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Thermal treatment study of vanadium-loaded hydrotalcites employing *in situ* DXAS

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Abstract

A comparative study was made in which two hydrotalcites were loaded with vanadium employing different procedures: (1) aqueous phase impregnation, with vanadyl sulfate solution in pH 6.5 or 9.5; (2) solid phase mixing, with vanadyl sulfate or vanadium pentoxide physically mixed up. TPR investigation revealed that vanadium-loaded hydrotalcites obtained by aqueous phase impregnation in two distinct pH, resulted in different reduction profiles. The vanadium-loaded hydrotalcites were characterized by FTIR, XRD and TGA–DTA analysis. *In situ* dispersive XAS (DXAS) spectra obtained during thermal treatment in air showed that, for the physical mixture of solids, vanadium is oxidized above 350 °C. For the samples prepared by aqueous phase impregnation, the effect of alkaline pH was to produce polymeric vanadium species deposited onto the HT in comparison with the isolated vanadium species in acidic conditions. The influence of both, the hydrotalcite interlayer anion type and the vanadium loading procedure, on the reducibility of vanadium species is also discussed.

Keywords: Hydrotalcite; Vanadium; Catalyst; XAS; DXAS; FTIR

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1. Introduction

The formation and dispersion of vanadium species on the hydrotalcites (HTs) perform an important role on the catalytic properties of HT-based catalysts. Hydrotalcites are cited in the literature as anionic clays which have several applications [1] and a review about its preparation, characterization and properties was issued previously [2,3]. Hydrotalcites are combined with other ingredients in order to produce absorbents, pharmaceuticals, cosmetics, surfactants and catalysts. They can be used a.s. (as such) or, most often, after mild thermal treatment that results in a homogeneous mixture of oxides with very small crystal size and high surface area. Besides basic, HT shows the property of *memory effect*, restoring its starting structure after calcinations followed by re-hydration. Nevertheless, if undergoing calcinations above 600 °C, it yields irreversibly a mixture of oxides. HT has a layered structure, which can accommodate M(II) and M(III) ions among OH groups, forming brucite-like layers. The hydrotalcite most cited in the literature has the general formula $Mg_6Al_2(OH)_{16}CO_3\cdot n(H_2O)$ ($n = 2$–5). Moreover, it has been published a myriad of studies about synthesis and characterization of hydrotalcite-like compounds (HTlc), which can be made up of oxides mixtures of varied compositions [4]. Spectroscopic techniques such as XAS, EXAFS, FTIR and Raman have been widely used in studies involving the anions of the interlayer [5] and the cations distribution in the layers [6,7]. Despite the large number of characterization studies issued, many basic questions still remain unexplained, as the oxidation states and the coordination geometries of chemical species on the surface and the influence of HT composition on the reactivity. More recently, several studies have been reported

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about the investigation of vanadium supported HTs and HTlcs to catalyze oxidative dehydrogenation of alkanes to form olefins, catalytic selective reduction of NO_x to form NH_3 and controlled oxidation of SO_2 to form SO_3. The good catalytic activity and selectivity showed by such materials are ascribed to the alkalinity and to the presence of isolated species of tetrahedral V^{5+} located on the surface of the catalyst [8].

The knowledge of the interactions between vanadium and its neighborhood environment in oxides and common minerals has been reviewed and published in the literature [3]. Spectroscopic methods, as FTIR and synchrotron radiation analysis (XANES, DXAS, EXAFS), have been useful tools to carry out *in situ* thermal treatment studies in order to investigate vanadium coordination changes [9].

Some articles and monographies cite the use of V–HT to reduce the NO_x and SO_x emissions [10,11]. In these applications, vanadium oxides are deposited on HT to furnish active sites for redox reactions, such as the oxidation of SO_2 to SO_3 to promote its uptake as sulfates on the alkaline sites and the reduction of the metal sulfate to H_2S. On the other hand, mobile vanadium species are a great poison for fluid cracking catalysts (FCC). It is necessary a thorough knowledge of the chemistry involved between vanadium and the catalyst surface in order to improve the vanadium tolerance of the catalyst. For example, it was suggested that the deposition of a layer of Al_2O_3 on the USY zeolite surface can passivate vanadium, based on the deposition of the Keggin ion, a species too large to penetrate into the zeolite canals or pores [12] and that shows preferential absorption for V^{4+}.

