Infrared Spectroscopic Studies of the Formation and Catalytic Activity of Nd_2O_3

Gamal Abdel-Halim Mohamed HUSSEIN* and Hamdy Mahmoud ISMAIL
Department of Chemistry, Faculty of Science, Minia University, El-Minia 61519, Egypt
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Nd_2O_3 catalyst was obtained as a final product of the thermal decomposition of $Nd(CH_3COO)_3 \cdot 2H_2O$. The decomposition processes up to 800 °C were characterized by means of TG, DTA, XRD, and IR spectroscopy of the gas and solid phase products. The activation energy values were determined non-isothermally for thermal events involved in the decomposition course. The results indicate that $Nd(AcO)_3$ is completely decomposed to Nd_2O_3 at 670 °C through five different intermediates; $Nd(OH)(CH_3COO)_2$ at 310 °C, $NdO(CH_3COO)$ at 320 °C, $Nd_2(CO_3)_3$ at 350 °C, $Nd_2O(CO_3)_2$ at 385 °C, and $Nd_2O_2(CO_3)$ at 410 °C. The oxide, Nd_2O_3, obtained at 800 °C possesses higher surface area (30 $m^2 g^{-1}$) than that obtained at 1000 °C (10 $m^2 g^{-1}$).

Thus, the oxide obtained at 800 °C was tested qualitatively and quantitatively as a catalyst towards the decomposition of 2-propanol at 100—400 °C by IR-spectroscopy. The results indicate that Nd_2O_3 catalyses 2-propanol dehydrogenation (forming acetone) at <300°C and dehydration (forming propene) at >250°C. At >350°C, acetone was involved in a secondary surface reaction, presumably with the surface hydroxyl groups, to give CH_4 and CO_2 in the gas phase.

Finely divided metal oxide catalysts are often produced by thermal decomposition of supported or unsupported inactive precursors.[1—3] The existence of special fast transport ways for volatile constituents leads eventually to porous materials,[2,3] lattice imperfections and other characteristics that are necessary for surface reactivity.[4—6] The hexagonal-structured Nd_2O_3, whose thermal genesis is to be studied in the present investigation, finds some applications in various fields. For instance, it is used as a catalyst for dehydration of 2-alkanols to form 1-olefins.[7] It is also used as a support material for metals catalysts for the formation of methanol from CO_2 and H_2.[8]

Thermal decomposition of metal acetates is occasionally adopted as a mean of preparing metal and metal oxide catalysts, some of which are of industrial important.[9] On the other hand, metal acetates are common surface intermediates, and their thermal behavior is important for understanding processes involved in the adsorption, and surface reactions of many oxygenated compounds.[10,11] A thorough survey of the literature revealed only a study,[12] in which thermal decomposition of $Nd(AcO)_3$ was studied. The results indicate that $Nd(AcO)_3$ dehydrates at 250 °C, and then decomposes to form Nd_2O_3 at 750 °C via two different intermediates. The first is NdOAc at 380 °C, while the second is $Nd_2O_2(CO_3)$ at 460 °C.

The present investigation examines the decomposition course of $Nd(CH_3COO)_3 \cdot 2H_2O$ to the onset of formation of Nd_2O_3 using TG, DTA, and IR spectroscopy. In addition, the energy of activation (ΔE) was determined non isothermally for decomposition processes involved.

The surface area (S_{BET}) of Nd_2O_3 obtained at 800 and 1000 °C was determined by N_2-adsorption isotherms at −195 °C. The catalytic activity of Nd_2O_3 obtained at 800 °C was tested qualitatively and quantitatively towards the decomposition of 2-propanol using IR-spectroscopy.

Experimental

Neodymium Acetate: $Nd(CH_3COO)_3 \cdot 2H_2O$ (donated $Nd(AcO)_3$) used was a 99.9% pure Aldrich Product, (U.S.A). In view of the thermal analysis results (see below), solid-phase decomposition products were obtained by heating at 200—1000 °C for 1 h in a dynamic atmosphere of air. For convenience, the calcination products are indicated by a combination of the precursor designation and the calcination temperature applied. For example, $Nd(AcO)_3$800 refers to the calcination product of $Nd(CH_3COO)_3 \cdot 2H_2O$ at 800 °C for 1 h.

