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PHASE TRANSITION IN NIOBIUM PENTOXIDE SUPPORTED ON SILICA-ALUMINA

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Nb_2O_5 supported on SiO_2–Al_2O_3 were prepared with a wide loading range (2, 5, 10, 15, 20 and 25 mass%) and analyzed by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). The materials presented a phase transition close to 1364°C. This phase transition was studied by XRD, FTIR and Raman spectroscopy. A mixture of orthorhombic (T) and monoclinic (H and M) crystalline phases was evidenced in the supported samples, which is coverage dependent, in contrast to the formation of only the monoclinic phase (H and M) when pure Nb_2O_5 is heated under the same conditions. These results indicate the stabilization of Nb_2O_5 on silica-alumina surface.

Keywords: *niobium pentoxide, phase transition, silica-alumina, supported catalyst, thermal analysis*

Introduction

Niobium pentoxide supported on high surface area oxides is used as an acid-redox catalyst for a variety of chemical reactions (e.g., esterification, hydration, etc.) [1–3]. Depending on the surface coverage, mono-oxo isolated, polymerized or bulk species may be formed [4]. These surface species are responsible for the new properties and enhanced catalytic activity of these materials [5].

Thermal stabilities of the supported oxides change dramatically in comparison with the bulk oxide. For instance, a mixed oxide containing 25 mass% of Nb_2O_5 and 75 mass% of SiO_2 heated at 1000°C forms a hexagonal (TT) phase of Nb_2O_5, while pure Nb_2O_5 forms the same phase at 450–500°C [6]. The phase transition of Nb_2O_5 can be used as a criterion to establish the degree of interaction between the two oxides [6].

The polymorphism in Nb_2O_5 is temperature dependent and crystallization is influenced by the starting material, impurities, and interaction with other components. The main crystalline forms of Nb_2O_5 are hexagonal (TT), orthorhombic (T or γ), monoclinic (M or β), and monoclinic (H or α) [7]. There is some controversy whether TT and M phases are really crystalline forms. Nevertheless, the existence of these polymorphs is important for the reactivity of any niobium containing material [6].

The structure of niobium oxide supported on silica-alumina has recently been characterized [8]. A phase transition for the material pre-calcined at 800°C was observed about 1356°C by simultaneous TG/DTA analysis. Even though the process occurred at high temperature, the crystalline form of supported niobium pentoxide was not fully characterized. Therefore, the goal of this work was to characterize in detail the crystalline phase formed using thermal analysis, X-ray diffraction (XRD), infrared (FTIR) and Raman spectroscopy.

Experimental

Preparation of Nb_2O_5 supported on SiO_2–Al_2O_3

An aqueous solution of ammonium niobium oxalate, $NH_4[NbO(C_2O_4)_2(H_2O)_2](H_2O)_n$, obtained from Companhia Brasileira de Metalurgia e Mineração (CBMM), was added to a glass round bottom flask containing silica-alumina (Aldrich) at 1:10 mass ratio of solid to water. Silica-alumina was activated by calcination at 550°C for 12 h in order to transform it from ammonium to protonated form. The amount of niobium precursor was calculated to obtain 2, 5, 10, 15, 20 and 25 mass% loadings of Nb_2O_5. The system was stirred at 80°C until the water had completely evaporated. The solid was removed, ground to finer particles and placed in an oven at 150°C for 2 h before further analysis.

Thermoanalytical, XRD and spectroscopic analyses

Thermal analysis data were obtained in a simultaneous TG-DTA model SDT 2960 from TA Instruments, at a scan rate of 10°C min^{-1} in the 25–1400°C range under nitrogen (99.999%) flow of 110 mL min^{-1}. Platinum

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pans with about 20 mg of sample were used in all runs with α-Al_2O_3 as reference. At least three replicate experiments were recorded and the samples collected to obtain enough material for the spectroscopic analyses.

X-ray powder diffraction patterns were recorded on a Rigaku D/Max-2A/C spectrometer with CuKα radiation of 1.5418 Å (40 kV and 20 mA). A 2θ range from 2 to 60° was scanned at 1.8° min^{-1}. Crystalline phases were identified by comparison with PDF database from ICDD included in the software JADE 3.0.