This work aims to contribute to the fundamental aspects of employing HTs as additives to FCC catalysts. It was investigated the interaction between HTs and vanadium, that is, the influence of the vanadium loading procedures and the effect of temperature treatment on such systems. Thus, the HT-vanadium systems were compared, notably the following parameters being considered:

(1) Interlayer anion type—hydroxyl versus carbonate.
(2) Vanadium introduction procedure—aqueous phase impregnation versus physical mixture of solids.

2. Experimental

2.1. Materials and methods

In this work two HTs were used, both produced according to patent applied by Akzo-Nobel [13]. The HTs interlayer anions were, respectively, hydroxyl (HT-OH^-, sample code HT20) and carbonate (HT-CO_3^{2-}, sample code HT21). The vanadium sources were vanadyl sulfate ($VOSO_4 \cdot 5H_2O$) and vanadium pentoxide (V_2O_5), both P.A. grade and supplied by Aldrich.

From HT-OH^- and HT-CO_3^{2-} two series of samples were prepared via liquid phase impregnation, to obtain V–HTs containing, respectively, 4 and 10 wt% of vanadium. For the impregnation, 10 g d.b. (dry basis) of HT in aqueous suspension (20 wt% solids) was maintained at 50 °C under stirring. Then, the necessary stoichiometric amount of $VOSO_4$ dissolved in 30 g of distillated water was added. The resulting pH 6.5 was measured during the preparations. Depending on the case, it was dosed simultaneously a solution 12 wt% of ammonium hydroxide to maintain the pH 9.5. The stirring was held further during half an hour. Afterwards, the suspension was filtered and the cake dried at 120 °C overnight.

From HT-CO_3^{2-} an additional series was prepared from simple physical mixture of HT a.s. with either $VOSO_4 \cdot 5H_2O$ (HT-CO_3^{2-} + $VOSO_4$, sample code FRC015) or V_2O_5 (HT-CO_3^{2-} + V_2O_5, reference sample), in the proportion 1:1 of solids.

The vanadium content of the samples was determined by X-ray fluorescence (XRF) by an analyzer Phillips, model PW 2400. The measurement of mesopores and BET surface area were determined by an Analyzer Gemini, model 2360. Before measuring, the samples were pre-treated inside the analyzer, in an inert atmosphere, at 300 °C, for 1 h. X-ray diffraction (XRD) analyses of the samples were obtained in an X-ray diffractometer Philips; model PW 1710, with the Cu Kα radiation. The infrared spectra were obtained from samples waivers in KBr, in a Fourier transform infrared (FTIR) Spectrometer Nicolet, model Magna-IR 760. Thermogravimetric and differential thermoanalysis (TGA–DTA) were carried out in an instrument Universal TA, model TGA 2960, between 20 and 1000 °C, with 10mg of sample, heating rate = 20 °C/min and air flow rate = 100 ml/min.

2.2. DXAS study—thermal treatment up to 600 °C

Some vanadium containing samples underwent thermal treatment in air, in an induction oven, heating rate 10 °C/min, flats at 200, 350, 450, and 600 °C. This thermal treatment was monitored by *in situ* measurements in the K-edge of vanadium (5465 eV), at the D06A-DXAS line of the Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil). The energy resolution was estimated to be 0.8 eV. During the measurements, the synchrotron radiation beam was focused on a self-supported thin sample pellet, in a quartz sample holder mounted inside the induction oven. The systems investigated were:

(1) HT-CO_3^{2-} + $VOSO_4$ (1:1);
(2) HT-CO_3^{2-} + V_2O_5 (1:1), as reference;
(3) HT-CO_3^{2-} and HT-OH^-, respectively, with 10 wt% of V, obtained by $VOSO_4$ impregnation in pH 6.5 or 9.5.

2.3. TPR study—thermal treatment up to 800 °C

Temperature programmed reduction (TPR) was carried out in some vanadium containing samples, in a quartz reactor attached to a mass spectrometer (MS). Inside the reactor, the sample contacted a gas stream composed of 1.51 vol% of hydrogen in argon, flow rate = 60 ml/min. Heating increased at 10 °C/min up to 800 °C and was held at this temperature for 2 h. The variation of the gas stream composition was measured by the MS and allowed drawing graphics of hydrogen consumption as a function of temperature.

