LOW TEMPERATURE SINTERING STUDIES OF AMMONIUM MOLYBDATE, NICKEL HYDROXIDE AND NICKEL MOLYBDATE

Samih A. HALAWY, Khalaf Alla M. ABD EL-SALAAM and Hesham M. RAGIH

Department of Chemistry, Faculty of Science, Qena, Egypt

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The thermal decomposition of ammonium molybdate, nickel hydroxide and MoO_3–NiO 50 mole % mixture were studied by means of TG and DTG non-isothermally, in a dynamic atmosphere of N_2. The activation energy of the thermal process of such samples, also, were evaluated using Maple's theory, in isothermal condition. The variation of S_{BET} with time, during heating ammonium molybdate, nickel hydroxide and MoO_3–NiO 50 mole % mixture at different temperatures, in the range 200 – 400 °C, was monitored, and the activation energy for the sintering process of each compound were calculated from the Arrhenius plot. The final products of heating each sample at the sintering temperatures after 6 h, were characterized by IR and XRD analyses. MoO_3 was formed clearly at 350 °C, while Ni forms a mixture of nickel(II) and -(III) oxides at the same temperature. $NiMoO_4$ was produced, also, at 350 °C in MoO_3–NiO 50 mole % mixture sample.

Sintering is the term that indicates a decrease in the surface area of a porous solid powdered material. Two types of sintering, usually, can be identified, type I shows a continuous decrease in surface area with increasing heating temperature, and type II shows a maximum value of the surface area of the resulting compound in a heating process[1]. Some authors[2,3] studied the phase and structural changes accompanying the thermal dehydration of metal hydroxides, and others studied the sintering of metal-supported catalysts[4]. Babu et al.[5] characterized the metal-supported interactions in Ni–Silica catalysts, using IR spectroscopy.

Flynn et al.[6,7] developed a model of sintering of a supported metal catalyst, and applied it to several theoretical particle size distributions. It is concluded that the rate of sintering increases as the surface velocity and the metal loading increases.

Sintering behaviour, of the most compounds of transition metals, is very sensitive to the heating temperatures, and also the calculated value of the activation energy of the sintering process. The sintering of ammonium molybdate (AM), as well as of $NiMoO_4$, at low temperatures have received no attention in the literatures.

In the present work the thermal decomposition of ammonium molybdate (AM), $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture, in air, is studied using the non-isothermal technique. The surface area of the resulting materials, heated at different temperatures of each duration, is measured using the BET method. The activation energy for both isothermal decomposition and sintering processes are calculated for each material. X-Ray and IR spectroscopy analyses have been used to confirm the formation of the proposed compounds.

EXPERIMENTAL

All the reagents employed were of analytical grade materials. Ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ (AM) was heated in air at 250, 300, 350 and 400 °C for various durations. Nickel hydroxide was prepared according to Teichner and Morrison[8], then heated at 200, 250, 300 and 350 °C for various durations. MoO_3–NiO 50 mole % mixture was prepared by the impregnation method. Calculated amounts of ammonium molybdate (AM) and nickel hydroxide were mixed together by deionized water. The homogeneous paste was dried at 120 °C in an oven overnight to a constant weight. The resulting solid material was heated in air at 200, 250, 300 and 350 °C for 1/2, 1, 2, 4 and 6 h durations.

Thermogravimetric measurements were carried out through heating of known weights of samples (about 50 mg each), with heating rate 5 °C/min in a dynamic atmosphere of N_2 (40 ml/min). The system was described previously[9] as follows: The sample is hanged in the pan of an electronic analytical balance model ER-120A (U.S.A.). The sample is being heated inside cylindrical furnace, therefore the weight measurements were performed against the temperature of the sample. Temperature (±0.1 °C) was measured using a digital multimeter model HC-5010 EC (Japan). Other samples were heated, in the same atmosphere at some selected temperatures in order to study their isothermal decomposition.

The surface area of all the prepared samples were determined, by using N_2 adsorption at –196 °C, with the aid of a conventional volumetric gas adsorption apparatus[10].

X-Ray diffraction analysis was carried out using a Philips Diffractometer (P.W. 2103/00) with Ni-filtered CuKα radiation ($\lambda = 1.542$ Å).

