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Esterification of acetic acid with alcohols using supported niobium pentoxide on silica–alumina catalysts☆

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Abstract

Supported niobium pentoxide catalysts are active for a variety of acid and redox catalyzed reactions such as dehydration, hydrogenation and esterification. In this work, niobium pentoxide has been supported on silica–alumina using two methods: grafting in CH_2Cl_2 or ethanol solution with $NbCl_5$ precursor, and impregnating in aqueous solution with ammonium niobium oxalate. XRD, TG/DTG/DTA, FTIR, DRIFTS, FT-Raman, and calorimetric titration with pyridine were used to characterize the materials. Calcination of the materials at 800 °C produced crystalline Nb_2O_5 (T-phase) for the samples prepared by grafting, while a mixture of T- and H-phases are formed by aqueous impregnation, indicating the higher stability of the former materials. Thermal analysis confirmed a stronger interaction of niobium oxide species on the silica–alumina surface for the grafting procedure. On the other hand, partial neutralization of hydroxyl groups occurred on the support surface by grafting process, and the neutralization reaction is practically complete at 25 wt.% of Nb_2O_5 by impregnation. The catalysts with about 10 wt.% of Nb_2O_5 prepared by aqueous impregnation reached the monolayer, while by grafting it predominates bulk Nb_2O_5, as demonstrated by FT-Raman. These catalysts also showed the highest acidity, when calcined at 300 °C. Based on these results, liquid phase esterification reactions of acetic acid were carried out with different alcohols (ethanol, *n*-butanol, and *iso*-pentanol). The yields were about the same, independent of the preparation method for 10 wt.% Nb_2O_5 catalysts. The conversions using molar ratio 2:1 (acid:alcohol) after 8 h showed good results (83, 87, and 91%, respectively) and 100% selectivity for all esters.

Keywords: Esterification; Niobium pentoxide; Silica–alumina; Supported catalyst; Solid acid

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1. Introduction

Many catalysts based on niobium have been applied on different processes due to the high activity, selectivity, and stability of these materials [1–3]. Reactions such as hydrogenation, hydrocarbon conversion, selective oxidation, condensation, and esterification are reported among others [4–7]. In addition, water tolerant properties of niobium pentoxide are important for applications involving water in the medium [8].

Supported niobium oxides are interesting catalysts because they have surface properties dependent on the niobium content, nature of support, calcination temperature, etc. In most of the cases, it is possible to differentiate the surface species that are formed by different preparation methods through the use of in situ techniques [9]. Those species are responsible for the new active sites generated on the material surface and may act selectively for certain types of reactions [10]. As supported phase, the interaction of Nb_2O_5 with the surface depends on the nature of the support. Acidic supports react via hydroxyl groups (Brønsted sites) and basic supports react preferentially on the Lewis sites [11,12].

Esters obtained from small chain acid and alcohols are very important industrially. For example, *n*-butyl acetate is used in

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large scale as solvent in the manufacturing of plastics, films and varnishes [13,14]. The esterification reactions to obtain these esters are usually catalyzed by sulphuric or *p*-toluenesulphonic acid. Although these acids are very active, major problems are related to environmental concerns, besides the corrosive nature and difficulties to separate them from the reaction mixture [15–18].

Lately, the use of solid acids has gained attention. Examples of solid acids catalysts for esterification reactions include: ion exchange resins (e.g., amberlyst 15, smopex-101), zeolites (e.g., Y, USY, BEA, MOR, ZSM-5), sulphated oxides (e.g., SO_4/ZrO_2), niobic acid, and supported heteropolyacids (e.g., $H_4SiW_{12}O_{40}/ZrO_2$) [19–21]. Even though the esterification reaction looks simple, it is an equilibrium process (with low equilibrium constant), and in order to get improved yields much engineering should be done [22].

The main goal of this work is to produce suitable catalysts for liquid phase esterification processes. Supported Nb_2O_5 on silica–alumina were recently prepared by aqueous impregnation and characterized [23,24]. Preliminary activities for these materials were observed in our laboratory. Thus, a complete study involving different preparation methods, characterization of the materials, and three esterification reactions (acetic acid with ethanol, *n*-butanol, and *iso*-pentanol, respectively), is presented here.