Thermal Analysis: TG and DTA curves were obtained on heating up to 800 °C at various rates (θ=2—20°C min^{-1}) in a dynamic atmosphere of air (20 $cm^3 min^{-1}$), using an automatically recording (model 30 H) Shimadzu (Japan). Small portion (ca. 20 mg) of $Nd(AcO)_3$ were used for the TG, and highly sintered α-Al_2O_3 was the thermally inert reference material used for the DTA.

Shifts observed in the DTA peak temperature (T_{max}) as a function of the heating rates (θ°C min^{-1}) was implemented with Kissinger's equation,[13] to calculate the corresponding activation energy (ΔE/kJ mol^{-1}).

X-Ray Diffractometry (XRD): Powder diffractograms of $Nd(AcO)_3$ and its calcination products were obtained by means of a model JSX-60 PA JEOL (Japan) diffractometer, equipped with a source of Ni-filtered Cu $K\alpha$ radiation. For identification purposes, diffraction patterns [($I/I°$) versus d spacing (Å)] obtained were matched with relevant ASTM standards.

Infrared Spectroscopy (IRA): All the IR spectra were obtained at a resolution of 5.3 cm^{-1}, over the frequency range from 4000 to 400 cm^{-1}, using a model 580B Perkin–Elmer spectrophotometer (U.K.), equipped with a 3500 PE data station for spectra acquisition and handling.

I. Gas phase decomposition products were identified by means of IR spectra (4000—600 cm^{-1}) taken from the atmosphere surrounding a 0.5-g portion of $Nd(AcO)_3$ being heated at 10 °C min^{-1} to various temperatures (150—600 °C) for 5 min in a specially designed IR-cell.[14] The cell was

equipped with NaCl windows and evacuated briefly to 10^{-3} Torr prior to heating the sample (1 Torr=133.322 Pa).

II. IR spectra for solid phase products decomposition were taken from KBr-supported discs (<1 wt%; 20—30 mg cm^{-2}).

III. IR-spectra of 2-propanol and its catalytic decomposition gaseous products were taken with the same IR-cell,[14] where the catalyst could be heated in situ at various temperatures The following standard procedure was adopted. The catalyst (100-mg portion in a finely divided form) was heated in a stream of oxygen at 700 °C for 1h to clean the surface from carbonate contamination,[8] and cooled to room temperature under vac. (10^{-3} Torr). With the help of a specially designed, all-glass gas/vacuum handling system,[15] 10 Torr of the 2-propanol vapor was allowed into the cell at the following temperatures, 150, 200, 250, 300, 350, and 400 °C, and maintained for 10 min in contact with the catalyst.

The 2-propanol and its decomposition gas products were quantitatively analyzed using the standard Quant software of Perkin–Elmer and the on-line data acquisition system. Accordingly, amounts of the gas phase components (reactant and products) were determined varsus calibration curves relating the IR absorbance at a certain analytical frequency to the calibrate gas phase pressure (Torr).

The calibration curves were derived from IR spectral data obtained for authentic samples of each of the gas phase components under identical spectroscopic conditions. The absorbance was measured at 3664±5 cm^{-1} for 2-propanol, 1740±5 cm^{-1} for acetone,[11] (the alcohol dehydrogenation product) and at 912±5 cm^{-1} for propene (the dehydration product).[11]

Surface Area Measurements (S_{BET}): Surface area measurements for $Nd(AcO)_3$800 and 1000 °C were carried out by analyzing N_2 adsorption isotherms determined at −195 °C, using the BET method.[16]