Infrared spectra were recorded on a Bruker Equinox 55 spectrometer with 128 scans and spectral resolution of 4 cm^{-1} in dried 1 mass% KBr (Merck) pellets. FT-Raman spectra of samples were obtained at room temperature (25°C) with 128 scans at a resolution of 2 cm^{-1} on a Bruker FRA 106/S module attached to the Equinox 55 spectrometer. The wavelength and laser (Nd-YAG) power were 1064 nm and 126 mW, respectively. A liquid nitrogen cooled Ge detector collected the Raman signal. Infrared and Raman spectra were obtained under ambient conditions and baseline corrected.

Results and discussion

Preliminary analysis

The theoretical monolayer of supported Nb_2O_5 on silica-alumina (475 m^2 g^{-1}) is close to 39.6 mass% loading, which may be calculated based on the dimension of the Nb_2O_5 crystal unit reported in the literature (0.32 nm^2) [9]. Nonetheless, the experimental data based on XRD and Raman measurements established that the actual monolayer is obtained with Nb_2O_5 loading between 10 and 15 mass% [8]. Thus, the materials with 2 and 5 mass% are below the monolayer while those with 15–25 mass% are above monolayer.

In order to look at the effects of loading and decomposition of the precursor on the support, previous studies revealed that pure crystalline oxalate has an amorphous pattern at heating temperatures of 300–400°C for 6 h. This pattern is also observed for Nb_2O_5/SiO_2–Al_2O_3 heated at 300°C/6 h. Thus, the decomposition of oxalate groups is expected to occur close to 300°C and it is highly dependent on the degree of interaction with the support during thermal treatment. Further details regarding this decomposition will be provided in the following sections.

Simultaneous TG/DTA

The DTG curves of Nb_2O_5/SiO_2–Al_2O_3 are presented in Fig. 1 and display a profile that depends on the initial loading of the niobium precursor. For the samples with low contents (2–10%) there are two mass loss peaks centered close to 60 and 300°C associated with the desorption of physically and chemically adsorbed water and the decomposition of oxalate, respectively. On the other hand, the samples with 15–25% showed a displacement of the maximum temperature to higher values and fine characteristics in the range of 200–400°C (peaks at 202, 280 and 353°C). All these events are related to complete decomposition of the supported ammonium niobium oxalate precursor, as comprised by FTIR analysis of the samples calcined up to 400°C [8].

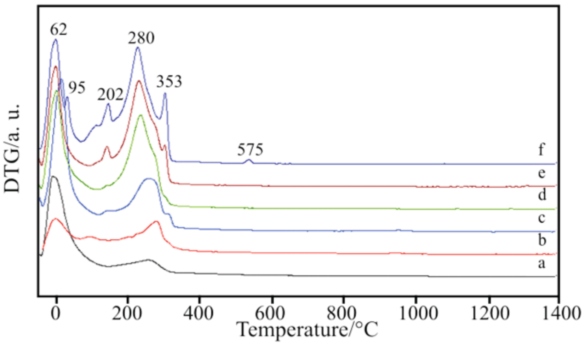

Fig. 1 DTG curves of the samples with: a – 2, b – 5, c – 10, d – 15, e – 20 and f – 25 mass% loadings of Nb_2O_5/SiO_2–Al_2O_3, respectively

In order to be sure on these assignments and to compare the DTG/DTA profile obtained with the behavior of the niobium precursor a DTG/DTA curve is provided for pure ammonium niobium oxalate (Fig. 2). The DTG curve shows basically six mass loss peaks, which correspond to five events in DTA curve: *i*) four endothermic peaks at 167, 240 and 268°C, which are related to the release of physisorbed and chemisorbed water, and ammonium desorption, respectively; *ii*) two exothermic peaks at 268 and 541°C, attributed to partial and total decomposition of oxalate, respectively. The mass loss at offset (~610°C) of the highest temperature peak is consistent with the complete conversion of the ammonium oxalate to niobium pentoxide, as calculated by the theoretical value. Those assignments are in agreement with other works related to oxalate precursor decompositions [10, 11].