2. Experimental

2.1. Methods for preparation of supported $Nb_2O_5/SiO_2–Al_2O_3$

The supported catalysts were prepared either by grafting or impregnation procedures. Both methods used silica–alumina (Aldrich, catalyst support grade 135, 12 wt.% Al_2O_3, >90% AS-100 mesh, and specific surface area (BET) of 465 $m^2\ g^{-1}$). Silica–alumina was activated at 550 °C for 12 h into a muffle furnace, in order to transform it from ammonium to protonated form. The precursors were weighted in the required amount in order to produce a final concentration of Nb_2O_5 equivalent to 5, 10, 15, and 25 wt.%. This nominal composition was confirmed by niobium elemental analysis (ICP-AES), which showed slight differences (3–6%). Therefore, all niobia loadings refer to the nominal values. All niobium reagents were provided by CBMM (Companhia Brasileira de Mineração e Metalurgia, Araxá, Brazil).

Grafting procedure consisted of weighting $NbCl_5$ (under nitrogen atmosphere) and adding to 50 ml of solvent (either CH_2Cl_2 or 0.5 mol l^{-1} of acetic acid in ethanol) inside a glass round-bottom flask containing activated silica–alumina. The system was kept under reflux at 70 °C (dichloromethane) or 80 °C (ethanol) for 19 h under nitrogen atmosphere. After that, the solid was filtered, washed consecutively with 1.0 mol l^{-1} HNO_3 and distilled water. Next, the materials were dried in an oven (100 °C) for 4 h and finally calcined either at 300 or 800 °C/6 h.

Aqueous impregnation procedure used $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_n$ as precursor. Ammonium niobium oxalate was weighted and added to a glass round-bottom flask with activated silica–alumina and distilled water. The slurry was kept at 80 °C until all water had evaporated. Next, the solid was ground to finer particles, dried in an oven (100 °C) for 4 h, and finally calcined either at 300 or 800 °C/6 h. Other details for this impregnation procedure can be found elsewhere [23]. Table 1 summarizes the sample preparations and composition.

Table 1
Nomination, method, and preparation condition for the different catalysts

Nomination	Preparation method	Solvent/precursor
NbSiAl–DM	Grafting/reflux	$CH_2Cl_2/NbCl_5$
NbSiAl–ET	Grafting/reflux	CH_3CH_2OH[a]/$NbCl_5$
NbSiAl–AQ	Impregnation/ evaporation	$H_2O/NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot(H_2O)_n$

[a] 0.5 mol l^{-1} of CH_3COOH in ethanol.

2.2. Thermal, XRD, and spectroscopic analyses

The calcinations were performed in a muffle furnace (Sybron Thermoline, model FA 1630) under static conditions in porcelain crucibles at ~13 °C min^{-1}.

Thermal analysis data were obtained in a simultaneous TG-DSC (TA Instruments, model SDT 2960) with scan rate at 10 °C min^{-1}, from room temperature (~25 °C) to 1400 °C under nitrogen (99.999%) flow of 100 ml min^{-1}.

XRD patterns were obtained using a Rigaku D/Max-2A/C with Cu Kα radiation of 1.5418 Å (40 kV and 20 mA). A 2θ range from 2° to 60° was scanned at 1.8° min^{-1}.

FT-Raman spectra were obtained at room temperature (25 °C) with 256 scans and resolution of 2 cm^{-1} on a Bruker FRA 106/S module attached to a Bruker Equinox-55 spectrometer. The laser excitation (Nd:YAG) wavenumber and power were 1064 nm and 126 mW, respectively. The signal was detected by a liquid nitrogen cooled Ge detector. Raman spectra were baseline corrected and smoothed using polynomial functions.

Infrared spectra were recorded using pellets of dried 1 wt.% KBr (Merck) on a Bruker Equinox-55 spectrometer equipped with a DTGS detector under ambient conditions. The resolution was 4 cm^{-1} and 256 scans were acquired.

DRIFTS spectra were obtained at 25 °C within a Harrick diffuse reflectance accessory (The Praying Mantis^{TM}), equipped with high temperature chamber with windows of KBr. Before acquisition, each solid was heated at 450 °C under dry nitrogen (99.999%) flow for 30 min and then cooled. Each spectrum was acquired as reflectance against an alignment mirror and then converted to Kubelka–Munk units after baseline correction. The resolution was 4 cm^{-1} and 256 scans were collected for each spectrum.

