CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201200268

Acid/Vanadium-Containing Saponite for the Conversion of Propene into Coke: Potential Flame-Retardant Filler for Nanocomposite Materials

Luca Ostinelli,[a, c] Sandro Recchia,*[a, c] Chiara Bisio,[b, c] Fabio Carniato,[b] Matteo Guidotti,[c] Leonardo Marchese,[b] and Rinaldo Psaro[c]

Abstract: Vanadium-containing saponite samples were synthesized in a one-pot synthetic procedure with the aim of preparing samples for potential application as fillers for polymeric composites. These vanadium-modified materials were prepared from an acid support by adopting a synthetic strategy that allowed us to introduce isolated structural V species (H/V-SAP). The physicochemical properties of these materials were investigated by XRD analysis and by DR-UV/Vis and FTIR spectroscopy of CO that was adsorbed at 100 K; these data were compared to those of a V-modified saponite material that did not contain any Brønsted acid sites (Na/V-SAP). The surface-acid properties of both samples (together with the fully acidic H-SAP material and the Na-SAP solid) were studied in the catalytic isomerization of α-pinene oxide. The V-containing solids were tested in the oxidative dehydrogenation reaction of propene to evaluate their potential use as flame-retardant fillers for polymer composites. The effect of tuning the presence of Lewis/Brønsted acid sites was carefully studied. The V-containing saponite sample that contained a marked presence of Brønsted acid sites showed the most interesting performance in the oxidative dehydrogenation (ODH) reactions because they produced coke, even at 773 K. The catalytic data presented herein indicate that the H/V-SAP material is potentially active as a flame-retardant filler.

Keywords: alkenes · clays · coke · saponites · vanadium

Introduction

One important limit for the utilization of polymers in several domains of everyday life is their low thermal stability and relative high flammability. Different families of inorganic compounds have been used as additives to increase the flame resistance of polymer matrices. In the past, halogenated materials, in particular containing Cl- and Br species, were employed because, during combustion, such additives preferentially release specific radicals, which stop the free-radical mechanism that is responsible for the thermal decomposition of the polymer. Nevertheless, halogenated compounds are often toxic and have a negative impact on both the environment and human health.[1]

For this reason, in the recent literature, the use of alternative halogen-free flame-retardant additives that display different physical- and/or chemical effects on the mechanism of polymer combustion has been proposed.[1] Inorganic hydroxides, such as $Mg(OH)_2$ and $Al(OH)_3$,[1,2] that induce a temperature decrease by heat consumption, along with silica particles,[3] naturals clays,[4] silsesquioxanes,[5] and borates,[1] which promote the formation of inorganic protective layers between the combustion zone and the solid phase, have been exploited to increase the flame-resistance of polymers.

Moreover, acidic clays and metal-containing polyhedral oligomeric silsesquioxanes, which partially decompose the polymer chains, have also been proposed.[6–8] These materials catalyze oxidative dehydrogenation (ODH) reactions, thereby leading to the formation of protective charring layers.

Clay materials have attracted particular interest over the past few decades because they show both physical- and chemical flame-retardance action.[1] In fact, Camino and coworkers[9] reported that the promising behavior of clays was mainly owing to two synergetic effects: the creation of a protective inorganic layer on the surface of the polymer matrix and the formation of charred laminar structures caused by acid sites, which are particularly active in hydrogen-transfer reactions.[10] Among the wide family of layered materials, acidic saponite clays (especially those of synthetic origin) display interesting features as additives for polymer-based nanocomposite materials. Indeed, synthetic saponite solids have high surface acidity (relevant for cracking[11] or epoxide-ring-opening reactions[12]), as well as a tunable morphology and textural properties.[13] In addition, the synthesis of

---

[a] Dr. L. Ostinelli, Prof. S. Recchia
Dipartimento di Scienza e Alta Tecnologia
Università dell'Insubria
Via Valleggio, 11, 22100 Como (Italy)
Fax: (+39) 0312386449
E-mail: sandro.recchia@uninsubria.it

[b] Dr. C. Bisio, Dr. F. Carniato, Prof. L. Marchese
Dipartimento di Scienze e Innovazione Tecnologica and
Nano-SiSTeMI Interdisciplinary Centre
Università del Piemonte Orientale "A. Avogadro"
Viale Teresa Michel, 11, 15121, Alessandria (Italy)

[c] Dr. L. Ostinelli, Prof. S. Recchia, Dr. C. Bisio, Dr. M. Guidotti, Dr. R. Psaro
Istituto di Scienze e Tecnologie Molecolari (ISTM-CNR)
via C. Golgi 19, 20133 Milano (Italy)

these materials can be easily adapted to facilitate the introduction of metal centers that are able to promote redox reactions, thus improving the flame retardance of polymers.

Among the transition-metal ions, vanadium has largely been investigated because of its redox properties: it can be used to catalyze various oxidative dehydrogenations (i.e., MeOH into formaldehyde,[14] ethane into acetaldehyde/acrolein,[15] ethyl benzene into styrene[16]). Therefore, the introduction of vanadium sites on acidic saponite materials can be relevant to enhance the formation of charring products when opportunely dispersed in polymeric matrices, such as poly(olefin)s.

Recently, some of us reported a new vanadium-containing synthetic clay, which is a potentially interesting material for these kinds of applications.[17] This material is a synthetic saponite and contains both vanadium ions, by partially replacing silicon ions in the tetrahedral sheet, and extra-framework vanadium species (Figure 1).

The co-presence of vanadium- and silicon atoms in the same layer generates Brønsted acid sites that are able to produce coke from propene.[17] Thus, the ODH reaction of propene was used as a test reaction for a fast screening of additives because it can improve the capacity of a given catalyst to favor: 1) the production of volatile oxygenated products, 2) the production of coke, and 3) the total combustion of propene. This reaction was actually a model reaction for the evaluation of the flame-retardant properties of polyolefin matrices because the thermal degradation of polypropylene starts with the release of propene.[18]

Nevertheless, as stated above, these preliminary studies were conducted on a V-saponite (V-SAP) solid that was characterized by the presence of both extra-framework- and structural vanadium species, along with surface acid sites, which rendered the comprehension of the catalytic behavior of the V-modified clay difficult. Herein, vanadium-modified materials are prepared by exploiting a fully acidic support and by adopting a synthetic strategy that essentially leads to the formation of isolated structural V sites. Our purpose was to drive the catalytic conversion of propene into coke by exploiting the positive features of both acidic saponite sites and vanadium centers. The catalytic performance of vanadium–saponites in the ODH reaction of propene was compared with that obtained over different metal-free sodium- and acidic saponites (that contain different amounts of Brønsted acid sites). Finally, the acid-catalyzed isomerization of α-pinene oxide was chosen as a test reaction to evaluate the nature of the acid sites.