Table 1
Characteristics and codes of investigated samples

Sample code	HT anion type	V (%)	SO_4 (%)	pH of the impregnation	BET SA (m^2/g)		Meso SA (m^2/g)	
					Fresh	800 °C	Fresh	800 °C
HT20	Hydroxyl	0	0.19	n.a.	39	140	87	277
HT21	Carbonate	0	0.08	n.a.	49	188	48	171
FRC003	Hydroxyl	10	n.d.	6.5	161	n.d.	172	n.d.
FRC004	Hydroxyl	10	n.d.	9.5	162	n.d.	293	n.d.
FRC007	Hydroxyl	4	4.15	6.5	36	171	79	191
FRC008	Carbonate	10	n.d.	6.5	140	n.d.	105	n.d.
FRC009	Carbonate	10	n.d.	9.5	136	n.d.	108	n.d.
FRC012	Carbonate	4	1.62	6.5	78	204	55	78
FRC015	Carbonate	16	19	n.a.	n.d.	n.d.	n.d.	n.d.

Notes: (1) n.a. = not applicable; (2) n.d. = not determined.

3. Results and discussions

Table 1 shows that the area of the samples is low due to the presence of interlayer material, which is in part removed as the samples are submitted to temperature increase, resulting in a higher surface area.

XRD results issued earlier [14] showed higher crystallinity for HT-CO_3^{2-}. The XRD diffractograms remained unchanged after $VOSO_4$ loading. After calcinations at 800 °C, all impregnated samples showed BET surface area increase and very similar XRD diffractograms, suggesting that the calcination leads to the formation of a mixture of the oxides composed of Al_2O_3, MgO and, additionally for V–HTs, V_2O_5.

The HTs showed quite intense absorptions in the FTIR spectra, below 800 cm^{-1}, ascribed to vibrations of the anion CO_3^{2-} and of the chemical bonds Mg–O and Al–O [2]. Fortunately, they did not show intense bands in the range between 1000 and 1300 cm^{-1}, allowing the V–HTs characterization through an intense band attributed to the stretching vibration of the V═O bond near 1110 cm^{-1} (Figs. 1 and 2), also observed in the $VOSO_4$ spectrum. The force constant of this vibration is very sensitive to bond length variations [15]. A shifted V═O band was observed in the FTIR spectra of the V–HTs prepared in acidic pH. The weakening of the V═O band observed in the spectrum of HT-CO_3^{2-} + $VOSO_4$ sample impregnated in basic pH (FRC009) evidenced the partial decomposition of vanadyl during the impregnation (Fig. 2).

Considering the stability of vanadium(IV) species in aqueous solution as a function of pH [16], one can verify that, above pH 9.5, species such as $[(VO)_2(OH)_5]^-$, $[(VO)_4(OH)_{10}]^{2-}$ and $[(VO)_2(OH)_6]^{2-}$ are predominating, as well as the yellow-brown $[V_4O_9]^{2-}$ and $[VO_4]^{4-}$. On the other hand, below pH 6.5, the predominating species is $[(VO)_2(OH)_2]^{2+}$. It is also known and reported in the literature [3] that several vanadium species condensate yielding polymeric oxygen-sharing compounds [17]. Thus, vanadium loading in those pHs should lead to different V–HT interactions. However, the presence of V^{5+} species in the samples investigated was detected by DXAS (no variation of the pre-edge peak energy), even before the temperature treatment, as it will be discussed thereinafter. Therefore, one assumes the vanadium can undergo oxidation, from +4 to +5, during the impregnation process.

The two peaks observed in the TGA–DTA, at 205 °C (loss of water from the interlayer) and 410 °C (loss of hydroxyls from the brucite-like layers and loss of anions from the interlayer),

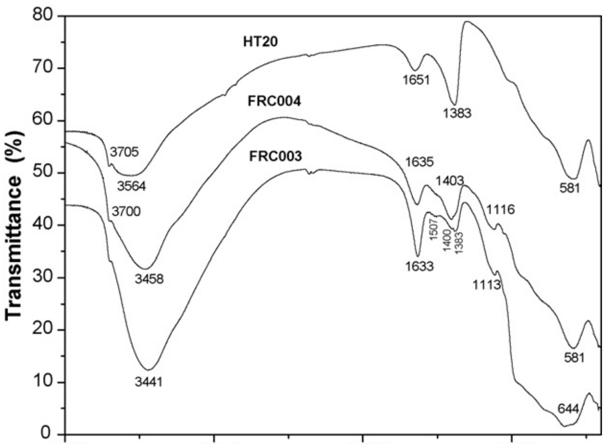

Fig. 1. FTIR spectra of HT-OH^- a.s. (HT20) and impregnated with 10% of vanadium in pH 6.5 (FRC003) and pH 9.5 (FRC004).