2.3. Calorimetric measurements

The heat measurements were generated in a model ISC 4300 calorimeter from Calorimetry Sciences Corporation, using the following procedure: inside an inert atmosphere glove box filled with dry nitrogen, 0.5 g of the samples were weighed and transferred to an isothermal calorimetric cell, followed by the addition of 50 ml of anhydrous cyclohexane. A calibrated syringe (Hamilton, 5 ml) was filled with a known concentration of pyridine solution (e.g., 0.1 mol l^{-1}). Cell and syringe were inserted into the calorimeter holder, which were immersed in a regulated thermal bath at 26.000 °C. The calorimeter was connected to a computer, and the experiment set-up was made using the software provided by the manufacturer. The addition of pyridine solution was done in the incremental mode. The measured heats were obtained by a calibration curve before each titration. Other details of experimental set-up have been published elsewhere [25].

2.4. Esterification reactions

The esterification reaction of acetic acid with each alcohol was carried out in a stirred batch reflux system. A 50-ml glass round-bottom flask was charged with acetic acid and the respective alcohol, both weighted sequentially, followed by the addition of the pre-activated catalyst (0.2 g). The reagent amounts were calculated according to the desired molar ratio for each reaction (2:1 acid:alcohol). Then, the system was heated up to the reflux temperature, the reaction was carried out for 8 h, and finally the products were collected and analyzed by a gas chromatograph (Shimadzu, model GC 17A) equipped with a flame ionization detector (FID) and a fused silica capillary column with dimethyl polysiloxane as stationary phase. The identification of the products was confirmed by GC coupled with a mass spectrometer (Shimadzu, model QP5050A).

3. Results and discussion

3.1. Comparative characterization of the catalysts

Preparation of $Nb_2O_5/SiO_2–Al_2O_3$ catalysts based on impregnation with ammonium niobium oxalate aqueous solution was recently reported [23]. In this case, the stability of the new catalysts were compared to pure Nb_2O_5, which is amorphous up to ~450 °C. Supported on silica–alumina, niobium pentoxide showed much more resistance to form a crystalline phase. Only when calcined at 800 °C/3 h, supported Nb_2O_5 exhibited a mixture of predominantly orthorhombic (T) and the monoclinic (M and H) crystalline phases. In addition, it was possible to detect crystalline forms for Nb_2O_5 with contents at or above 15 wt.%, indicating that the monolayer surface for this supported catalyst had been overcome.

In order to verify the influence of the preparation method on the surface structure of supported niobium pentoxide and thus the activity of the catalyst, two grafting methods were investigated. The materials prepared by grafting showed the same behavior of the aqueous impregnation, i.e., calcination at or above 800 °C showed crystallization of niobium pentoxide. Figs. 1 and 2 show the XRD of the different catalysts. It can be observed that the catalysts prepared in CH_2Cl_2 or ethanol presented a crystalline pattern as low as 5 wt.% of Nb_2O_5. This is in contrast to the system prepared by aqueous impregnation, which exhibits a crystalline pattern at concentrations above 10 wt.%. However, unlike the materials prepared in aqueous solution, which showed a mixture of orthorhombic (T) and the monoclinic (M and H) phases of niobium pentoxide [23], the catalysts prepared in dichloromethane exhibit characteristic reflections of T-Nb_2O_5 ($2\theta = 22.6°$, 28.4°, 28.9°, 36.6°, and 46.3°). In addition, the materials prepared in ethanol showed not only the reflections related to T-phase, but also a single reflection at $2\theta = 24.9°$ that is found in the M- or H-Nb_2O_5. These phase assignments were obtained comparing the PDF files from the International Centre for Diffraction Data (ICDD) with the obtained experimental powder diffraction patterns.