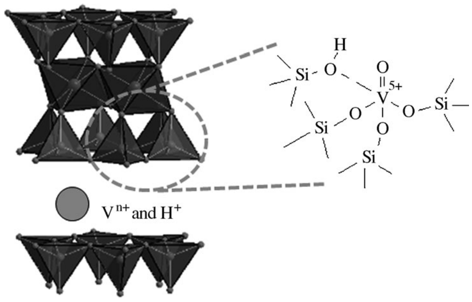


Figure 1. Structure of a synthetic vanadium-containing saponite.

Abstract in Italian: In questo lavoro è stato sintetizzata tramite metodologia “one-pot” una saponite contenente in struttura vanadio, di interesse come additivo per compositi polimerici. La metodologia di sintesi adottata ha permesso di ottenere un solido acido contenente siti di vanadio strutturale isolati (H/V-SAP). Le proprietà chimico-fisiche di tale materiale sono state studiate tramite XRD, DR-UV-Vis e FT-IR di CO adsorbito a 100 K e confrontate con quelle di una V-saponite priva di acidità di Brønsted (Na/V-SAP). Le proprietà acide di entrambi i materiali (e di saponiti acidi H-SAP e sodica Na-SAP) sono state investigate sottoponendo i campioni ad un test catalitico di isomerizzazione dell’ ossido di α-pinene. I campioni contenenti vanadio sono stati infine testati come catalizzatori per la reazione di deidrogenazione ossidativa del propene, con l'obiettivo di valutarne i loro potenziale uso come additivi ritardanti di fiamma per compositi polimerici. La saponite contenente vanadio strutturale e caratterizzata da una marcata acidità di Brønsted ha mostrato le migliori prestazioni catalitiche, producendo prodotti carboniosi anche ad alte temperature di esercizio (773 K). I dati catalitici qui mostrati indicano che il campione H/V-SAP è potenzialmente attivo come ritardante di fiamma per compositi polimerici.

Results and Discussion

Physicochemical Characterization of Vanadium-Containing Saponites

A series of three vanadium-containing saponites (V-SAP, Na/V-SAP, and H/V-SAP) and four vanadium-free saponites (Na-SAP, H-SAP-0.01, H-SAP-0.1, and H-SAP-1) with acidic and redox properties were prepared.

The chemical composition of the vanadium-containing materials are reported in Table 1. The V-SAP sample is characterized by a lower Na content (0.015 $mmol\,g^{-1}$) with respect to the synthetic gel (about 1 $mmol\,g^{-1}$), which suggests that, beside Na^+ ions, the negative charge of the saponite layers is balanced by other counterions (i.e., Mg^{2+}, Al^{3+}, and H^+ ions). The amount of vanadium in V-SAP is 0.06 $mmol\,g^{-1}$.

Results obtained on the Na/V-SAP sample, which was prepared by ion-exchange of the V-SAP solid in a saturated solution of NaCl, indicate that the V-SAP sample contains

Table 1. Na- and V content [$mmol\,g^{-1}$] in V-SAP, Na/V-SAP, and H/V-SAP.

	V-SAP	Na/V-SAP	H/V-SAP
Na	0.015	0.50	0.04
V	0.06	0.05	0.05

a small amount of extra-framework V species, as attested by the fact that the ion-exchange procedure leads to a drop in the total vanadium content (from 0.06 mmol$\,g^{-1}$ for V-SAP to 0.05 mmol$\,g^{-1}$ for Na/V-SAP). In this sample, the amount of Na^+ ions is significantly higher than in the parent, as-synthesized V-SAP solid, thus indicating that extra-framework species, such as Mg^{2+} or Al^{3+} ions, are substituted with Na^+ cations.

Under acidic conditions, the ion-exchange procedure that was used to prepare the H/V-SAP sample (0.01 M HCl solution) resulted in a significant decrease in the Na^+-ion content (from 0.50 to 0.04 mmol$\,g^{-1}$), thus indicating that a large proportion of the interlayer Na^+ ions were replaced by protons. This treatment did not affect the total vanadium content, thereby confirming that all of the extra-framework vanadium ions were replaced in the previous ion-exchange procedure in NaCl solution.

The structural properties of V-SAP before- and after the ion-exchange procedure in both NaCl and acidic solutions were investigated by X-ray diffraction.

According to a literature report,[13] the X-ray pattern of V-SAP (Figure 2 A, curve a) showed (001), (110), (201), and (060) reflections that are typical of a trioctahedral clay, which suggests that the introduction of vanadium into the synthesis gel does not affect the layered saponite structure. The position of the (001) reflection at $2\theta = 6.5°$ indicates that the interlayer spacing in the V-saponite is about 1.3 nm, which is slightly higher than that reported for the Na-SAP sample (11 Å),[13] which showed a broad signal at about $2\theta = 7.8°$ (Figure 2, dashed line). Moreover, the basal reflection of V-SAP is more intense and well-defined with respect to the Na-SAP sample, thus suggesting a more ordered stacking of the clay layers, according to data reported in the literature for metal-containing clay samples.[19]

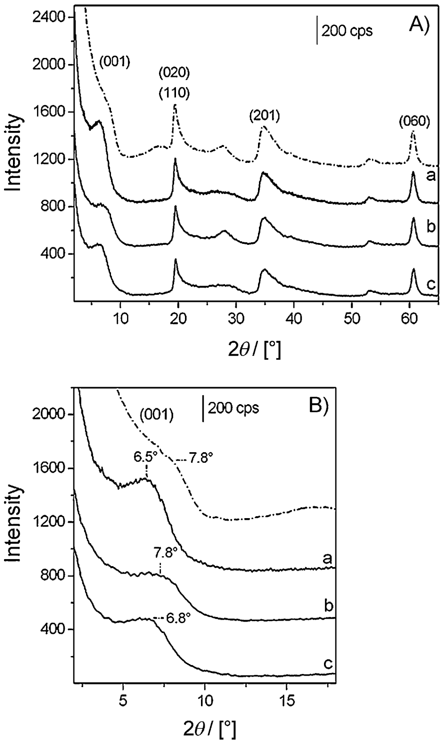


Figure 2. A) XRD profiles of V-SAP (a), Na/V-SAP (b), H/V-SAP (c) and Na-SAP (dashed line); B) expanded view in the range 2–18°.

