al]-MCM-22	–	–	60	–	–	0.02	–
Na-[Al]-MCM-22	–	–	62	–	–	0.28	–
K-[Al]-MCM-22	–	–	69	–	–	0.04	0.89
[V,Al]-MCM-22	0.57	Aggregates	40	473	12	0.09	–
H-[V,Al]-MCM-22	0.25	Isolated	30	1036	35	0.02	–
Na-[V,Al]-MCM-22	0.27	Isolated	34	999	30	0.20	–
VO-[Al]-MCM-22	0.14	Isolated	42	1886	45	0.02	–

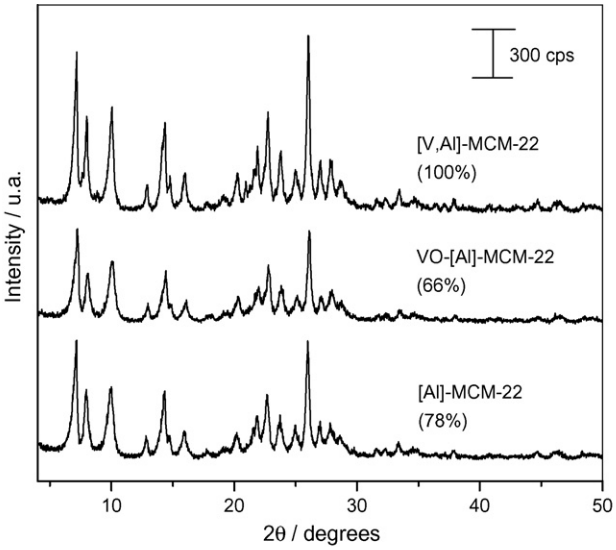

Fig. 1. XRD of [V,Al]-MCM-22, VO-[Al]-MCM-22 and [Al]-MCM-22, with crystallinity values of 100%, 66% and 78%, respectively.

Fig. 1. Sample VO-[Al]-MCM-22 presents a profile similar to parent [Al]-MCM-22 (similar band widths) although the diffractogram presents general lower intensity. The procedure of ion-exchange of VO^{2+} ions in acid media probably causes a decrease in the crystallinity of the sample, which, comparatively to [V,Al]-MCM-22 is of 66%. Loss of crystallinity in this case may be due to the ion-exchange procedure adopted and not to a large concentration of VO^{2+} ions in the structure, as vanadium content in this material is low (Table 1).

On the other hand, calcined [V,Al]-MCM-22 present a higher crystallinity degree in comparison to [Al]-MCM-22, 100% and 78%, respectively. The presence of heteroatoms other than aluminum in [Al]-MCM-22 seems, thus, to promote a higher cristallinity degree, as already observed for aluminum itself [13].

Although cristallinity degrees from XRD are higher for vanadoaluminosilicates, micropore volumes of aluminosilicates are similar or slightly higher than for vanadium-containing catalysts (Table 2), which is an indication that vanadium incorporation does not cause very important changes due to micropore occlusion. After ion-exchange procedure and thermal treatment a decrease in micropore volume is observed, due to the formation of extra-framework Al species that may partially block the catalyst micropores. As reported previously, [V,Al]-MCM-22 also presents more densely packed aggregates in comparison to [Al]-MCM-22, which may also interfere in textural parameters [14].

Table 2
Micropore volume of the catalysts

Sample	Micropore volume ($cm^3\ g^{-1}$)
H-[Al]-MCM-22	0.14
Na-[Al]-MCM-22	0.14
K-[Al]-MCM-22	0.13
[V,Al]-MCM-22	0.14
H-[V,Al]-MCM-22	0.11
Na-[V,Al]-MCM-22	0.12
VO-[Al]-MCM-22	Not analysed

The number of acid sites and the total relative acidity was determined by NH_3-TPD. All samples presented two desorption bands, whose presence indicates the existence of two different types of acid sites—one of higher strength, which desorbs ammonia at higher temperatures and one of lower strength, at lower temperatures. In the specific case of zeolites the band at lower temperatures can be related to ammonia interacting with silanols and the band at higher temperatures to the interaction with Si-(OH)-Al groups. Ammonia interacts also with Lewis acid sites that exist by the presence of aluminum, vanadium, sodium or potassium, but it is not possible to differentiate them from the Brønsted sites by this technique [15]. The characterization of the nature of acid sites in [V,Al]-MCM-22 has already been performed by FTIR with CO adsorption [12,14].