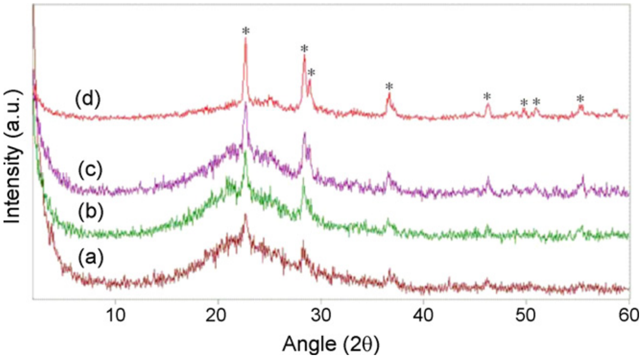

Fig. 1. XRD patterns for $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–DM) with (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.% and (d) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h. The * denotes T-phase (orthorhombic) for Nb_2O_5.

The results imply that a stronger interaction between niobium pentoxide and silica–alumina occurs by grafting process, compared to aqueous impregnation. This is mainly based on the lower mobility of Nb_2O_5 crystallites over silica–alumina surface by the grafting method. Since orthorhombic (T) is the predominant crystalline phase for grafting preparations, it indicates a stronger interaction between Nb_2O_5 and silica–alumina surface than the aqueous impregnation process that forms a mixture of orthorhombic (T) and monoclinic (M and H) phases. Monoclinic phase takes place at higher temperature than orthorhombic, so that the higher temperature phase niobium pentoxide reaches the weaker interaction on the support occurs [26].

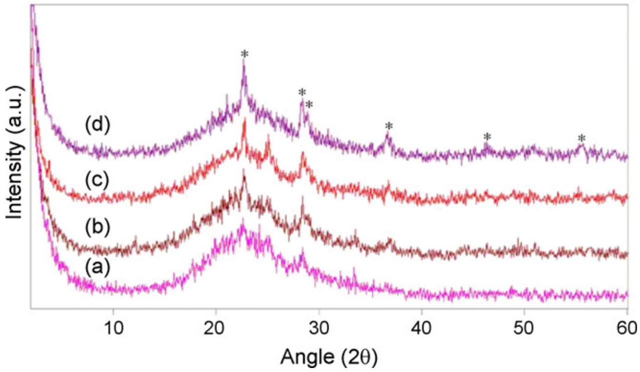

Fig. 2. XRD patterns for $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–ET) with (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.% and (d) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h. The * denotes T-phase (orthorhombic) for Nb_2O_5.

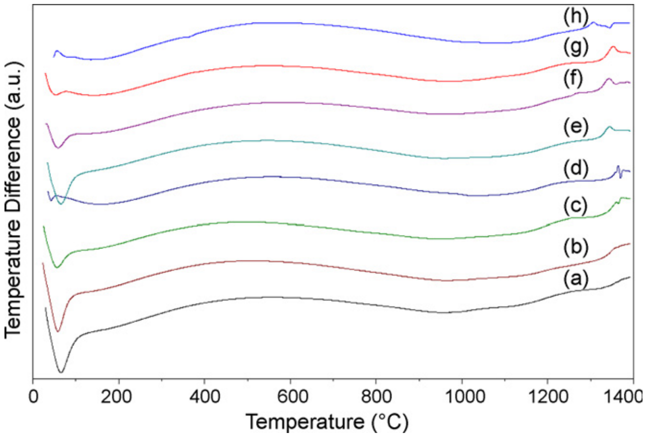

Fig. 3. DTA curves of $Nb_2O_5/SiO_2–Al_2O_3$ with 5 wt.%, 10 wt.%, 15 wt.%, and 25 wt.% of Nb_2O_5 prepared in dichloromethane (a–d) and ethanol (e–h), respectively. All samples were calcined at 800 °C/6 h.

Thermal analysis provided interesting results for comparison of the material stabilities, according to the preparation method. It was observed before for pure Nb_2O_5 [23] that there was a sharp exothermic peak at 567 °C in the DTA curve, which was attributed to a phase transition (no mass loss observed in the TG/DTG curves). In addition, no transition phase is observed for silica–alumina in the DTA curve. In this case, TG/DTG curves for the protonic sample, freshly calcined at 550 °C, show a mass loss centered about 100 °C (due to physical desorption of water) and no other event up to 700 °C.