By replacing the interlayer V cations by Na^+ ions in the Na/V-SAP sample, a more-disordered structure is obtained (Figure 2, curve b), as indicated by a decrease in the intensity and slight broadening of the basal reflection. In addition, the (001) basal reflection shifted to a higher angle (from $2\theta = 6.5°$ to 7.8°) as a consequence of the decrease in interlayer distance.

Treatment under mildly acidic conditions does not significantly alter the structure of the layered material, as indicated by the fact that the XRD profile of the H/V-SAP is similar to that of the parent Na/V-SAP material (Figure 2, curve c). After H^+-ion exchange, the basal reflection is found at $2\theta = 6.8°$, thus indicating a slight increase (of about 0.17 nm) in the interlayer distance compared to Na/V-SAP (Figure 2 c), as has previously been observed for similar samples.[11]

The coordination and oxidation state of the vanadium species in V-SAP and in the exchanged materials (Na/V-SAP and H/V-SAP) were investigated by DR-UV/Vis spectroscopy (Figure 3). As-synthesized V-SAP (Figure 3 a) is characterized by the presence of a broad absorption in the range of 200–350 nm, with a maximum at 230 nm and a shoulder at 270 nm. These bands are assigned to charge-transfer (CT) transitions from oxygen to V^{5+} in distorted (pseudo)tetrahedral oxovanadium $(SiO)_3V{=}O$ species. Three broad bands at about 340, 430, and 600 nm are also observed. The first two bands indicate the presence of V_2O_5-like oligomers, which are probably located in extra-framework positions, whilst the broad absorption at higher wavelength is related to d–d transitions of the V^{4+} cations, thus indicating that the solid contains both V^{5+} and V^{4+} species.[17,20]

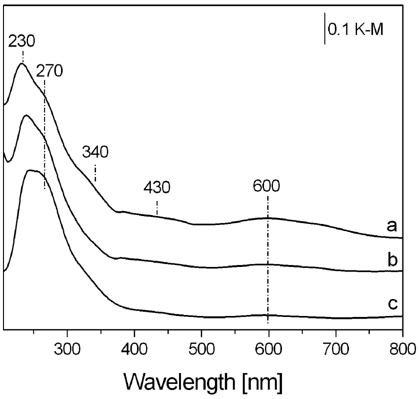


Figure 3. DR-UV/Vis spectra of V-SAP (a), Na/V-SAP (b), and H/V-SAP (c) diluted in a $BaSO_4$ matrix (10 wt.%). The spectra were collected at room temperature after treatment under vacuum conditions at room temperature for 1 h.

The intensity of the band at 600 nm drastically decreases after ion-exchange in NaCl solution (Figure 3b). This evidence suggests that V^{4+} species are mainly located inside the interlayer space of V-SAP and act as countercations of the negative saponite layers. In addition, a marked decrease in the band intensity, which is attributed to the presence of extra-framework V_2O_5 species, is also observed in the UV/Vis spectrum of Na/V-SAP.

The DR-UV/Vis spectrum of H/V-SAP is similar to that of Na/V-SAP (Figure 3c). Nevertheless, in this case, a different ratio of the intensities of the bands at 230 and 270 nm is observed. This change could be assigned to the effect of acid treatment on the local organization of the structural V^{5+} sites.

IR spectroscopy was used to study the redox behavior of the vanadium ions in Na/V-SAP and H/V-SAP materials. IR spectra that were collected upon CO adsorption at 100 K on Na/V-SAP and H/V-SAP pellets, that were oxidized under oxygen at 853 K, are shown in Figure 4. Adsorption of CO onto the Na/V-SAP sample results in changes in the original bands—owing to the formation of surface OH groups—at 3740 and 3700 cm^{-1} (negative bands in Figure 4A),[11] as well as in the broad absorption at about 3625 cm^{-1}; the associated Δν(OH) shifts are equal to about 115 and 75 cm^{-1}, respectively. A precise Δν(OH) shift cannot be given on the basis of the experimental data owing to the broadness of the absorption that is formed upon CO interaction and to its partial overlapping with bands that are characteristic of saponite OH surface groups. These estimated shifts in the OH stretching are related to the interactions between CO and the surface SiOH groups of saponite.

In the ν(CO) stretching region (Figure 4A′), the spectrum is dominated by an intense absorption at 2170 cm^{-1} with a shoulder at about 2160 cm^{-1}. The band at 2170 cm^{-1} can be assigned to CO molecules that are adsorbed onto (or polarized by) Na^+ ions that are present in the interlayer space of the saponite clay, whereas the absorption that is centered at 2160 cm^{-1} is due to the stretching mode of CO in interactions with silanol species.[13]

In addition, a broad band at 2140 cm^{-1}, owing to the stretching vibration of CO that is condensed in a liquid-like state inside the saponite porosities that are generated by particle aggregation, is also observed.[13,17]

The IR spectrum, that is collected upon CO adsorption (60 mbar) at 100 K on the reduced Na/V-SAP sample, shows similar bands to that of the oxidized sample (Figure 5). Nevertheless, a new absorption in the CO stretching region at 2190 cm^{-1}, which disappears after re-oxidation (Figure 5), is observed, which is ascribed to CO interacting with V^{4+} ions that are derived from the reduction of structural V^{5+} species.

A similar study was carried out for the oxidized H/V-SAP sample; the IR spectra that were collected upon CO adsorption at 100 K are shown in Figure 4B,B′.

Beside the absorption at 3630 cm^{-1}, as already observed for the oxidized Na/V-SAP sample, which is more intense for the H/V-SAP sample, two positive absorptions at 3400 and 3250 cm^{-1} appear in the difference spectrum of oxidized H/V-SAP (Figure 4B). The broad band at 3400 cm^{-1} is assigned to the stretching mode of CO molecules that interact with Al−OH and V^{5+}−OH species with medium acidity, in which the Al and V ions are partially extra-framework.[21] The component at 3250 cm^{-1} is associated to the presence of sites with high Brøntsed acidity. According to data reported in the literature for the as-synthesized V-SAP sample,[17] this band can be assigned to the stretching mode of hydroxy groups that are generated by the presence of $Si(OH)V^{5+}$ and Al(OH)Si species that interact with CO probe molecules. The large shift in frequency upon CO absorption ($\Delta\nu = 340\ cm^{-1}$) indicates that the surface acidity of this material is comparable to that of the acid saponites.