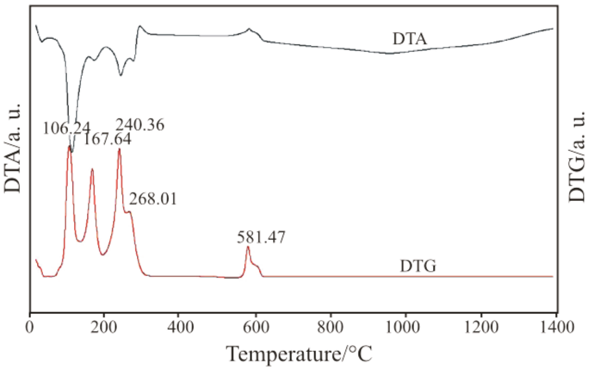

Fig. 2 DTG/DTA curves of ammonium niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)_2](H_2O)_n$)

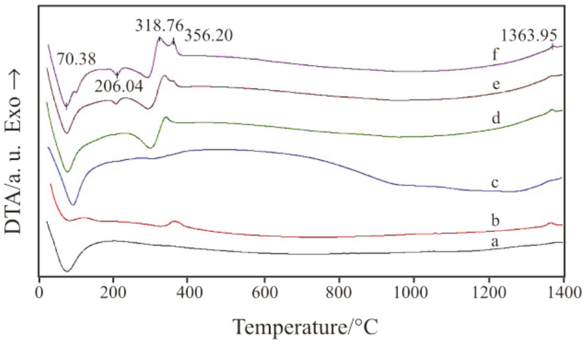

Fig. 3 DTA curves of the samples with: a – 2, b – 5, c – 10, d – 15, e – 20 and f – 25 mass% loadings of $Nb_2O_5/SiO_2–Al_2O_3$, respectively

The DTA curves (Fig. 3) display, for the samples with 15–25% a large endothermic peak centered about 70°C (in the range of 30–150°C) relative to water desorption processes. In addition, there are two endothermic peaks at about 206 and 300°C, which are assigned to ammonia desorption and CO and/or CO_2 from the catalyst surface during the decomposition of the niobium complex, respectively. Moreover, there are three additional exothermic peaks. The ones at 319 and 356°C are attributed to oxalate decomposition and the third one around 1364°C is related to a phase transition (no mass loss in the DTG curve). The profile of DTA curves for the samples with 2–10% is different in temperatures higher than 150°C. No marked peaks for the precursor decomposition were observed, probably because of the large background signal of DTA and the low initial oxalate content. Moreover, no transition phase for the sample with 2% was observed.

A phase transition peak was observed (at about 1356°C) for the $Nb_2O_5/SiO_2–Al_2O_3$ samples pre-calcined at 800°C [8] with a larger area, indicating that previous calcination facilitates the formation of Nb_2O_5 crystallites. This phase transition is attributed to Nb_2O_5 since pure $SiO_2–Al_2O_3$ did not show any thermal event under the same temperature range studied. Characterization of the crystalline phase formed in the TG/DTA experimental conditions was performed by XRD, FTIR and Raman techniques.

X-ray powder diffraction

In order to confirm that the exothermic peaks displayed in the DTA curves represent phase transitions, XRD of the samples was taken before and after TG/DTA experiments. The samples of $Nb_2O_5/SiO_2–Al_2O_3$ after impregnation but without calcination did not show any XRD pattern of the crystalline ammonium niobium oxalate or niobium pentoxide crystalline phase (Fig. 4). These results confirmed that the impregnation process generates either a very disperse and amorphous supported niobium complex or particles that are too small to be detected by powder XRD. Pure Nb_2O_5 showed a crystalline pattern equivalent to monoclinic form (H and M) after TG/DTA experiment (Fig. 5). Silica-alumina did not show any phase transition when heated under the same temperature range and established an amorphous pattern with or without [8] calcination (Fig. 4).