Results and Discussion

Decomposition Processes and Products of $Nd(AcO)_3$: TG and DTA curves (Fig. 1) monitor nine weight loss (WL) processes (designated I—X) in the decomposition course of, $Nd(CH_3COO)_3 \cdot 2H_2O$. Four of these process (V—VIII) are exothermic, whereas the others are shown to be endothermic. The WL effected via the first three processes (I—III) accounts for a stepwise dehydration of $Nd(AcO)_3$, in such a way that both process-I (WL=2.5%, T_{max}=80°C), and process-II (WL=5%, T_{max}=100°C), leads to removal of one mole of H_2O, whereas process-III (WL=10%, T_{max}=175°C) involves the removal of the other mole of water.

The corresponding activation energy (Table 1) has values (52.5 (I), 58.4 (II), and 65.1 (III) kJ mol^{-1}) within the range characteristic of dehydration process.[17]

Consistently, the IR-gas-phase spectrum at 150 °C (Fig. 2), displays a broad absorption centered around 3440 cm^{-1} and a sharper absorption at 1630 cm^{-1}, due respectively to ν(OH) and δ(HOH) vibrations of H_2O molecules.[18] These absorptions also appear in the 200 °C spectrum.

Table 1. The energy of activation (ΔE, kJ mol^{-1}) determined non-isothermally for the processes encountered throughout the decomposition course of $Nd(CH_3COO)_3 \cdot 2H_2O$

Process	I	II	III	IV	V	VI	VII	VIII	X
ΔE	52.5	58.4	65.1	151.8	158.4	162.3	168.1	186.7	302.3

The weak absorptions appearing at 1795, 1760, 1420, 1195, 1130, 1030, 655, and 640 cm^{-1} in the gas phase spectrum at 200 °C are due to acetic acid molecules.[19] They may imply occurrance of hydrolysis of surface acetates, which may explain the weak endotherm located at 220 °C (Fig. 1). In support, the IR spectrum obtained for $Nd(AcO)_3$200 (Fig. 3), exhibits bands at 1800—400 cm^{-1} for the various modes of vibration of CH_3COO^- species.[18] XRD of $Nd(AcO)_3$200 (Fig. 4) shows a sole pattern of diffraction peak due to crystalline anhydrous $Nd(CH_3COO)_3$ (ASTM No. 23-420).

On, a further heating up process-IV ocurrs and gets overlapped by rapid exothermic WL processes V—VIII (Fig. 1). It takes place arround 310 °C, and amounts to a total WL of 21.1%, accounting for the conversion of $Nd(CH_3COO)_3 \cdot 2H_2O$ into $Nd(OH)(CH_3COO)_2$ (expected WL is ca 21.8%). The energy of activation determined for process IV is 151.8 kJ mol^{-1}.

The IR gas-phase spectrum at 300 °C (Fig. 2) exhibits weakening of water absorptions, and reinforcement of absorptions bands due to acetic acid. Thus, the formation of acetic acid at this stage, could be seen to occur via the possible intervention of ketene (CH_2=C=O),[20] as follow:

$$Nd(CH_3COO)_3(s) \rightarrow Nd(OH)(CH_3COO)_2(s) + CH_2{=}C{=}O(g), \quad (1)$$

$$CH_2{=}C{=}O(g) + H_2O(g) \rightarrow CH_3COOH(g), \quad (2)$$

where (s)=surface and (g)=gas.

Process-V is exothermic, WL and overlaps largely with both processes IV and VI. It maximizes at 320 °C. The total WL determined on completion of process V is 37.6%, which is close to that 38.6% expected for the formation of $NdO(CH_3COO)$. Thus process V is responsible for the decomposition of NdOHAc into NdOAc. This is in good agreement with Paul et al.,[12] who reported the formation of acetate oxide intermediate in the decomposition course of $Nd(AcO)_3$ at 320 °C.

The IR gas-phase spectrum at 300 °C (Fig. 2) detects the appearance of both acetone and CO_2 as a results of the decomposition of the $Nd(OH)(CH_3COO)_2$.