Supported $Nb_2O_5/SiO_2–Al_2O_3$ displays a very different profile. Fig. 3 shows the DTA curves for the supported Nb_2O_5 catalysts prepared in CH_2Cl_2 and ethanol under nitrogen atmosphere. The DTA curves of the calcined samples (800 °C) display an endothermic peak about 100 °C (related to water desorption) and a phase transition (no mass loss associated with this exothermic peak) in the temperature region 1306–1363 °C, which is dependent on the niobium content and the preparation method. Table 2 exhibits each phase transition temperature for a better comparison. The phase transition temperatures for the samples obtained by grafting Nb on ethanol solution are slightly lower than the other ones under different preparations. Also, the preparation in dichloromethane produces materials with slightly higher transition phase temperatures (or even no transition phases, as for 5 and 10 wt.% Nb_2O_5 samples) in relation to aqueous impregnation process. This is in agreement with the XRD results, which demonstrate that the formation of crystalline Nb_2O_5 phase on silica–alumina material is more resistant for the samples prepared in CH_2Cl_2. Thus, the DTA results indicate that the preparation in CH_2Cl_2 solvent produces materials with stronger bondings, based on the absence of phase transition or higher temperature for that transition. The same samples showed similar DTA curve profiles, before calcination, except for the preparation in aqueous solution. In this latter case, decomposition of the niobium precursor took place with peaks at about 100 °C (water physically adsorbed) and at about 300 °C (related to decomposition of the oxalate ligands of Nb precursor). This demonstrates that longer treatments at 300 °C lead to the complete degradation of the niobium oxalate complex to niobium oxide [24].

Table 2
Phase transition temperatures obtained by DTA under nitrogen atmosphere for $Nb_2O_5/SiO_2–Al_2O_3$ catalysts, pre-calcined at 800 °C

Catalyst	Composition	T (°C)
NbSiAl–AQ	5% Nb_2O_5·95% $SiO_2–Al_2O_3$	1349
	10% Nb_2O_5·90% $SiO_2–Al_2O_3$	1353
	15% Nb_2O_5·85% $SiO_2–Al_2O_3$	1354
	25% Nb_2O_5·75% $SiO_2–Al_2O_3$	1362
NbSiAl–DM	5% Nb_2O_5·95% $SiO_2–Al_2O_3$	N.O.
	10% Nb_2O_5·90% $SiO_2–Al_2O_3$	N.O.
	15% Nb_2O_5·85% $SiO_2–Al_2O_3$	1360
	25% Nb_2O_5·75% $SiO_2–Al_2O_3$	1363
NbSiAl–ET	5% Nb_2O_5·95% $SiO_2–Al_2O_3$	1343
	10% Nb_2O_5·90% $SiO_2–Al_2O_3$	1343
	15% Nb_2O_5·85% $SiO_2–Al_2O_3$	1353
	25% Nb_2O_5·75% $SiO_2–Al_2O_3$	1306

N.O.: not observed.

FTIR spectra of the different catalysts were obtained for both samples calcined at 300 or 800 °C and preparation methods. Both spectra displayed similar characteristics, independent of the calcination temperatures or the preparation method. The stronger absorptions of the support make the niobium pentoxide bands basically obscured, i.e., the calcined silica–alumina absorptions (ν_{as}Si–O ~1100 cm^{-1}, with a shoulder ~1200 cm^{-1}, external νSi–O^- ~930 cm^{-1}, ν_sSi–O^- ~805 cm^{-1}, external δSi–O^- ~576 cm^{-1}, and δSi–O–Si ~467 cm^{-1}) predominate [23]. However, the most prominent change occurs in the absorptions at 903 cm^{-1} (shifted from 930 cm^{-1}) and 567 cm^{-1} (shifted from 576 cm^{-1}), which had already been observed for the catalysts prepared in aqueous solution [23]. These shifts can be explained by the reaction of niobium precursors with SiOH forming new surface bondings Si–O–Nb. The shift took place to a lower energy vibration because of the smaller electronegativity of Nb in relation to H.