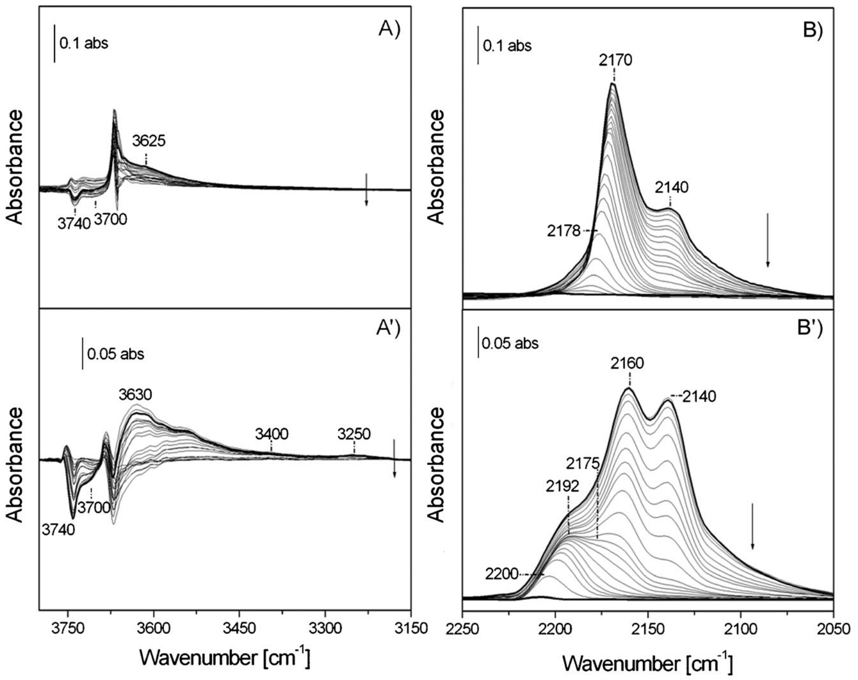


Figure 4. IR spectra of CO that was adsorbed at 100 K (maximum coverage at 60 mbar) on Na/V-SAP and H/V-SAP pellets that were oxidized under an oxygen atmosphere at 853 K. Difference spectra in the ranges 3800–3200 cm^{-1} and 2240–2045 cm^{-1} for Na/V-SAP (A and A′) and H/V-SAP (B and B′) were obtained by subtracting the spectra of the materials before interactions with CO. Arrows indicate decreasing CO pressure.

In the range of 2240–2045 cm^{-1} (Figure 4B′), the spectrum after CO adsorption

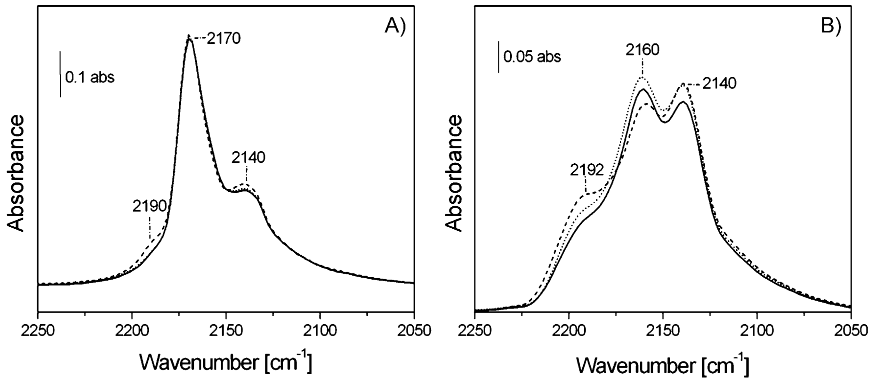
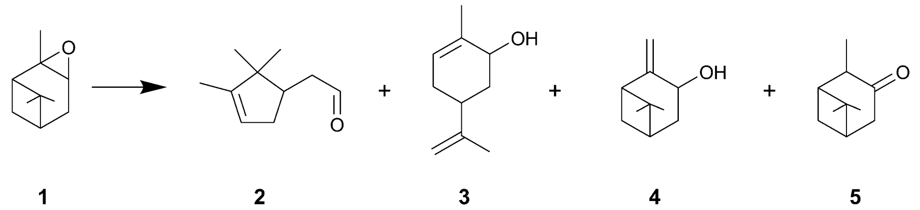


Figure 5. IR spectra of CO adsorbed at 100 K (maximum coverage at 60 mbar) on oxidized- (solid line), reduced- (dashed line), and re-oxidized samples (dotted line) of Na/V-SAP (A) and H/V-SAP (B). Difference spectra in the range 2240–2045 cm^{-1} were obtained by subtracting the spectra of the materials before interactions with CO.

onto the oxidized sample shows an intense band at 2175 cm^{-1}, which is assigned to the stretching mode of CO molecules that interact with both Si(OH)V^{5+} and Si(OH)Al acid sites, as well as bands at 2140 and 2160 cm^{-1}, which were previously observed for the oxidized Na/V-SAP sample. Moreover, the broad and complex component in the range 2200–2192 cm^{-1}, which becomes more evident at low CO pressures, can be associated to the stretching mode of CO molecules that are polarized on the V^{5+} and Al^{3+} sites that are present in the solid.



Scheme 1. Acid-catalyzed isomerization of α-pinene oxide.

As far as the reduced sample is concerned, the band at 2192 cm^{-1} becomes more intense owing to the interactions of CO molecules with V^{4+} ions that are formed during the reduction process (Figure 5), according to that observed for reduced Na/V-SAP. The re-oxidation process of H/V-SAP restores the vibrational profile of oxidized H/V-SAP to a large extent, thus indicating the reversibility of the redox cycle.

Evaluation of the Acidic Character of the Saponite Samples: Isomerization of α-Pinene Oxide

The acidic character of the V-containing saponite samples (Na/V-SAP and H/V-SAP) was also evaluated by using the catalytic isomerization of α-pinene oxide (**1**) in the liquid phase as a test reaction (Scheme 1). The acidity of these solids was compared with that of metal-free acid saponites that were prepared by ionic-exchange in HCl solutions of different concentrations (H-SAP-1, H-SAP-0.1, and H-SAP-0.01; see the Experimental Section and Ref. [11]) and with the Na-SAP sample.

In the presence of acid sites, α-pinene oxide (**1**) easily isomerizes into a series of different compounds: campholenic aldehyde (**2**), carveol (**3**), pinocarveol (**4**), and pinocamphone (**5**). The strength and nature of the acid sites (Lewis or Brønsted) have a direct influence on the amount and distribution of the products formed. Indeed, the use of mild Lewis acid sites largely favors the production of compound **2** together with compounds **4** and **5** as the major side-products, whilst Brønsted acid sites enhance the formation of compound **3** with the main product (**2**).[22–25]

All of the materials show good activity: In all cases, at room temperature, the isomerization is almost complete within 15 minutes (Table 2). In particular, the catalytic activity follows the trend: H-SAP-0.01 ≈ H-SAP-0.1 > H/V-SAP > H-SAP-1 ≈ Na-SAP > Na/V-SAP.