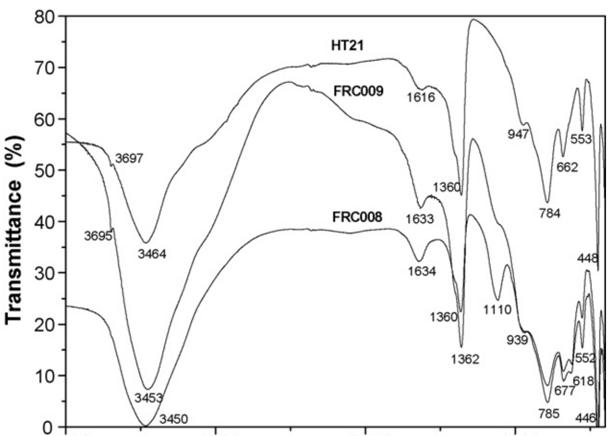

Fig. 2. FTIR spectra of HT-CO_3^{2-} a.s. (HT21) and impregnated with 10% of vanadium in pH 6.5 (FRC008) and pH 9.5 (FRC009).

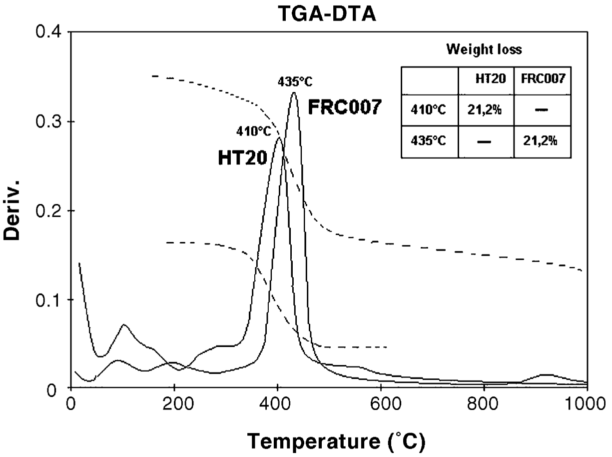

Fig. 3. TGA–DTA of HT-OH$^-$ a.s. (HT20) and impregnated with 4% of vanadium in pH 6.5 (FRC007).

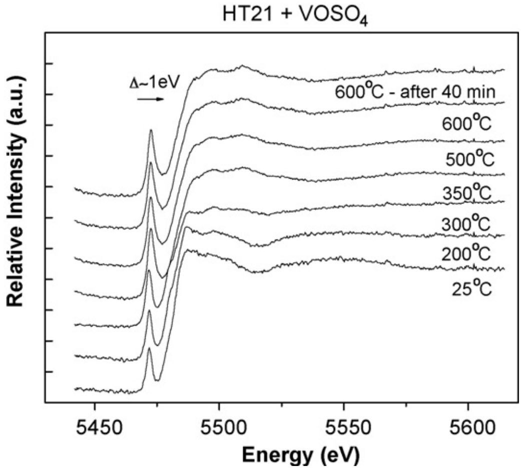

Fig. 5. DXAS spectra of the sample HT-CO$_3^{2-}$ + VOSO$_4$ (FRC015), V-loading in solid state.

suggest the presence of only one phase in the HTs samples (Figs. 3 and 4) [18]. In the case of HT-CO$_3^{2-}$, the second peak displays an overlap of three peaks, respectively, at 325, 380 and 415 °C. The first two peaks represent the exclusion of carbonate, species which is absent in HT-OH$^-$. V–HTs and HTs showed peaks correspondingly similar, but it was observed a shift of the second peak of about +20 °C.