In Table 3 are reported the values of NH_3 desorbed per gram of each sample, this value is proportional to the number of acid sites of the samples. There can also be seen in Table 3 the values that refer to each one of the principal bands, calculated by deconvolution of the TPD curve, done with aid of the software PeakFit for Windows—Science, and also the maximum temperatures at which each of the desorption occurs.

According to total NH_3 values for aluminosilicate MCM-22 samples, the order observed for number of acid sites is H-[Al]-MCM-22 > VO-[Al]-MCM-22 > Na-[Al]-MCM-22 > K-[Al]-MCM-22. It is worth noting that, as observed by elemental analysis, exchange with K^+ ions is more efficient as with Na^+ ions (90% and 30%, respectively); K^+ ions substitute more efficiently the bridging H^+ ions, diminishing the number of acid sites in a better way. Besides, potassium exchanged [Al]-MCM-22 is the sample that presents the lower value of NH_3 desorbed at higher temperature, which indicates that besides having the lower number of acid sites, it is also the sample that presents the lower quantity of strong Si-(OH)-Al type sites.

Of the vanadoaluminosilicates, the sample that contains the higher number of acid sites is [V,Al]-MCM-22. This occurs because this is the sample that has the higher quantity of vanadium atoms and therefore, the higher total quantity of Brønsted and Lewis acid sites. The order for number of acid sites in this case is [V,Al]-MCM-22 > H-[V,Al]-MCM-22 > Na-[V,Al]-MCM-22. The sample H-[V,Al]-MCM-22

Table 3
Partial and total values of ammonia desorbed during TPD of the samples and maximum temperature observed for the first and the second bands

Sample	Desorbed NH_3 ($\times 10^{-4}$ mol $NH_3\ g^{-1}$)			Temperature (°C)	
	Total	1st band	2nd band	1st band	2nd band
H-[Al]-MCM-22	9.22	5.82	3.40	220	441
Na-[Al]-MCM-22	8.62	5.45	3.17	210	411
K-[Al]-MCM-22	5.94	4.76	1.18	211	403
[V,Al]-MCM-22	10.2	6.27	3.93	247	467
H-[V,Al]-MCM-22	10.0	4.48	5.52	240	442
Na-[V,Al]-MCM-22	8.34	5.32	3.02	246	442
VO-[Al]-MCM-22	9.00	4.95	4.05	223	434

presents the larger concentration of ammonia desorbed at high temperatures, suggesting that this sample is the one with higher Brønsted acidity, due to a higher number of aluminum atoms compensated by protons, in comparison to H-[Al]MCM-22 and/or to the presence of sites of the type V-OH or V· · ·(OH)-Si [16].

The temperatures that refer to each of the bands (Table 3) may be used to qualitatively evaluate the acid strength of the sites. The higher the temperature, the higher the energy necessary to desorb ammonia and, therefore, the stronger the interaction of the acid site with the probe molecule. It is interesting to note that the three samples that contain structural V atoms presents higher temperature values for the first band in comparison to aluminosilicate samples and present, in general, stronger acid sites. It is not possible, however, to relate the higher acidity of these samples with the presence of vanadium atoms, as a higher quantity of aluminum atoms is also present.

Vanadoaluminosilicates present a higher number of acid sites than aluminosilicates and have a higher content of aluminum atoms (Table 1). They also present higher acidity values in comparison to aluminosilicates. This fact may be related to the presence of a higher quantity of Lewis acid sites, which increase the global acidity of the samples. Sample VO-[Al]-MCM-22 is the one that possesses the lowest vanadium content (Table 1) and presents, however, acidity comparable to that of aluminosilicates.