In order to confirm that hydroxyl functionality of silica–alumina has reacted to form a new layer containing niobium oxide species, DRIFTS spectra were taken for the different catalysts. Pure silica–alumina in the protonic form has two major absorptions: ~3740 cm^{-1} (isolated silanols) and ~3580 cm^{-1} (hydrogen bonded silanols). On the other hand, niobium pentoxide shows a spectrum that is very dependent on the calcination conditions. When Nb_2O_5 is calcined at 800 °C/6 h, up to five bands were observed in the hydroxyl region [23], but the strongest bands are at about 3748 (wide), 3525, and 3420 cm^{-1}. Calcined at 300 °C/3 h, only a broadband was observed in DRIFT spectrum of niobium pentoxide, probably because of the large amount of adsorbed water on the surface.

Reaction of niobium precursors with the silica–alumina hydroxyl functionality showed a selective neutralization of the OH groups. The most basic sites (higher wavenumbers) reacted first. The spectra for catalyst preparations in CH_2Cl_2 and ethanol are presented in Figs. 4 and 5, respectively. It should be noted that even at higher niobium contents (25 wt.% of Nb_2O_5), the hydroxyls on silica–alumina surface are not completely neutralized, unlike the process that took place in aqueous

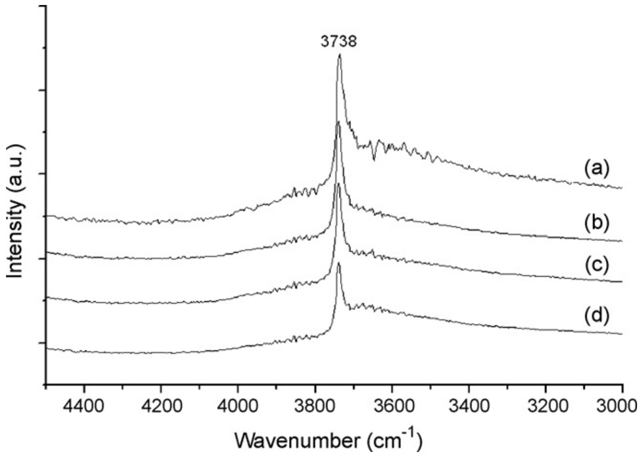

Fig. 4. DRIFTS spectra of $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–DM) with (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.% and (d) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h.

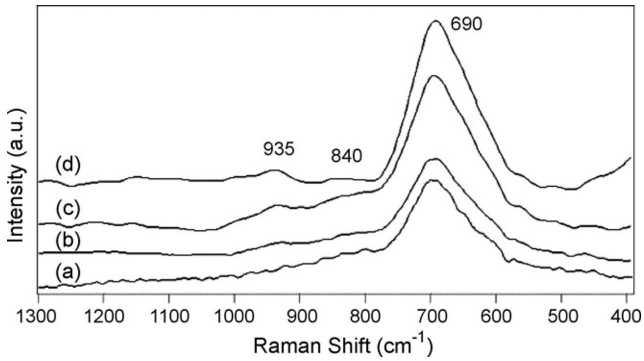

Fig. 6. FT-Raman spectra of $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–DM) with (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.%, and (d) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h.

solution [23]. For aqueous preparation, at 10–15 wt.% of Nb_2O_5, practically all OH surface groups have reacted. This demonstrates that the interaction of the precursor with the support sites is not complete for dichloromethane or ethanol systems, so that the surface has voids with the characteristic original sites from the support. This conclusion is in agreement with the XRD of observed patterns that showed, even for lower Nb_2O_5 contents, the presence of crystalline phases for niobium pentoxide. It probably indicates that the formation of larger agglomerates on silica–alumina surface was predominant under grafting process than the aqueous one.