Processes VI, VII, and VIII, are exothermic and strongly overlapping. They are maximized at 350 (VI), 385 (VII), and 410 °C (VIII). These processes bring the total WL up to 46.1% which is very close to that 46.7% expected for the formation of $Nd_2O_2(CO_3)$ most probably it takes place as follows,

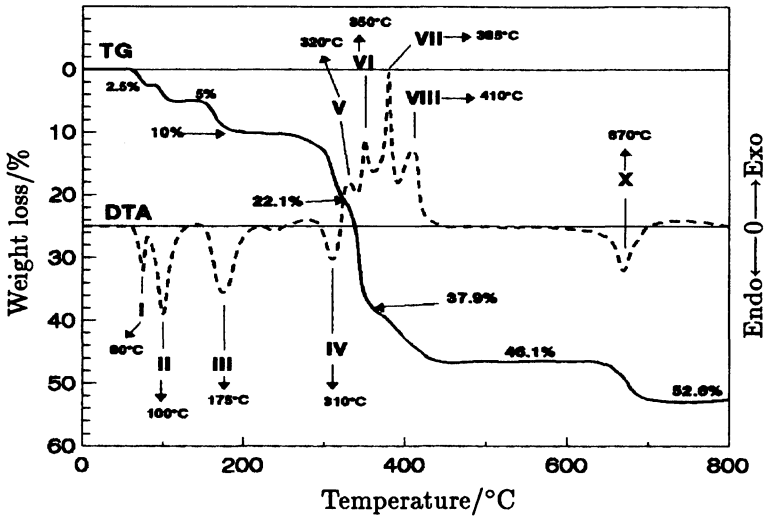

Fig. 1. TG and DTA curves for $Nd(AcO)_3$, in a dynamic (20 ml min^{-1}) atmosphere of air.

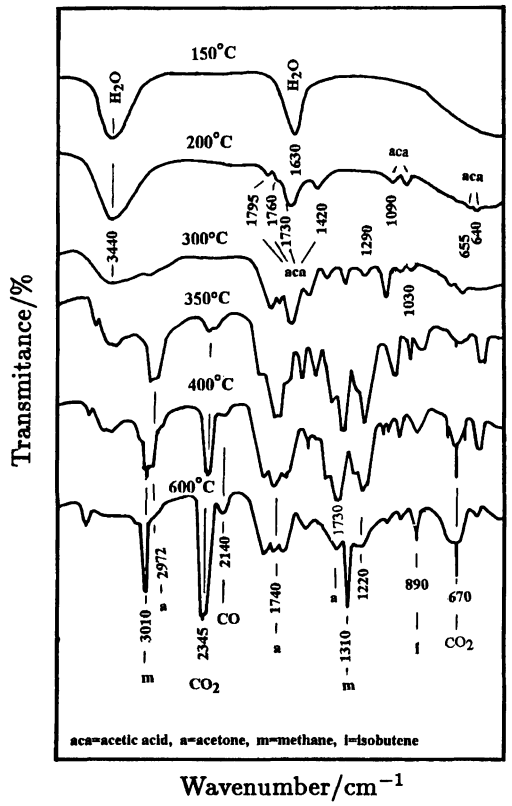

Fig. 2. IR-spectra from the gas phase surrounding a 0.5 gm portion of $Nd(AcO)_3$ heated at 10 °C min^{-1} to the temperatures indicated.

$$2Nd_2O(CH_3COO) \xrightarrow[VI]{350^\circ C} Nd_2(CO_3)_3 \searrow CH_3COCH_3(g)$$
$$\xrightarrow[VII]{385^\circ C} Nd_2O(CO_3)_2 \searrow CO_2(g) \qquad \xrightarrow[VIII]{410^\circ C} Nd_2O_2(CO_3). \searrow CO(g) \qquad (3)$$