Still regarding aluminosilicates, it can be observed that the temperature for the second NH_3 TPD band decreases as the alkaline ion-exchange degree increases (compare K-[Al]-MCM-22 to Na-[Al]-MCM-22 in Tables 1 and 3), because ion-exchange occurs preferentially at stronger acid sites, leaving the weaker sites free.

Regarding vanadoaluminosilicates, it can be observed that H-[V,Al]-MCM-22 presents lower second band temperature in comparison to [V,Al]-MCM-22. This fact must be due to the difference in vanadium content between these two samples, as both present similar aluminum content (Table 1). In this way, the presence of V_2O_5 domains in [V,Al]-MCM-22 [12], which are absent in H-[V,Al]-MCM-22 (Table 1) increases global acidity of the sample, making ammonia desorb at higher temperatures.

Catalytic tests in propane ODH have been performed. All samples presented activity in the temperature range studied (Figs. 2 and 3); the formation of propene, carbon oxides (CO and CO_2), ethene and methane was observed. The selectivity to all products at 500 °C are reported in Table 4. The values of reaction rate evaluated at 500 °C are also listed in order to give a direct comparison of the catalysts activity.

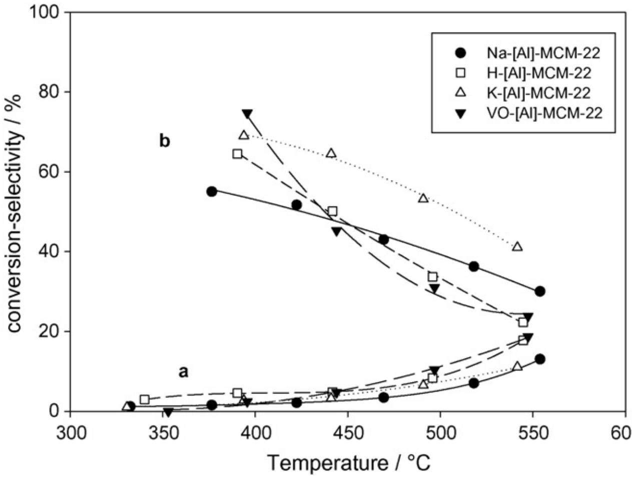

Fig. 2. Conversion of propane (a) and selectivity to propene (b) vs. temperature for [Al]-MCM-22 samples exchanged with Na^+, K^+, H^+ and VO^{2+}.

It is worth noting that high ethene and methane selectivity are associated to a high cracking activity. [Al]-MCM-22 samples presented formation of cracking products directly related to their order of acidity: H-[Al]-MCM-22 > Na-[Al]-MCM-22 > > K-[Al]-MCM-22. Samples that contain structural vanadium presented a lower cracking activity as their correspondent aluminosilicates, which is surprising because vanadoaluminosilicates possess higher number of acid sites (compare the values of Table 4 with Table 3). H-[V,Al]-MCM-22, for instance, presents a higher number of Brønsted acid sites as H-[Al]-MCM-22 (Table 3), but the last presents a higher tendency to cracking (Table 4). Structural vanadium in this way inhibits cracking reactions in conditions of equal number of acid sites. The sample VO-[Al]-MCM-22, inversely, behaves in a similar way as the samples that do not contain vanadium.

The comparison of the values of the reaction rate shows that vanadoaluminosilicates are more active than aluminosilicates suggesting that Brønsted acid sites can activate propane but that vanadium provides additional activity. In general, except for Na-[V,Al]-MCM-22, the catalytic activity, and as a consequence the reaction rate, is approximately linearly proportional to the total acidity of the material which, on the other hand, is enhanced by vanadium incorporation in the MCM-22 structure. These results are therefore an indication that vanadium atoms possess a very important role for the catalytic activity in these samples, but the species that are active are the isolated ones, that are the predominant species in Na^+ and H^+ exchanged [V,Al]-MCM-22 samples (Table 1) [12]. It can be concluded