Table 2. Catalytic performance of the saponite materials in the liquid-phase isomerization of α-pinene oxide.

Catalyst	Conversion[a]	Selectivity[b]			
	1 [%]	**2** [%]	**3** [%]	**4** [%]	**5** [%]
H-SAP-0.01	>98	51	27	7	15
H-SAP-0.1	>98	49	29	6	16
H-SAP-1	43	53	25	11	11
Na-SAP	46	55	18	13	14
Na/V-SAP	22	58	12	24	6
H/V-SAP	72	45	31	9	15

Conditions: catalyst (50 mg), α-pinene oxide (100 mg), toluene (8 mL), RT, 5 min. [a] conversion; [b] selectivity for products **2**–**5**.

The materials H-SAP-0.01 and H-SAP-0.1 are particularly active and reactant **1** disappears completely after five minutes. Compound **2** is formed as the major product, together with relevant amounts of carveol (**3**), thus indicating a marked and strong Brønsted character of these samples. H/V-SAP displays a high, albeit less-marked, acid character. Over this solid, the formation of compound **3**, which is favored by the presence of Brønsted sites (i.e., Si(OH)V^{5+} and Si(OH)Al), is maximized. Conversely, the lower activity of H-SAP-1, comparable with that of the sodium-containing Na-SAP, can be ascribed to the dramatic loss of the layered structure that is caused by the treatment in concentrated 1 M HCl solution during the preparation process.[12] Over H-SAP-1, the product-distribution pattern is typical of sites with intermediate Brønsted acid character. On the contrary, over Na-SAP and Na/V-SAP, the formation of products through Lewis acid catalysis is more marked, which is a clue that the ion-exchange process with Na^+ ions leads to a decrease in the Brønsted acid character. Finally, Na/V-SAP is the least-active solid in the isomerization of compound **1** because the thorough treatment of V-SAP with an aqueous solution of NaCl suppresses most of the Brønsted activity, thereby leaving a modest Lewis acid character.

In summary, the highest activity in the isomerization of α-pinene oxide was recorded over vanadium-free protonic saponites. Nevertheless, the H/V-SAP sample also displayed potentially interesting acid character, albeit weaker than purely protonic materials. Conversely, sodium-exchanged samples showed poor activity owing to the extensive exchange treatment by Na^+ cations that largely suppressed the Brønsted acidity in favor of some residual Lewis acid character.

Oxidative Dehydrogenation Tests

The catalytic performance of saponite-based materials for the oxidative dehydrogenation (ODH) of propene are reported in Table 3 and compared to those of a natural montmorillonite clay. Because montmorillonite is known to be a good char-producing flame retardant, it was tested as a "reference" to evaluate the performance of these saponite-based materials.

The behavior of all of the tested catalysts can be described by Equations (1–4):

$$C_3H_6+3\,O_2 \leftrightarrow 3\,CO+3\,H_2O \qquad (1)$$

$$2\,C_3H_6+9\,O_2 \leftrightarrow 6\,CO_2+6\,H_2O \qquad (2)$$

$$2\,C_3H_6+3\,O_2 \leftrightarrow 3\,C+6\,H_2O \qquad (3)$$

$$C+O_2 \leftrightarrow CO_2 \qquad (4)$$

In this four-reaction scheme, C represents carbonaceous coke deposits that are formed/consumed during the ODH tests.

Whereas CO and CO_2 are always reaction products, coke may be formed in reaction (3) and consumed in reaction (4). This property means that the rate of coke formation can be positive, if reaction (3) is faster than reaction (4), or negative, in the opposite case. Thus, a negative rate, which, in principle, does not possess a physical meaning, conventionally indicates that the system is burning the coke that was previously accumulated.

As expected, montmorillonite shows high propene conversion, with the production of coke, CO, CO_2, and water.

The activity of montmorillonite was the highest of all of the observed activities for saponite-based materials but, in spite of this high activity, the final amount of coke that was found on it after the reaction was not the highest. In fact, elemental analysis clearly showed that coke-deposition during the reaction for some saponite samples was higher than that of montmorillonite (Table 3). This result can be explained by looking at the coke-deposition rate: montmorillonite always shows lower rates of coke production than almost all saponite-based materials (Table 3). In particular, the rate of coke deposition already becomes negative (that is, coke is burnt) at 723 K. Thus, if we only look at the coke-production data, we may conclude that all of the saponite-based materials are potentially more interesting than montmorillonite for coke production and, thus, that these samples may have potential interest as flame-retardant fillers.

Some differences can be observed between the saponite materials. For the sake of clarity, the most relevant parameters (Table 3) are shown in Figure 6.

The main factors that affect the reactivity of the samples are: 1) the layered structure of saponite, which is fundamental for promoting the formation of coke layers; 2) the presence of both Lewis- and Brønsted acid sites that catalyze hydrogen-transfer reactions during combustion;[26] and 3) the presence of vanadium, which is known to be active in the ODH of propene.[27,28]

Sodium-containing saponite (Na-SAP) was tested to evaluate the activity of a vanadium-free- and Brønsted-site-free solid. Na-SAP shows the lowest activity at low temperatures and the lowest overall coke production (Figure 6). From the characterization data and the isomerization experiments of α-pinene oxide (see above), this material possesses a layered structure and modest Lewis acid character. Thus, the non-negligible ODH catalytic activity of Na-SAP is likely related to these two main features because both of them can play a positive role in coke production.

Table 3. Catalytic performance of the saponite materials and montmorillonite in the ODH reaction of propene.

Catalyst	Conversion [%]			Coke-formation/consumption rate[a]			CO-formation rate[b]			CO_2-formation rate[c]			Coke deposition[d]
	623 K	723 K	773 K	623 K	723 K	773 K	623 K	723 K	773 K	623 K	723 K	773 K	[wt. %]
H/V-SAP	7	14	21	0.22	0.11	0.02	0.015	0.036	0.061	0.016	0.049	0.078	5.46
Na/V-SAP	4	10	18	0.2	0.04	−0.09	0.004	0.029	0.060	0.006	0.034	0.065	2.04
H-SAP-0.01	5	11	18	0.26	0.17	−0.06	0.006	0.022	0.052	0.007	0.034	0.073	6.10
H-SAP-0.1	5	13	22	0.27	0.21	−0.25	0.003	0.021	0.051	0.005	0.048	0.118	3.39
Na-SAP	2	7	17	0.08	0.02	−0.01	0.002	0.021	0.052	0.003	0.024	0.061	1.55
montmorillonite	11	53	63	0.16	−0.07	−0.57	0.032	0.219	0.303	0.027	0.147	0.177	3.82

[a] Formation/consumption rates expressed in (mmol C) $g_{cat}^{-1}\,min^{-1}$; [b,c] formation rates expressed in (mmol CO) $g_{cat}^{-1}\,min^{-1}$; and (mmol CO_2) $g_{cat}^{-1}\,min^{-1}$, respectively; [d] coke deposition determined by elemental analysis of the exhaust catalysts.