IR absorption spectra of samples heated at different temperatures, were obtained using Perkin–Elmer 599B IR spectrophotometer, by the KBr disc technique, in the region 1600 – 400 cm^{-1}.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TG) and Derivative Thermogravimetry (DTG)

Thermogravimetric and derivative thermogravimetric curves of AM are shown in Fig. 1*a*. The thermal decomposition of AM takes place in three consecutive clear steps, these steps start to occur at 70, 180 and 267 °C, respectively. The first step represents a loss of 1.46% of the original sample weight, this can be attributed to a loss of water molecule. The second step shows weight loss of 4.3%, and this is related to the evolution of two molecules of ammonia and one molecule of water accompanying it $[2\,(NH_3) + H_2O]$ (ref.[11]). The last step gives weight loss of 8.93%, and this can be related to the loss of $2\,[2\,(NH_3) + H_2O]$, where the final product was MoO_3.

The DTG of AM shows a small broad peak at 101.8 °C, which corresponds to the dehydration step in the TG curve, and there are two peaks with maxima at 214.5 and

240 °C, followed by another one at 306 °C. They are related to the maximal rate at which [2 (NH_3) + H_2O] were evolved and the formation of MoO_3 as a final product as concluded from the TG curve of AM.

The TG curve of $Ni(OH)_2$ shows one decomposition step, Fig. 1*b*, with total weight loss of 19.5%, giving a final product as NiO.

The DTG curve of $Ni(OH)_2$ gives a single peak at 310.3 °C, which is related to the temperature of the maximum rate of formation of NiO.

Mixing of MoO_3 and NiO with 50 mole % each, shows another thermal behaviour, differing from that of the parent materials, Fig. 1*c*. The weight loss goes smoothly up to 209 °C, this process is followed by another step starting at about 248.5 °C and the weight loss attained a constant value of 16.7% without any further loss at 390 °C, where $NiMoO_4$ is clearly formed as indicated from XRD and IR analyses.

The DTG curve of MoO_3–NiO 50 mole % mixture shows a broad peak at 209 °C, and a shoulder at 293 °C before the last clear peak at 332 °C, that corresponds to the maximum rate of formation of nickel molybdate.

The kinetics of the isothermal decomposition of AM, $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture were monitored in the temperature range 200 – 325 °C in N_2 atmosphere. All the results are in good agreement with Mampel's theory[12] over the decay period which corresponds to 80 – 90% of the complete decomposition.

Table I summarized the Arrhenius parameters of the isothermal decomposition of AM, $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture. The values of the activation energy

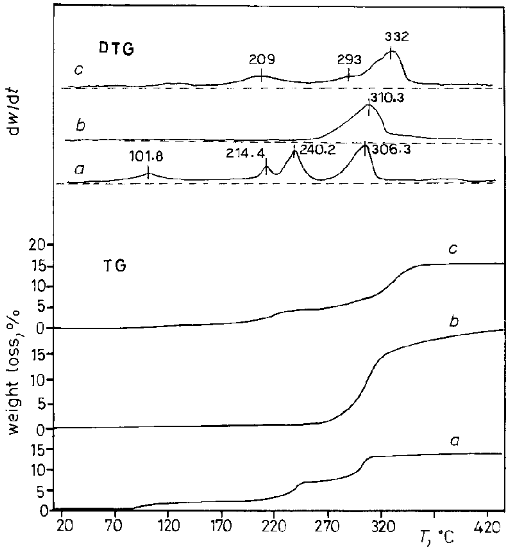

FIG. 1

TG and DTG curves for the decomposition of: *a* ammonium molybdate, *b* $Ni(OH)_2$ and *c* MoO_3–NiO 50 mole % mixture, carried out at 5 °C/min in a dynamic atmosphere of dry N_2 (40 ml/min) are calculated to be 27.98, 68.32 and 35.15 kJ/mol for AM, $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture, respectively.

Sintering of Ammonium Molybdate (AM), Ni(OH)2 and NiMoO4 at Low Temperatures

In order to calculate the activation energy of the sintering process of the samples under investigation, the rate constant of sintering should be determined at different calcination temperatures[2].

The variation of S_{BET} of AM with heating time is shown in Fig. 2*a*. At 250 °C, the surface area increases reaching a maximum value after 4 h heating time, whereas heat-