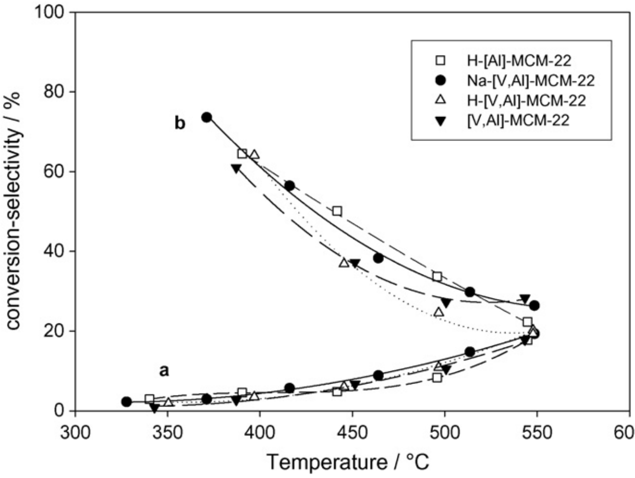

Fig. 3. Conversion of propane (a) and selectivity to propene (b) vs. temperature for [V,Al]-MCM-22 samples exchanged with Na^+, H^+ and non-exchanged [V,Al]-MCM-22 in comparison to H-[Al]-MCM-22.

Table 4
Selectivity to reaction products and reaction velocities at 500 °C

Sample	*s* C_2H_6 (%)	*s* CO (%)	*s* CO_2 (%)	*s* C_2H_4 (%)	*s* CH_4 (%)	*R* at 500 °C ($\times10^{-7}$ mol C_3H_8 s^{-1})
H-[Al]-MCM-22	33.8	10.4	25.6	21.7	8.5	4.54
Na-[Al]-MCM-22	36.2	15.8	22.6	17.9	7.5	4.22
K-[Al]-MCM-22	53.1	21.5	17.2	8.2	0.0	3.55
[V,Al]-MCM-22	27.3	35.8	24.7	8.9	3.3	5.83
H-[V,Al]-MCM-22	24.9	27.0	27.1	15.5	5.5	6.23
Na-[V,Al]-MCM-22	29.8	33.0	26.1	8.2	2.9	8.38
VO-[Al]-MCM-22	31.2	22.9	19.0	18.4	8.5	5.66

that the presence of both Brønsted acid sites and vanadium atoms is important to promote the activity of these catalysts.

In Table 4, in addition to the selectivity to cracking products, the selectivity to propene and carbon oxides is reported. In general, the formation of CO and CO_2 is higher for the most active catalysts suggesting that active sites for the ODH reaction are also active for the further oxidation of propene.

The conversion of propane and the corresponding selectivity to propene in the whole range of temperature explored are reported in Figs. 2 and 3. In Fig. 2 the curves relative to [Al]-MCM-22 exchanged with Na^+, K^+, H^+ and VO^{2+} are reported while in Fig. 3 the curves of the vanadoaluminosilicate samples are reported, in comparison to H-[Al]-MCM-22.

As expected, conversion increases and selectivity to the primary product decreases with the reaction temperature, however, although conversion curves are very close to one another, selectivity curves are more spaced. In order to understand if selectivity is simply correlated to conversion through a mechanism of consecutive reactions, i.e. the more propane is converted the more it is oxidized to by-products, or if the cracking of propane taking place at the same time may affect the selectivity, in Fig. 4 the selectivity to propene is reported as a function of propane conversion for all catalysts. It is worth noting that samples inhibiting cracking reactions (K-[Al]-MCM-22, Na-[V, Al]-MCM-22) show the curves with the best olefin yield thus suggesting that when the parallel cracking of the hydrocarbon is hindered better selectivity to propene can be obtained for the same conversion level.