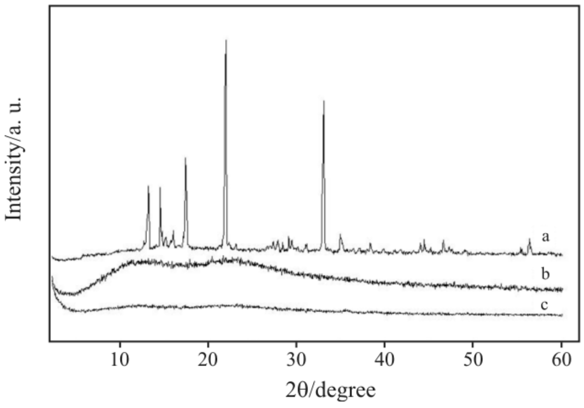

Fig. 4 XRD of: a – $NH_4[NbO(C_2O_4)_2(H_2O)_2]\ (H_2O)_n$, b – 25% $Nb_2O_5/SiO_2–Al_2O_3$ without calcination, c – silica-alumina after TG/DTA experiment

The supported samples with 15–25% of Nb_2O_5 displayed reflections that had contributions from the predominantly monoclinic (H and M) together with orthorhombic (T) crystalline structures (Figs 5e–g). The support imposes less mobility to Nb_2O_5 because of its interaction with silica-alumina. Thus, the reactivity of supported niobium pentoxide, regarding phase transitions, decreases when compared to the pure oxide, since it forms a crystalline phase that is usually obtained at a lower temperature. This reactivity is coverage dependent [8] and formation of high temperature phases is attributed to a weaker interaction with the support [6]. This is demonstrated by the behavior of the supported samples with 2–10% of

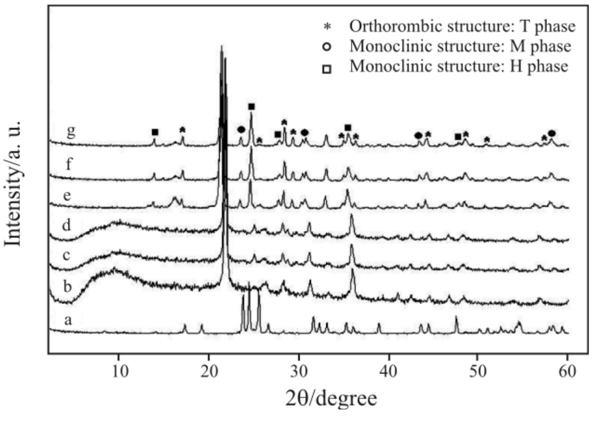

Fig. 5 XRD pattern of the samples: a – pure Nb_2O_5 and supported with: b – 2, c – 5, d – 10, e – 15, f – 20 and g – 25 mass% loadings of $Nb_2O_5/SiO_2–Al_2O_3$, after TG/DTA experiments. Note that the most intense peak of supported samples shifts from 2θ=22.6 (T-phase, b–d) to 2θ=22.3 (H-phase, e–g)

Nb_2O_5, which are composed of predominantly orthorhombic (T) phase and presence of monoclinic (H and M) crystalline structures (Figs 5b–d). It should be noted that the most intense reflection peak shifts from 2θ=22.6 (T-phase) to 2θ=22.3 (H-phase) with the increase in Nb_2O_5 loading.

FTIR and Raman spectroscopy

The changes in the spectra of supported Nb_2O_5 on silica-alumina obtained after calcination at 800°C are subtler [8], but the same samples display new absorptions after the TG/DTA experiments. Silica-alumina has strong peaks at ~1096 cm^{-1} ($\nu_{as(Si–O)}$), with a shoulder at ~1200, ~930 cm^{-1} (external ν_{Si-O^-}), ~805 cm^{-1} ($\nu_{s(Si-O^-)}$), and weak peaks at ~720 cm^{-1} ($\nu_{Al–O}$), ~576 cm^{-1} (external δ_{Si-O^-}), and ~467 cm^{-1} ($\delta_{Si–O–Si}$) [12]. The supported samples (15–25%) after thermal analysis experiments showed additional absorptions (Fig. 6). These absorptions at ~950 and 850 cm^{-1} ($\nu_{Nb=O}$ of highly distorted NbO_6), ~714 cm^{-1} (Nb–O–Nb chain linkages) and ~620 cm^{-1} ($\nu_{Nb–O}$ of slight distorted NbO_6) [13] are assigned to the presence of bulk niobium pentoxide species. For the lower supported samples (2–10%) not all absorptions are present. The main bands are assigned at 990, 790, 620 and 490 cm^{-1} (except 10%, which has an additional band at 850 cm^{-1}). These samples are loaded below monolayer, and thus the bands are related to the presence of either isolated or polymerized Nb_2O_x species on the silica-alumina surface [8].