Raman spectroscopy was used to further investigate the nature of species on silica–alumina surface. Due to low polarizability of its light atoms and the relative ionic character of Si–O and Al–O bonds, silica–alumina shows weaker Raman bands, in contrast to stronger IR absorptions. Raman spectra of Nb_2O_5 have been used either to assign different phases or to identify the surface species present on supported oxides [27,28]. Figs. 6 and 7 display the Raman spectra of both grafting preparations in CH_2Cl_2 (DM) and ethanol (ET), respectively. NbSiAl–DM catalysts present absorptions at 690, 840, and 935 cm^{-1} attributed to T-phase of niobium pentoxide [28]. Besides, the assigned band vibrations corresponding to stretching modes of different niobia polyhedra such as NbO_6, NbO_7, and NbO_8, slightly distorted NbO_6 Octaedra, and Nb=O stretching bands of highly distorted octahedra. Similar spectra were observed for NbSiAl–ET catalysts, except for the absorption at 998 cm^{-1} (Nb=O stretching) and the sample with 5 wt.% of Nb_2O_5, which exhibited broadbands in the Raman spectrum. These results confirm that the structure formed on the silica–alumina surface catalysts prepared by grafting process resembles the bulk phase of niobium pentoxide, in accordance with the other experimental data. This is in contrast to the formation of isolated species (2–5 wt.%) and polymerized species (10–15 wt.% of Nb_2O_5) on silica–alumina surface by aqueous impregnation method [23]. Therefore, it may be concluded that a better dispersion on the silica–alumina surface sites can be achieved with the aqueous impregnation process. The monolayer is reached with 10–15 wt.% of Nb_2O_5 in contrast to about 5 wt.% loading when the supported catalysts are prepared by grafting.

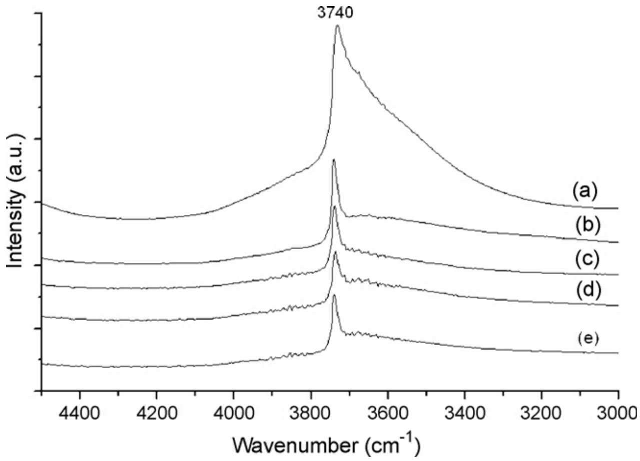

Fig. 5. DRIFTS spectra of $SiO_2–Al_2O_3$ (a) and $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–ET) with (b) 5 wt.%, (c) 10 wt.%, (d) 15 wt.%, and (e) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h.

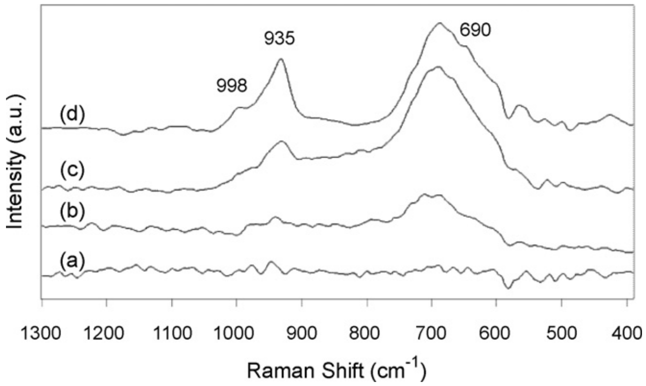

Fig. 7. FT-Raman spectra of $Nb_2O_5/SiO_2–Al_2O_3$ (NbSiAl–ET) with (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.%, and (d) 25 wt.% of Nb_2O_5. All samples were calcined at 800 °C/6 h.

3.2. Catalytic activity for esterification

Esterification is a typical Brønsted acid catalyzed reaction. Since the series of produced catalysts have intrinsic Brønsted acidity (both Nb_2O_5 and SiO_2–Al_2O_3 are solid acids), a preliminary acidity study of these catalyst materials was performed. Titration of the solid acid in cyclohexane slurry with pyridine solution was performed for each material at two calcination conditions: 300 and 800 °C. Previous titration tests with Nb_2O_5 showed that calcination at higher temperatures dehydroxylate its surface lowering its Brønsted but increasing its Lewis acidity, as described in the literature using other techniques [5]. Calcined at 300 °C, the interaction of Nb_2O_5 with pyridine rendered an average enthalpy (ΔH_{av}) of about -71.1 kJ mol^{-1}, while at 800 °C the same interaction drops to about -46.0 kJ mol^{-1}. On the other hand, SiO_2–Al_2O_3 in the protonic form and calcined at 300 °C presented a reaction enthalpy with pyridine around -92.1 kJ mol^{-1}. These values should be taken as averages of the strongest sites for each solid acid, since no complete data treatment was carried out yet.