Wong et al. [19] showed that the main-edge energy position in the XAS spectra of vanadium compounds contains information about the valence of the V cation, and the pre-edge intensity informs about the vanadium coordination. Symmetrical vanadium-ligand coordinations with inversion of the symmetry, such as strictly regular [VO$_6$] octahedra, do not present pre-edge peaks, while coordinations without symmetry inversion, such as genuine [VO$_4$] tetrahedra, display the highest pre-edge intensities. Deviations from regular octahedral symmetry, five-coordinated species and distorted tetra-coordinated environments are therefore expected to afford a range of pre-edge peaks intensities, which could be used as a probe for vanadium coordination. Thus, the *in situ* DXAS study would allow the verification of changes in vanadium closest neighborhood, due to the oxides mixture formation mentioned previously, as well as the vanadium oxidation during the thermal treatment up to 600 °C.

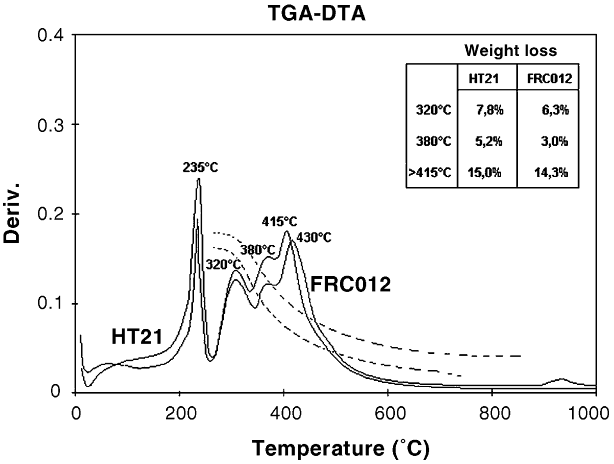

Fig. 4. TGA–DTA of HT-CO$_3^{2-}$ a.s. (HT21) and impregnated with 4% of vanadium in pH 6.5 (FRC012).

From the spectra of the sample HT-CO$_3^{2-}$ + VOSO$_4$ (physical mixture of solids, sample code FRC015), the peak intensity, I_0, determined from the pre-edge peaks height (5468–5469 eV), increased with the temperature, until 350 °C. Furthermore, the ratios between the peaks, I_1/I_0 ($I_1 = 5487$ eV) and I_2/I_0 ($I_2 = 5507$ eV), followed the inverse trend (Fig. 5 and Table 2). It means alteration of the vanadium neighborhood in the temperature range investigated. The shift of the pre-edge peak, about 1 eV towards higher energy, indicates that vanadium oxidizes from +4 to +5 at 350 °C [20,21]. Above this temperature, the pre-edge peak did not shift further and its intensity remained unchanged, indicating the vanadium neighborhood becomes stable. The DXAS spectrum obtained at 600 °C, even after 40 min in this temperature, is similar to the spectrum of the reference sample, HT-CO$_3^{2-}$ + V$_2$O$_5$ (not shown), which has comparable features to the spectra of V$_2$O$_5$ reported in the literature [9]. Moreover, the spectrum of the reference sample (HT-CO$_3^{2-}$ + V$_2$O$_5$) remained unchanged along the same experimental conditions.

The comparison between the spectra of the samples prepared with VOSO$_4$, by physical mixture and by aqueous solution, showed different patterns. The spectrum obtained at 25 °C from the sample prepared by physical mixture has comparable features to the spectra of VOSO$_4$ reported in the literature [9], whereas the spectra obtained at 25 °C from the samples

Table 2
Ratios between main-edge (I_1 and I_2) and pre-edge (I_0) peak intensities of the sample HT-CO$_3^{2-}$ + VOSO$_4$ (FRC015), V-loading in solid state

T (°C)	I_0	I_1	I_2	I_1/I_0	I_2/I_0
25	1.9	6.2	5.3	3.3	2.8
200	2.1	5.7	5.0	2.7	2.4
300	2.4	5.0	5.0	2.1	2.1
350	2.9	5.2	5.6	1.8	1.9
500	2.9	5.2	5.7	1.8	2.0
600	2.9	5.2	5.7	1.8	2.0

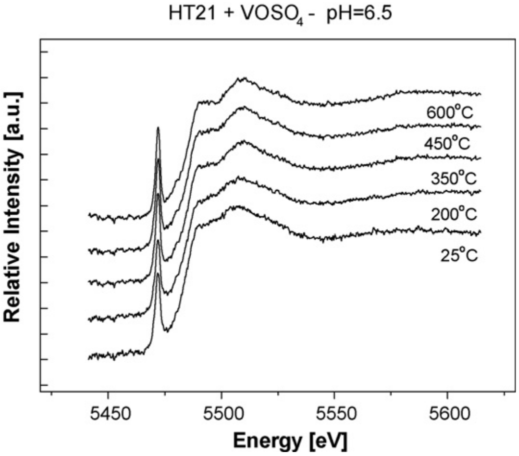

Fig. 6. DXAS spectra of the sample HT-CO_3^{2-} + $VOSO_4$ (FRC008), V-loading in aqueous phase in pH 6.5.