Further evidence of niobium oxide interaction on silica-alumina surface is obtained by the Raman spectra (Fig. 7). Silica-alumina has weak Raman bands in the range of 400–1000 cm^{-1} [8]. Supported samples with higher coverage (15–25%) displayed bands at 933 cm^{-1} (with shoulders at 955 and 995 cm^{-1}), and smaller bands at 795, 729, 605 cm^{-1}. These absorptions are attributed to terminal Nb=O bonds on highly distorted NbO_6 species, Nb–O bonds in slighted distorted NbO_6, NbO_7 and NbO_8 polyhedra species and Nb–O–Nb angle deformations, respectively [14–16] present on bulk Nb_2O_5. It is interesting to note that the Raman spectrum of Nb_2O_5 agrees with the formation of H phase (presence of a band at 995 cm^{-1}) [17, 18]. Thus, coupling Raman spectroscopy with XRD analysis enabled the conclusion that H-phase is the predominant form of niobium pentoxide after thermal analysis experiments. The samples with lower coverage (2–10%) have bands consistent with the presence of both isolated and polymerized species on the surface (main bands at 940 and 630 cm^{-1}), except the 2% sample that presents very broad bands consistent with the ones observed in materials with highly dispersed Nb_2O_x species [8].

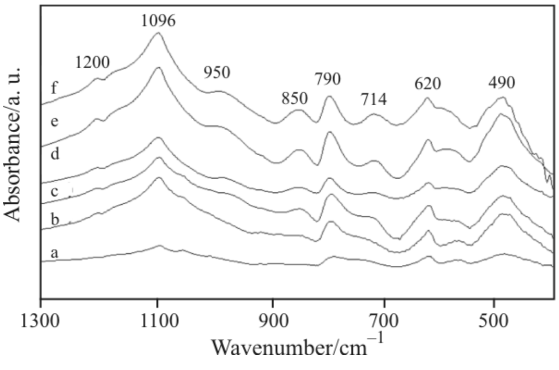

Fig. 6 FTIR spectra of the samples with: a – 2, b – 5, c – 10, d – 15, e – 20 and f – 25 mass% loadings of $Nb_2O_5/SiO_2–Al_2O_3$, after TG/DTA experiments

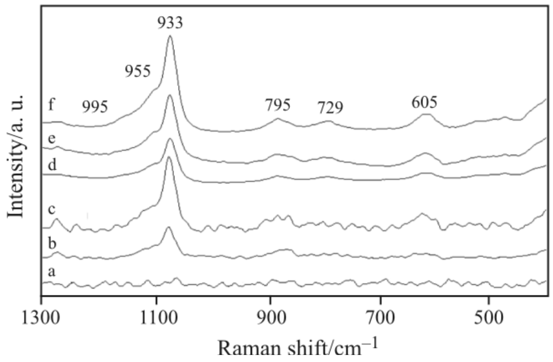

Fig. 7 Raman spectra of the samples with: a – 2, b – 5, c – 10, d – 15, e – 20 and f – 25 mass% loadings of $Nb_2O_5/SiO_2–Al_2O_3$, after TG/DTA experiments

Conclusions

Simultaneous TG-DTA analyses of $Nb_2O_5/SiO_2–Al_2O_3$ materials showed a phase transition at about 1364°C. This phase transition was studied by XRD, FTIR and Raman spectroscopy. Based on these results, a mixture of orthorhombic (T) and monoclinic (H and M) structures was evidenced in the supported samples, in contrast to the formation of only monoclinic phase (H) when pure Nb_2O_5 is heated under the same conditions. The degree of the mixture depends on the Nb_2O_5 loading, since T-phase predominates in samples with low coverage (2–10 mass%) while H-phase dominates in those with high coverage (15–25 mass%).

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