The corresponding activation energies (Table 1) were 162.3 (VI), 168.1 (VII), and 186.7 kJ mol^{-1} (VIII). The above values may give indication that the thermal stability of these intermediates may represented as follows,

$$Nd_2O(CO_3)_2\ (VIII) > Nd_2(CO_3)_2\ (VII) > NdO(CH_3COO).$$

The IR spectra of the gas phase at 350 and 400 °C show intensifying of the bands due to acetone, CO_2 and CO, gaseous decomposition products from reaction (3). In support with the above results, the XRD of Nd-$(AcO)_3$350 (Fig. 4) detects a growing pattern, which matches well with the reference pattern of standard $Nd_2O_2(CO_3)$ [ASTM No. 37-806]. Moreover, XRD of $Nd(AcO)_3$600 gives indication of a phase transformation of $Nd_2O_2(CO_3)$ (ASTM No. 25-567). Compatibly, IR spectra of $Nd(AcO)_3$350 and $Nd(AcO)_3$600 (Fig. 3) show only absorptions assignable to carbonate oxide species at 1560, 1450, 1370, 1050, and 870 cm^{-1}.[21] The strong absorptions emerging at 650—400 cm^{-1} are related to Nd–O vibrations modes.[21]

The IR spectrum of the gas phase at 400 °C (Fig. 2) displays more bands due to methane (3010 and 1310 cm^{-1}),[19] and isobutene (890 cm^{-1}).[19] The formation of both methane and isobutene is expected as a results of the involvement of acetone in surface mediated bimolecular reactions.[4,11] The reactions involved have been visualized,[4,11] as follow:

$$(CH_3)_2CO(s) + OH^-(s) + (CH_3)_2CO(g) \rightarrow (CH_3)_2C{=}CH_2(g) + CH_3COO^-(s), \qquad (4)$$

$$(CH_3)_2CO(g) + OH^-(s) \rightarrow CH_4(g) + CH_3COO^-(s). \qquad (5)$$

At >630°C, process X (Fig. 1) takes place endothermally. The WL, thus determined (52.6%) agrees well with the expected (52.9%) for an overall conversion of $Nd(AcO)_3$ into Nd_2O_3. Accordingly, the intermediate carbonate oxide $Nd_2O_2(CO_3)$, must have decomposed somewhere between 630 and 670 °C, with energy of activation of 302.3 kJ mol^{-1} to form Nd_2O_3.

The XRD for $Nd(AcO)_3$800 (Fig. 4), shows nothing but a sole pattern for crystalline Nd_2O_3 (ASTM No. 6-

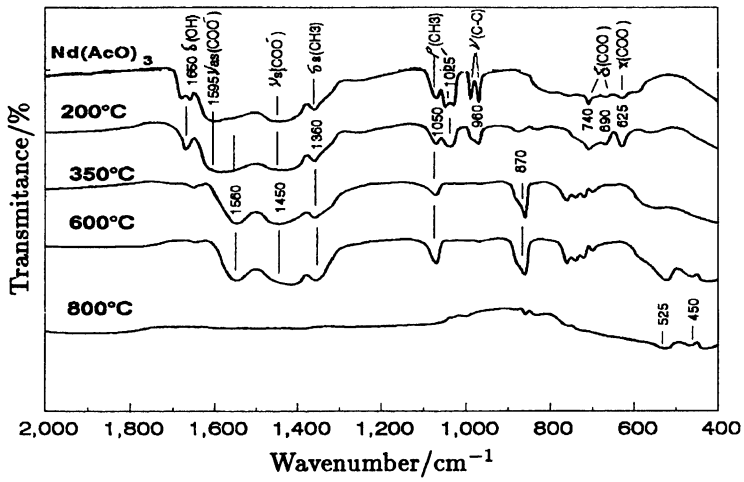

Fig. 3. IR-spectra from KBr supported samples of $Nd(AcO)_3$ and its solid decomposition products obtained by calcining for 1 h in air.