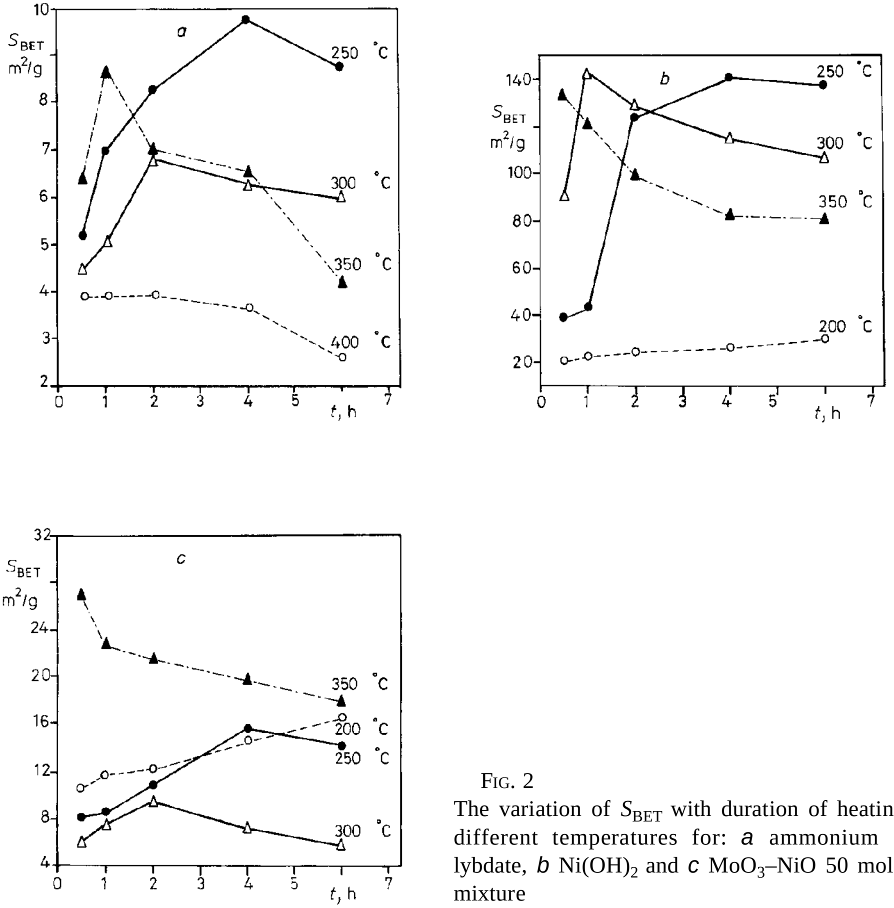

FIG. 2

The variation of S_{BET} with duration of heating at different temperatures for: *a* ammonium molybdate, *b* $Ni(OH)_2$ and *c* MoO_3–NiO 50 mole % mixture ing at 300 °C gives a maximum S_{BET} after 2 h, then it falls down with increasing the heating time. At 350 and 400 °C, the maximum S_{BET} attains early after one hour, then it decreases with increasing the heating time intervals.

In case of $Ni(OH)_2$ (Fig. 2*b*) the surface area at 200 °C increases gradually with increasing heating duration and reaches a maximum after 6 h, while at 250 °C the maximum value of S_{BET} is attained after 4 h. At 300 °C, the highest S_{BET} is reached after one hour, then it decreased steadily with increasing the heating time. The maximum S_{BET} at 350 °C is attained early after half-an-hour.

Figure 2*c* shows the variation of S_{BET} with heating time for MoO_3–NiO 50 mole % mixture sample, at different temperatures. The S_{BET} increases with increasing the heating time, reaching a highest value after 6 h heating at 200 °C. The surface area, at 250 °C, attains to its maximum value after 4 h, but at 300 °C, the maximum S_{BET} is reached after 2 h, then it decreased with increasing the time of heating. Finally, at 350 °C, the highest surface area is occured early after half-an-hour heating time, then it dropped as the time of heating is increased.

Using the equations mentioned elsewhere[2], the values of the rate of sintering (K) were calculated, from the slope of the straight lines resulted by plotting log S_{BET} against log t (time), then the activation energy (E_a, kJ/mol) for the sintering process of each sample were calculated from the Arrhenius plot and cited in Table I.

IR Analysis

IR spectra were performed to investigate the structure of the various samples, heated at different temperatures for 6 h in air.

TABLE I
The Arrhenius parameters of the isothermal decomposition and sintering processes of ammonium molybdate (AM), $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture

Sample	Isothermal decomposition				Sintering process			
	Temp. range, °C	E_a kJ/mol	ln A	r	Temp. range, °C	E_a kJ/mol	ln A	r
AM	200 – 325	27.98	2.68	0.96	250 – 400	24.83	2.27	0.99
$Ni(OH)_2$	275 – 375	68.32	9.28	0.99	200 – 350	35.56	5.57	0.99
MoO_3–NiO 50 mole %	200 – 235	35.12	3.98	0.98	200 – 350	37.04	6.59	0.98

Figure 3 shows the collected absorption spectra of AM, heated in the temperature range 250 – 400 °C. The absorption band at 1 400 cm^{-1}, which is related to the deformation vibrations of physically adsorbed water[13], disappeared in sample heated at 350 °C, while the intensity of the absorption band at 985 cm^{-1} increased with increasing the heating temperature. This band corresponds to Mo=O stretching mode, with molybdenum atom possessing an octahedral coordination[14]. A group of bands appeared in the range 850 – 605 cm^{-1}, with different intensities, which are attributed to the stretching vibrations of bridging oxygen ν(Mo–O–Mo).