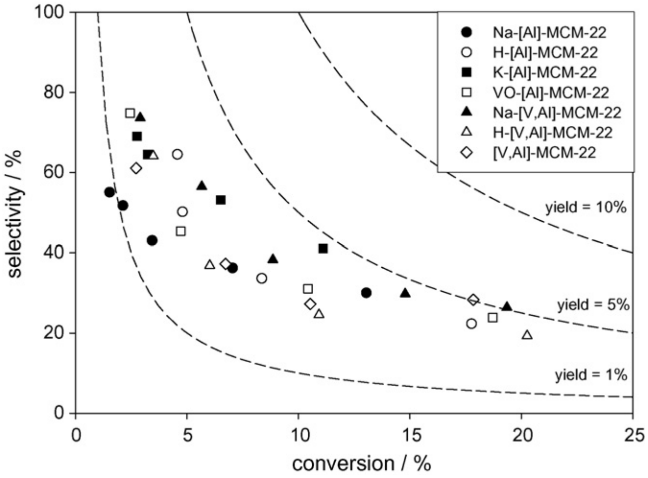

Fig. 4. Selectivity to propene vs. propane conversions for all samples.

It must be underlined that these samples have a low concentration of strong Brønsted acid centres. As a matter of fact Brønsted acid sites present in zeolitic structures possess different behaviour towards ODH reaction according to their acidity, as proposed by Bandiera et al. [17]. According to these authors, propane molecules are initially adsorbed binding preferentially by the C–H bond when the site is weak and by the C–C bond when the site is strong. Thus, dehydrogenation occurs in weak sites (via 1,3 cleavage) leading to propene production and cracking in strong sites (via 1,2 cleavage) leading to methane and ethene production [17].

Catalyst activity may also be compared by means of their turnover frequencies (TOF) at 500 °C (Table 5). Considering the active sites as a sum of the Brønsted acid sites of the type Si(OH)Al and vanadium atoms, the order observed for TOF values was K-[Al]-MCM-22 ≫ Na-[Al]-MCM-22 > Na-[V,Al]-MCM-22 > H-[Al]-MCM-22 > VO-[Al]-MCM-22 > [V,Al]-MCM-22 > H-[V,Al]-MCM-22. The first observation that can be done is that the catalysts containing alkaline cations as counterions, in special K^+, present higher TOF values, which suggests that these cations modify the acid-base characteristics of the catalysts, as already observed in TPD results, having also their activities modified. It is worth noting, for instance, that Na-[Al]-MCM-22 and Na-[V,Al]-MCM-22 have similar TOF values, but the former presents half the *R* value in relation to the last. Those facts show that vanadium ions are important catalytic sites for propane OD in these catalysts.

Considering as active only the vanadium sites, the TOF value observed for Na-[V,Al]-MCM-22, which is the highest obtained in this work (Table 5), is higher than, for instance, 2% niobia-supported vanadium oxide (18.10^{-3} s^{-1} at 425 °C) [18].

Table 5
Turnover frequency data at 500 °C

Sample	TOF ($\times10^{-3}$ s^{-1})[a]	TOF ($\times10^{-3}$ s^{-1})[b]
H-[Al]-MCM-22	0.91	–
Na-[Al]-MCM-22	1.18	–
K-[Al]-MCM-22	7.53	–
[V,Al]-MCM-22	0.78	9.28
H-[V,Al]-MCM-22	0.65	22.7
Na-[V,Al]-MCM-22	1.16	28.5
VO-[Al]-MCM-22	0.80	21.7

[a] Active sites = moles of vanadium + moles of Si(OH)Al (Brønsted sites).
[b] Active sites = moles of vanadium.

4. Conclusions

NH_3-TPD results showed that molecular sieves that contain structural vanadium atoms possess higher acidity in comparison to analogous materials that do not contain vanadium, as well as a higher total number of acid sites. Besides, samples exchanged with alkaline cations present weaker acid sites than samples containing only H^+ as a counter-ion.

When tested in propane oxidative dehydrogenation, vanadoaluminosilicates were more active than aluminosilicates, with similar propene selectivity values. Selectivity to propene may be affected by overoxidation of propane and/or propane, which increases in the presence of vanadium ions. Lowering the number of strong Brønsted acid sites of the molecular sieve can modulate the cracking tendency of the catalysts, enhancing its selectivity. This effect can be obtained by ion-exchange with alkaline cations, in this way removing the stronger acid protons from the structure.

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