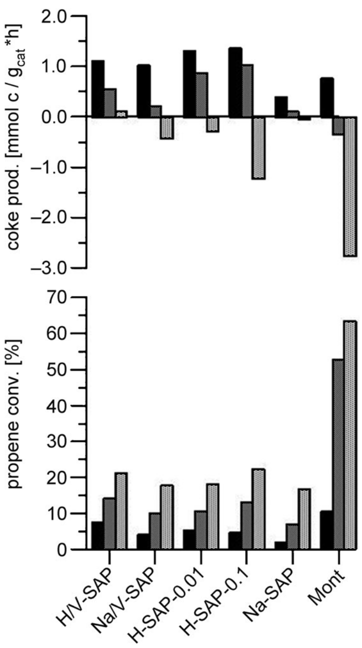


Figure 6. The ODH of propene was performed on various samples. Activity and coke-production data were determined at: 623 K (black), 723 K (gray), and 773 K (light gray).

The catalytic behavior of H-SAP-0.1 and H-SAP-0.01 (generated by ion-exchange reactions) can be easily explained by considering the beneficial effect that the Brønsted acid sites exert in terms of an increased aptitude toward coke formation (Figure 6). On these two latter catalysts, we observe the best low/medium-temperature coke production. At 773 K, both catalysts show a significant tendency towards burning the previously accumulated coke, which is markedly higher for H-SAP-0.1. Instead, H-SAP-1 is completely inactive: As mentioned above, this behavior is due to the observed complete loss of the layered structure (and, thus, of Brønsted acid character) of saponite for this sample. Notably, the isomerization of α-pinene oxide is less sensitive to this dramatic change in the saponite structure because H-SAP-1 shows only a significantly lower (yet non-zero) conversion in this reaction instead of the total loss of activity observed during the ODH tests.

Finally, the role of the co-presence of acid sites and vanadium ions was evaluated by testing the H/V-SAP and Na/V-SAP materials. H/V-SAP always shows higher activity than Na/V-SAP, which means that the presence of Brønsted acid sites increases the reactivity towards propene-conversion (Figure 6). In fact, from the isomerization of α-pinene oxide, Na/V-SAP only showed modest Lewis acid character. Moreover, H/V-SAP is the only sample that still maintains positive coke production at the highest temperature (773 K), which, in turns, prevents coke combustion, thus leading to the deposition of large amounts of coke. This behavior may be ascribed to the synergetic effect of the presence of structural vanadium ions and surface acid sites.

The lower overall amount of coke deposited for H/V-SAP (5.46 wt.%) with respect to H-SAP-0.01 (6.10 wt.%) should not lead to an incorrect interpretation of the compared performances of these two catalysts. In fact, we must keep in mind that both catalysts are only tested at the highest temperature for 30 min. It is reasonable to suppose that the results of a longer test could be significantly different because H/V-SAP still produces coke at 773 K, whilst H-SAP-0.01 burns coke at this temperature.

In summary, H/V-SAP is probably the most-interesting catalyst because it shows good performance at low temperatures (in both propene-conversion and coke-production) and because it is the only system that still produces coke at 773 K (Figure 6).

Conclusions

Herein, two different saponite clays that contain vanadium ions in structural positions have been successfully prepared by using a one-pot approach. In one case, Brønsted acid sites were generated by ion-exchange of Na/V-SAP under mild-acid conditions, with the aim of exchanging interlayer Na$^+$ ions with protons.

The introduction of V into the synthesized gel does not affect the final structure of the V-SAP sample, which is similar to that in classically prepared saponite clays.

The coordination and oxidation state of V in both samples were studied by DR-UV/Vis spectroscopy, which indicated that the samples contain V^{5+} ions in a distorted (pseudo)tetrahedral geometry. H/V-SAP and Na/V-SAP did not contain a significant amount of extra-framework species because they were removed during the exchange procedures.

The redox behavior of the samples was investigated by FTIR spectroscopic analysis of the adsorbed CO at 100 K. For both samples, most of the V ions underwent redox cycles.

The acidity of these V-containing saponites was evaluated on a model catalytic reaction (the isomerization of α-pinene oxide) and compared to that of fully acid H-SAP materials (which contain different amounts of Brønsted acid sites), as well as with Na-SAP. Na/V-SAP has a weak Lewis acid character, whereas H/V-SAP is characterized by a marked Brønsted acid character, even if this sample is less acidic than metal-free purely protonic H-SAP samples.

All of the samples were tested in the ODH reaction of propene to study their capability to form carbonaceous species, which are interesting for applications in flame-retardant materials in polymer science. All of the tested materials (i.e., V-containing samples, acid saponites, and Na-SAP) show interesting activities in propene-conversion and coke-formation (with different coke-formation rates depending on the chemical nature of the catalyst). Nevertheless, apart from the bifunctional H/V-SAP sample, all of the catalysts tend to decompose coke at a high working temperature because they favor coke-combustion reactions. On the contrary, H/V-SAP is the most interesting catalyst because it shows good activities at low temperatures and because it is the only system that still maintains a positive coke production at high temperature (773 K). This result indicates that, although the lamellar structure is fundamental to drive the ODH of propene toward the formation of coke, the overall performance of these materials significantly increases with the co-presence of V ions and Brønsted acid sites.

Experimental Section

Vanadium-Containing Saponite Samples

(V-SAP): Vanadium-containing saponite clay (gel composition $(Na)_{0.81}Mg_6(OH)_4(Al_{0.81}V_{0.07}Si_{7.11})O_{20}{\cdot}n\,H_2O$, H_2O/Si 20:1, nominal cationic exchange capacity (CEC): 104.9 milliequiv/100g was prepared according to an optimized literature procedure.[17]

Amorphous silica (SiO_2, 6.68 g, 99.8 %, Aldrich) and aluminum isopropoxide ($Al[OCH(CH_3)_2]_3$, 3.20 g, 98 %, Aldrich) were suspended in water (45 mL) that contained NaOH (0.63 g). After 1 h, magnesium acetate tetrahydrate ($Mg(CH_3COO)_2{\cdot}4\,H_2O$, 24.86 g, 99 %, Aldrich) was added to the suspension (gel 1). In parallel, vanadium(IV) oxide sulfate hydrate ($VOSO_4{\cdot}x\,H_2O$, 0.22 g, 97 %, Aldrich) was added to a suspension that was prepared by dissolving tetraethylorthosilicate (TEOS, 5.6 g, 98 %, Aldrich) in a small amount of EtOH (99.5 %, Aldrich). Two drops of HCl 37 % were added to the solution to promote the condensation of TEOS and $VOSO_4$.