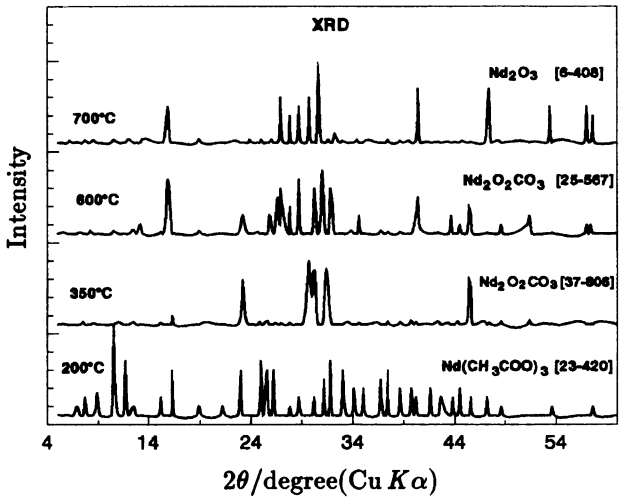

Fig. 4. X-Ray powder diffractograms of $Nd(AcO)_3$ and its decomposition products obtained by calcining for 1 h in air.

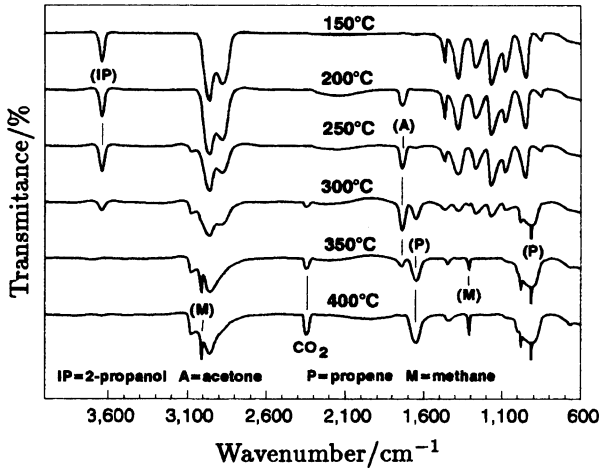

Fig. 5. IR-spectra from 10 Torr 2-propanol after being in contact with $Nd(AcO)_3$800 for 10 min at the temperatures indicated.

408). The corresponding, IR-spectrum (Fig. 3) declares the absence of detectable absorptions due to carbonate oxide and CO_3^{2-} species. However, it displays weak and ill-defined absorptions below 800 cm^{-1}, related to lattice modes of vibration of Nd_2O_3.[21]

The oxide obtained at 800 assumes a higher surface area (30 $m^2 g^{-1}$) than that of Nd_2O_3 obtained at 1000 °C (10 $m^2 g^{-1}$).

Catalytic Activity of Nd_2O_3: IR spectra taken from the gas phase of 2-propanol/Nd_2O_3 (800) at different temperatures (150—400 °C) for 10 min are given in Fig. 5. The room temperature and 150 °C spectra display the characteristic bands of 2-propanol.[19] At 200 °C, the spectrum displays a weak, but important, band at 1740 cm^{-1}. It is developed in the 250 spectrum with the appearance of a band at 1250 cm^{-1}.[19] The two bands mark the formation of acetone gas phase, and, accordingly, the dehydrogenation of 2-propanol started at 200 °C.

In the same spectrum (250 °C, Fig. 5), additional absorptions emerge at 1650 (doublet) and 915 cm^{-1}. At 300 °C, the 2-propanol absorptions became very weak, the absorptions at 1650 and 915 cm^{-1} stronger, and absorptions in the ν(CH) region (3100—2800 cm^{-1}) restructured. The 1650 and 915 cm^{-1} bands are due to propene gas phase. Hence, the dehydration of 2-propanol occur at >250°C.