Table 3
Ratios between main-edge (I_1 and I_2) and pre-edge (I_0) peak intensities of the sample HT-CO_3^{2-} + $VOSO_4$ (FRC008), V-loading in aqueous phase in pH 6.5

T (°C)	I_0	I_1	I_2	I_1/I_0	I_2/I_0
25	4.0	6.4	7.3	1.6	1.8
200	3.7	5.6	6.9	1.5	1.9
350	4.2	5.6	7.0	1.3	1.7
450	4.4	5.8	7.1	1.3	1.6
600	4.4	5.8	7.0	1.3	1.6

Table 4
Ratios between main-edge (I_1 and I_2) and pre-edge (I_0) peak intensities of the sample HT-CO_3^{2-} + $VOSO_4$ (FRC009), V-loading in aqueous phase in pH 9.5

T (°C)	I_0	I_1	I_2	I_1/I_0	I_2/I_0
25	3.5	5.5	5.8	1.6	1.7
200	4.5	6.0	7.1	1.3	1.6
350	5.0	6.3	7.5	1.3	1.5
450	5.0	6.5	7.9	1.3	1.6
600	4.6	6.4	7.2	1.4	1.6

prepared by aqueous solution impregnation have comparable features to the spectra of vanadates [6]. In fact, the DXAS spectra of the HTs impregnated in aqueous solution display nearly the same features, suggesting that the same type of vanadium 'building block' is present. As already mentioned before, the nature and predominance of vanadium species in the samples investigated depends on the pH of the impregnation.

From the point of view of the DXAS measurements, an important parameter is the homogeneity of the sample, considering the vanadium ions as probes and the atoms close to them as scatterers. The *in situ* DXAS study suggests that the dispersion of vanadium onto the support increases when the introduction of $VOSO_4$ is done in aqueous solution. The samples impregnated with $VOSO_4$ in either pH 6.5 or pH 9.5 (Figs. 6 and 7 and Tables 3 and 4) showed that the ratios between the intensities of the pre-edge peak at 5469 eV (I_0) and neighbor oscillations (I_1 and I_2) remained practically unchanged during the whole experiment. The spectra measured at 600 °C for both samples are illustrative of the even higher dispersion of vanadium when the impregnation is carried out in alkaline pH. The signal-to-noise ratio is much higher than for acidic pH. Indeed, for the sample impregnated in alkaline pH, the DXAS spectra indicate a higher degree of short- and medium-range order, whereas for the sample impregnated in acidic pH, the measurements point to the opposite direction, lower signal-to-noise ratio, being related to incoherent scattering by the less ordered vanadium neighborhood. However, the low energy resolution of the spectra does not allow further conclusions on the reducibility of the V–HTs obtained by aqueous phase impregnation in pH 6.5 and pH 9.5.

TPR confirmed that the interaction between vanadium and support depends on both the nature of species present in the HT interlayer and the pH during vanadium impregnation. The carbonate bonding in the HT interlayer is weaker than the hydroxyl bonding because carbonate is larger and bivalent. Therefore, it would be expected that besides the higher dispersion brought about by the liquid phase loading, vanadium fixation would be easier along the interlayer of HT-CO_3^{2-}. The impregnation in alkaline pH led to vanadium reduction at lower

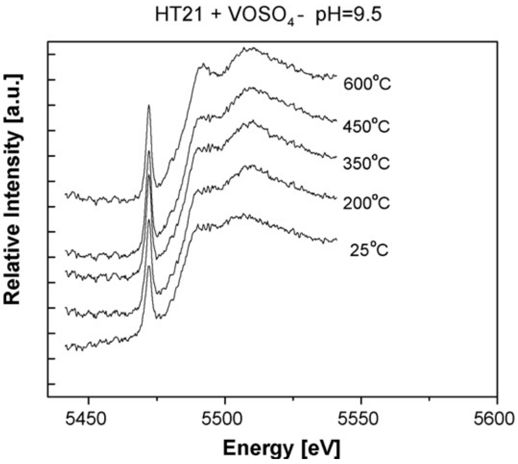

Fig. 7. DXAS spectra of the sample HT-CO_3^{2-} + $VOSO_4$ (FRC009), V-loading in aqueous phase in pH 9.5.