Finally, the solution was added to the gel and the mixture was poured into a PTFE cup in a sealed autoclave and heated at 513 K for 72 h.

After the hydrothermal crystallization process, the crystalline products were filtered and washed with deionized water to neutral pH value. The material was dried in an oven at 373 K for 24 h.

Na/V-SAP: V-SAP (1 g) was submitted to a classical ion-exchange process in a saturated solution of NaCl for 36 h at RT to completely replace the cations that were present in the interlayer space by Na^+ ions. Next, the solid was filtered and washed with deionized water until complete elimination of chloride had occurred (the presence of chloride was tested in all washings with $AgNO_3$).

H/V-SAP: Part of the Na/V-SAP solid underwent an ion-exchange process in acidic solution to activate the surface acidity through the replacement of interlamellar Na^+ ions by protons. Thus, Na/V-SAP was placed in contact with a 0.01 M HCl solution. The ion-exchange process was performed at RT under stirring for 36 h. H/V-SAP was obtained after filtration and washed until the chlorides had disappeared.

Sodium-Containing Saponite

Na-SAP: This solid was prepared according to a literature procedure.[11]

Acid Saponite Samples

H-SAP-0.01, H-SAP-0.1, and H-SAP-1: To replace the Na^+ ions with H^+ ions, Na-SAP (obtained as above described) was exchanged by using HCl solutions of different concentrations (0.01, 0.1 and 1 M, respectively). The ion-exchange reaction was performed for all saponite fractions under the synthetic conditions that were adopted for the H/V-SAP sample. These materials are named: H-SAP-0.01, H-SAP0.1, and H-SAP-1, according to the HCl concentration that was used for the ion-exchange.

ODH Reactions

The oxidative dehydrogenation (ODH) tests were performed under atmospheric pressure in a fixed-bed quartz tubular reactor (internal diameter: 4 mm). The feed was composed from a mixture of propene/oxygen/argon with a molar ratio of 3.75:7.5:88.75 and a total flow rate of 40 mL min^{-1}. The reactant mixture was generated by using three calibrated mass-flow controllers. The reported flows were chosen to work under various conditions, even with the most active catalyst. The catalytic tests were performed in the temperature range 623–773 K to evaluate the behavior of saponite-based materials immediately after the temperature at which polypropylene starts to decompose.[12] The reactants and gaseous reaction products were analyzed by using an online mass spectrometer (VG instruments, mod. VG2, m/z 0–200). In addition, a downstream cold trap (kept at 273 K) was inserted to eventually collect the condensable products. All tests were performed according to the following procedure: The solid catalyst (100(±1) mg) was introduced into the reactor (with a resulting catalyst-bed size of about 10–12 mm). The loaded catalyst was then degassed for 20 min at RT under a pure-Ar atmosphere. To allow for the calibration of the mass spectrometer, the reactor was isolated by using a bypass valve. Signals were then calibrated by using, in sequence, 2 % CO_2 (98 % Ar) and 2 % CO (98 % Ar) mixtures. Finally, propene and O_2 were calibrated by using the feeding gas mixture. Next, the reactor was inserted into the feeding flow and, after the complete stabilization of every mass channel, the reactor was heated at a ramp rate of 10 K min^{-1}. At 623 K, 723 K, and 773 K, the heating was temporarily stopped for 30 min to evaluate the catalytic behavior under steady-state conditions.

Conversions were calculated over the $m/z = 41$ (propene) channel. Moreover, we decided to show the rates of product-formation/depletion rather than selectivities because one of the products (coke) may also act as a reagent (see below). Formation rates (FR) were calculated according to Equation (5) and should be viewed as the average rate over the entire isothermal step. Coke-formation/depletion rates were calculated indirectly by taking into account the total carbon content as determined by elemental analysis.

$$FR = \frac{\text{mmol}_{\text{product}}}{\text{g}_{\text{catalyst}} \times \text{min}} \qquad (5)$$

Liquid-Phase Isomerization of α-Pinene Oxide

The isomerization reactions of (−)-α-pinene oxide (100 mg; 97 %, Aldrich) were performed in the liquid phase in a glass batch reactor (stirring rate: 1000 rpm) at RT by using toluene (8 mL; puriss., Riedel-de-Haën) that had previously been dried over molecular sieves (3 Å, Siliporite) as the solvent. The solid catalyst (50 mg) was pre-treated at 150 °C for 1 h in vacuo. The reaction was performed for 15 min and samples were taken after 5, 10, and 15 min. The reaction products were determined by GC analysis (HP5890; HP-5 column, 30 m × 0.25 mm; FID or MS detectors, head pressure: 160 kPa). The standard deviations in the conversion and selectivity values were (±2) % and (±3) %, respectively. Mesitylene (Fluka) was used as an internal standard.

Characterization Techniques

Chemical analysis of the materials was performed by using inductively coupled-plasma–mass-spectrometry (ICP-MS) and by atomic absorption spectroscopy (AAS) by ITECON laboratory (Nizza Monferrato, Italy).

X-ray diffraction (XRD) analysis was performed on a Thermo ARL ′XTRA-048′diffractometer by using a $Cu_{K\alpha}$ source. X-ray profiles were recorded at RT in the range $2\theta = 2$–65° with a rate of 1° min^{-1}.

Diffuse-reflectance UV/Vis (DR-UV/Vis) spectroscopy was performed on a Perkin–Elmer Lambda 900 spectrometer that was equipped with an integrating sphere accessory and by using a custom-made quartz cell that allowed analysis both under vacuum (residual pressure = 10^{-5} mbar) and under controlled gas atmospheres. Prior to the analysis, the sample was dispersed in anhydrous $BaSO_4$ (10 wt. %) and degassed at RT for 1 h.

After the ODH tests, a portion of the catalysts was analyzed with a Perkin–Elmer Series II elemental analyzer 2400 to quantify the carbon that was present on the catalyst surfaces.