Based on the niobium pentoxide behavior (i.e., lower enthalpies at higher calcination temperature), calcination of Nb_2O_5/SiO_2–Al_2O_3 materials was chosen at 300 °C in order to keep the strongest Brønsted sites. Thus, the materials were titrated with pyridine and the average values for all catalysts were similar (± 4 kJ mol^{-1}) for the same niobium pentoxide loading, independent of the preparation method. These results are in accordance with the overall characterization procedures, as already analyzed, since no significant difference was found for the active sites on the surface materials, except for those obtained with 10–15 wt.% of Nb_2O_5. The average values for the enthalpies were -104.6, -113.0, -96.2 and -83.7 kJ mol^{-1} for 5, 10, 15 and 25 wt.% of Nb_2O_5, respectively. This trend shows that the most acidic material contains 10 wt.% Nb_2O_5/SiO_2–Al_2O_3. As a result, these catalysts were submitted to catalytic esterification reactions.

Table 3 shows the conversion and selectivity results for esterification of acetic acid with ethanol, *n*-butanol, and *iso*-pentanol using 2:1 molar ratio (acid:alcohol) condition, respectively. Usually, the yield of the ester can be increased by additional use of either alcohol or acid. As the acetic acid is the less expensive reagent, it was used in excess in this study. The reactivity increases going from ethanol to *iso*-pentanol, which follows the known trend that tertiary alcohols react faster than primary or secondary. The conversion is about 83, 87, and 91% for ethanol, *n*-butanol and *iso*-pentanol, respectively. No by-products were detected, so that 100% selectivity for the respective ester was obtained. Because any esterification reaction proceeds without adding catalyst, blank tests without catalysts were performed. The yields were 40, 63, and 78% for ethanol, *n*-butanol and *iso*-pentanol, respectively. Esterification tests of acetic acid with ethanol were also conducted with silica–alumina or niobia as catalysts. The conversions were 74 and 59%, respectively, which demonstrates that the supported catalysts are more active than the isolated oxides.

Table 3
Conversion and selectivity for the esterification reactions of acetic acid with alcohols (2:1 molar ratio, respectively)

Alcohol	Temperature (°C)	Conversion (%)[a]	Selectivity (%)
Ethanol	~85	(DM) 82.8	100
		(ET) 83.0	100
		(AQ) 83.0	100
n-Butanol	~115–120	(DM) 86.6	100
		(ET) 87.6	100
		(AQ) 87.0	100
iso-Pentanol	~125–128	(DM) 91.5	100
		(ET) 90.0	100
		(AQ) 90.0	100

The conditions included: 8 h, 0.2 g of 10 wt.% Nb_2O_5/SiO_2–Al_2O_3 catalysts prepared in CH_2Cl_2 (DM), ethanol (ET), or water (AQ).

[a] Conversion is based on alcohol (mol%).

4. Conclusions

Catalysts based on Nb_2O_5/SiO_2–Al_2O_3 were prepared and compared by different methods (grafting in CH_2Cl_2 or ethanol, and aqueous impregnation). Considering the stability criterion, based on the niobium pentoxide crystalline phase formation on silica–alumina surface, the materials prepared by grafting were more stable, since they showed the presence of only T-phase (orthorhombic). In addition, thermal analysis provided evidence of stronger interaction between support and Nb_2O_5 when prepared by grafting in CH_2Cl_2. On the other hand, DRIFTS results indicated that not all surface hydroxyl of silica–alumina surface reacted with niobium precursor by the grafting process, which is in opposition to aqueous impregnation process. The catalysts produced by aqueous impregnation have better dispersion on silica–alumina surface as suggested by Raman and XRD data. Calorimetric measurements of the materials interacting with pyridine showed similar values for the same amount of Nb_2O_5 loading, independent of the preparation method. However, calorimetric data were able to prove that the most acidic catalysts are obtained with 10 wt.% Nb_2O_5 loading. These catalysts were applied to the esterification reaction of acetic acid with alcohols (ethanol, *n*-butanol, and *iso*-pentanol) and showed good conversions in 8 h (83, 87, and 91%, respectively).

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