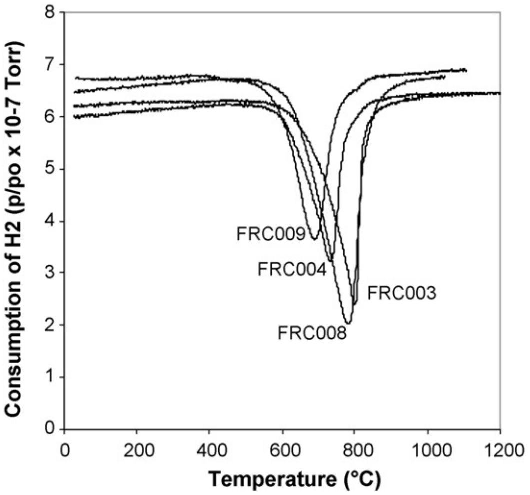

Fig. 8. TPR of HTs impregnated with 10% of vanadium in aqueous phase in pH 6.5 (FRC003 and FRC008) and pH 9.5 (FRC004 and FRC009).

Table 5
Temperature of the maximum point of TPR peaks of samples impregnated in aqueous phase

Sample code	HT anion type	pH of the impregnation	*T* (°C)
FRC003	Carbonate	6.5	798
FRC004	Carbonate	9.5	731
FRC008	Hydroxyl	6.5	781
FRC009	Hydroxyl	9.5	685

temperature (Fig. 8) in comparison to acidic pH, of about 100 °C in the case of HT-CO_3^{2-} (Table 5). The same effect was observed in the HT-OH^- impregnated samples, but less pronounced. These results allow to suggest that the formation of vanadium oligomers species, easier to reduce, are more favored by HT-CO_3^{2-} while the formation of V_2O_5 or predominance of isolated species of V^{5+}, harder to reduce, are favored by HT-OH^-.

The observation of the pronounced effect on the vanadium reduction profile combined to FTIR and DXAS analysis, also allow one to speculate about the modifications of the vanadium oligomerization degree. As the pH and vanadium concentration increase, in the conditions employed in this study, the oligomerization degree increases in the aqueous phase, leading to more oligomerized species deposited onto the HTs, that is, to more homogeneously dispersed vanadium neighborhood, as suggested by DXAS spectra. Such species would be reduced more readily, as evidenced by TPR measurements. In contrast, the impregnation in acidic solution leads predominantly to the formation of vanadium species that are more isolated, which would be more difficult to reduce.

4. Conclusions

Dispersive XAS, FTIR, TPR and thermoanalysis were employed to study the evolution of solid and aqueous phase loaded vanadium species supported, respectively, in two hydrotalcites, HT-OH^- and HT-CO_3^{2-}, during heating treatment in air. The DXAS spectra analysis combined to TGA–DTA results support that the oxidation of V^{4+} to V^{5+} occurs at 350 °C. Analysis of the results for V–HTs impregnated in acidic pH suggests that vanadium isolated species are predominant, while for V–HTs impregnated in alkaline pH affords vanadium polymeric species. The TPR study of the V–HTs impregnated in pH 9.5 showed that vanadium reduction takes place at much lower temperatures, about 100 °C less for HT-CO_3^{2-} and about 60 °C less for HT-OH^-, compared to their respective HTs impregnated in pH 6.5. Moreover, the changes observed at 600 °C in the DXAS spectra of the HTs impregnated in pH 9.5, as well with the weakening of the V=O band observed in the FTIR spectra, support the formation of larger oligomerized species of vanadium, which are known to undergo easier reduction.

The differences between the two HT types were also noted. The crystallinity of HT-CO_3^{2-} remained higher than the crystallinity of HT-OH^-, after impregnation in aqueous phase, even though after calcination at 800 °C both HTs yielded an amorphous mixture of oxides. The effect of pH during impregnation was very much pronounced for HT-CO_3^{2-} than for HT-OH^-. This information could be used to optimize the preparation of vanadium containing HT emission additives and will also provide the basis for comparison with the vanadium transferred to HT materials during regeneration, when using such additives.

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