FTIR analysis was performed on a Thermo Electron FT Nicolet 5700 Spectrometer that was equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm^{-1}. Before IR analysis, pelletized samples were oxidized and reduced according to the following procedure: Oxidized samples were obtained by treating the pellets under O_2 pressure (80 mbar) at 853 K for 3 h and reduced samples were obtained under H_2 pressure (80 mbar) at 773 K for 3 h. Finally, both of the oxidized and reduced samples were treated for 30 min under vacuum at 523 K and

773 K, respectively. After thermal treatment, the oxidized and reduced samples were cooled at 100 K in a custom-made IR cell that was connected to the vacuum line, which allowed all treatments and adsorption experiments to be performed in situ. Both the oxidized and reduced samples were characterized by CO adsorption at 100 K.

Acknowledgements

L.O., M.G., and R.P. acknowledge the Italian Ministry of Education and Scientific Research through the network “Rete Nazionale di Ricerca sulle Nanoscienze-ItalNanoNet” (project no. RBPR05JH2P) for financial support.

---

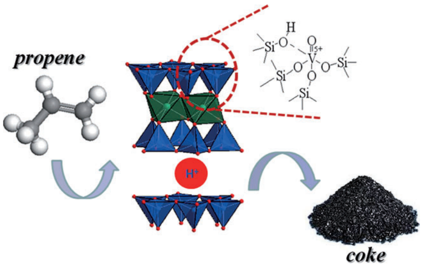
[1] F. Laoutid, L. Bonnaud, M. Alexandre, J.-M. Lopez-Cuesta, Ph. Dubois, *Mater. Sci. Eng.* **2009**, *63*, 100.
[2] L. Qiu, R. Xie, P. Ding, B. Qu, *Compos. Struct.* **2003**, *62*, 391.
[3] J. W. Gilman, T. Kashiwagi, R. H. Harris, Jr., S. Lomakin, J. D. Lichetenhan, P. Jones, A. Bolf in *Chemistry and Technology of Polymer Additives* (Eds.: S. Al-Malaika, C. Wilkie, C. A. Golovoy), Blackwell Science, London, **1999**.
[4] M. Zanetti, T. Kashiwagi, L. Falqui, G. Camino, *Chem. Mater.* **2002**, *14*, 881.
[5] S. Bourbigot, S. Duquesne, C. Jama, *Macromol. Symp.* **2006**, *233*, 180.
[6] J. W. Gilman, *Appl. Clay Sci.* **1999**, *15*, 31.
[7] L. A. Utracki, M. Sepehr, E. Boccaleri, *Polym. Adv. Technol.* **2007**, *18*, 1.
[8] A. Fina, H. C. L. Abbenhuis, D. Tabuani, G. Camino, *Polym. Degrad. Stab.* **2006**, *91*, 2275.
[9] H. O. Pastore, A. Frache, E. Boccaleri, L. Marchese, G. Camino, *Macromol. Mater. Eng.* **2004**, *289*, 783.
[10] R. Song, Z. Wang, X. Meng, B. Zhang, T. Tang, *J. Appl. Polym. Sci.* **2007**, *106*, 3488.
[11] C. Bisio, G. Gatti, E. Boccaleri, L. Marchese, L. Bertinetti, S. Coluccia, *Langmuir* **2008**, *24*, 2808.
[12] M. Guidotti, R. Psaro, N. Ravasio, M. Sgobba, F. Carniato, C. Bisio, G. Gatti, L. Marchese, *Green Chem.* **2009**, *11*, 1173.
[13] C. Bisio, G. Gatti, E. Boccaleri, L. Marchese, G. B. Superti, H. O. Pastore, M. Thommes, *Microporous Mesoporous Mater.* **2008**, *107*, 90.
[14] G. V. Isaguliants, I. P. Belomestnykh, *Catal. Today* **2005**, *100*, 441.
[15] Z. Zhao, Y. Yamada, Y. Teng, A. Ueda, K. Nakagawa, T. Kobayashi, *J. Catal.* **2000**, *190*, 215.
[16] N. R. Shiju, M. Anilkumar, S. P. Mirajkar, C. S. Gopinath, B. S. Rao, C. V. Satyanarayana, *J. Catal.* **2005**, *230*, 484.
[17] F. Carniato, C. Bisio, G. Gatti, S. Roncoroni, S. Recchia, L. Marchese, *Catal. Lett.* **2009**, *131*, 42.
[18] F. Carniato, A. Fina, D. Tabuani, E. Boccaleri, *Nanotechnology* **2008**, *19*, 475701.
[19] J. Breu, W. Seidl, A. Stoll, *Z. Anorg. Allg. Chem.* **2003**, *629*, 503.
[20] A. Albuquerque, L. Marchese, L. Lisi, H. O. Pastore, *J. Catal.* **2006**, *241*, 367.
[21] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Petrini, G. Leonfanti, M. Padovan, C. Otero Areàn, *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 2959.
[22] J. Kaminska, M. A. Schwegler, A. J. Hoefnagel, H. van Bekkum, *Recl. Trav. Chim. Pays-Bas.* **1992**, *111*, 432.
[23] K. Wilson, A. Renson, J. H. Clark, *Catal. Lett.* **1999**, *61*, 51.
[24] D. B. Ravindra, Y. T. Nie, S. Jaenicke, G. K. Chuah, *Catal. Today* **2004**, *96*, 147.
[25] N. Ravasio, F. Zaccheria, M. Guidotti, R. Psaro, *Top. Catal.* **2004**, *27*, 157.
[26] B. N. Jang, M. Costache, C. A. Wilkie, *Polymer* **2005**, *46*, 10678.
[27] P. Knotek, L. Čapek, R. Bulánek, J. Adam, *Top. Catal.* **2007**, *45*, 51.
[28] O. R. Evans, A. T. Bell, T. D. Tilley, *J. Catal.* **2004**, *226*, 292.

Received: March 28, 2012

Oxidative Dehydrogenation

*Luca Ostinelli, Sandro Recchia,**
Chiara Bisio, Fabio Carniato,
Matteo Guidotti, Leonardo Marchese,
Rinaldo Psaro ———— ■■■■–■■■■

Acid/Vanadium-Containing Saponite for the Conversion of Propene into Coke: Potential Flame-Retardant Filler for Nanocomposite Materials



A hard day's saponite: An acid/vanadium-containing saponite (H/V-SAP) was synthesized and its physicochemical properties were compared to those of a V-modified saponite material that did not contain acid sites. Both samples were tested in the oxidative dehydrogenation (ODH) reaction of propene to study the capability of the samples to form coke species. H/V-SAP was the most interesting catalyst for the production of coke.