When the temperature goes up to 350 °C (Fig. 5), absorptions due to both 2-propanol and acetone are hardly detectable. In contrast, the 915 cm^{-1} absorption intensifies, and new absorptions emerge at 1310 (sp), 2340 (doublet), and 3010 (sp) cm^{-1}. They intensify at 400 °C. The absorptions at 3010 and 1310 cm^{-1} indicate the formation of CH_4 gas phase,[22—24] whereas the absorption at 2340 cm^{-1} is due to CO_2. The formation of both CH_4 and CO_2 is due to surface reactions of acetone via an aldol-type of condensation,[22—24] such reactions involve adsorbed and gas phase acetone molecules, as well as nucleophilic surface-OH groups.

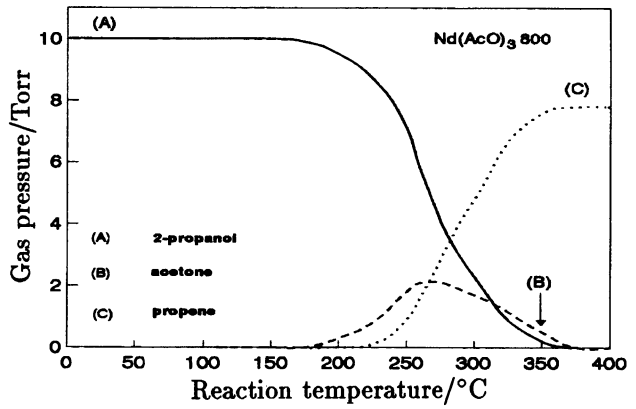

Fig. 6. IR-quantitative analysis of the gas phase composition showing the relation between the reaction temperature and the pressure (Torr), resulting from an initial dose of 10 Torr 2-propanol (A), giving products of acetone (B) and propene (C) after consecutive 10 min intervals at the temperatures indicated over the catalyst $Nd(AcO)_3800$.

The above results are represented, however on quantitative basis, in Fig. 6. It is shown that 2-propanol starts to decline at 175 °C, acetone emerges simultaneously at 175 °C and, then, propene at 225 °C. Rate of the alcohol decomposition appears to maximize at 300 °C, and so does the production of propene (ca. 80%) at 350 °C., and that of acetone (ca. 20%) at 265 °C. At 300 °C, the acetone commences to decrease in magnitude. It decomposed completely at 375 °C.

The qualitative (Fig. 5) and quantitative (Fig. 6) analyses of the catalytic conduct of Nd_2O_3 may conclude that, it acts as a duel dehydrogenation/dehydration catalyst, with a major dehydration selectivity.

Conclusion

The following conclusions can be drawn from the above presented and discussed results:

(1) The course of thermal formation of Nd_2O_3 from $Nd(CH_3COO)_3 \cdot 2H_2O$ may include the following pathways:

$$Nd(CH_3COO)_3 \cdot 2H_2O \xrightarrow{80^\circ C} Nd(CH_3COO)_3 \cdot 1.5H_2O$$
$$\xrightarrow{100^\circ C} Nd(CH_3COO)_3 \cdot H_2O \xrightarrow{175^\circ C} Nd(CH_3COO)_3$$
$$\xrightarrow{310^\circ C} Nd(OH)(CH_3COO)_2 \xrightarrow{320^\circ C} NdO(CH_3COO)$$
$$\xrightarrow{350^\circ C} Nd_2(CO_3)_3 \xrightarrow{385^\circ C} Nd_2O(CO_3)_2 \xrightarrow{410^\circ C} Nd_2O_2(CO_3)$$
$$\xrightarrow{670^\circ C} Nd_2O_3$$

(2) Evolution of acetic acid in the gas phase may be due to hydrolysis of i) surface acetates and ii) ketene (CH_2=C=O) formed through the formation of $Nd(OH)(CH_3COO)_2$.

(3) Nd_2O_3 obtained at 800 °C has higher surface area (30 $m^2\,g^{-1}$) than that obtained at 1000 °C (10 $m^2\,g^{-1}$).

(4) Nd_2O_3 obtained at 800 °C is strong 2-propanol dehydration catalyst (80%) at >300°C, with a lesser tendency towards dehydrogenation.

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