Figure 4 shows the IR absorption spectra of $Ni(OH)_2$ heated in air for 6 h, in the temperature range of 200 – 350 °C. The absorption band at 1 380 cm^{-1}, which is assigned to δ(OH) group still appears in the spectra of samples heated at 200, 250 and 300 °C, with gradual decrease in its intensity through increasing the heating temperature. The absorption bands of Ni–O stretching vibrations[15] at 510 and 440 cm^{-1} also appeared in all the spectra of the samples heated in the temperature range 200 – 350 °C.

The IR absorption spectra of MoO_3–NiO 50 mole % mixture heated in air for 6 h in the temperature range 200 – 350 °C are shown in Fig. 5. The absorption band of δ(OH) group at 1 390 cm^{-1}, appears in the spectra of samples heated at 200, 250 and 300 °C, then disappears in the last spectrum of sample heated at 350 °C. There are another groups of absorption bands in all the spectra in the range of 970 – 420 cm^{-1}, which are assigned to the different vibration modes of $NiMoO_4$, as mentioned previously by Cord et al.[16].

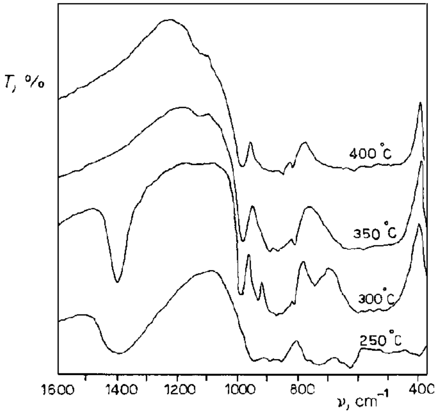

Fig. 3

IR absorption spectra of ammonium molybdate heated in air at different temperatures for 6 h

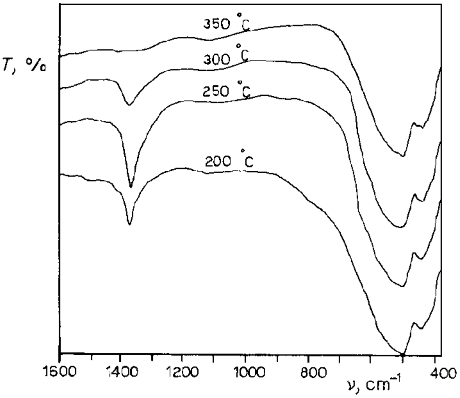

Fig. 4

IR absorption spectra of $Ni(OH)_2$ heated in air at different temperatures for 6 h

X-Ray Analysis

X-Ray diffraction patterns of AM, $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture heated at 350 °C in air for 6 h, together with the corresponding ASTM card data, are shown in Fig. 6.

AM heated at 350 °C have the same lattice structure of MoO_3, comparing the observed lines of this sample with those reported for standard pattern of MoO_3 (ASTM card no. 5-0508).

In case of $Ni(OH)_2$, heated at 350 °C, the X-ray pattern showed that the resulted nickel oxide is a mixture of NiO + Ni_2O_3. Some diffraction lines at d = 2.05, 1.55 and 1.09 Å are related to NiO (ASTM card no. 4-0835), while the diffraction line at d = 1.78 Å is related to Ni_2O_3 (ASTM card no. 14-481).

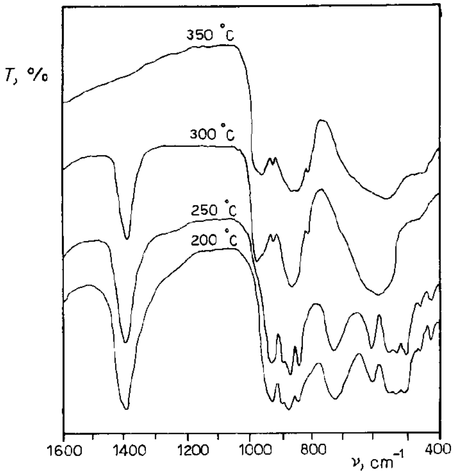

FIG. 5
IR absorption spectra of MoO_3–NiO 50 mole % mixture heated in air at different temperatures for 6 h

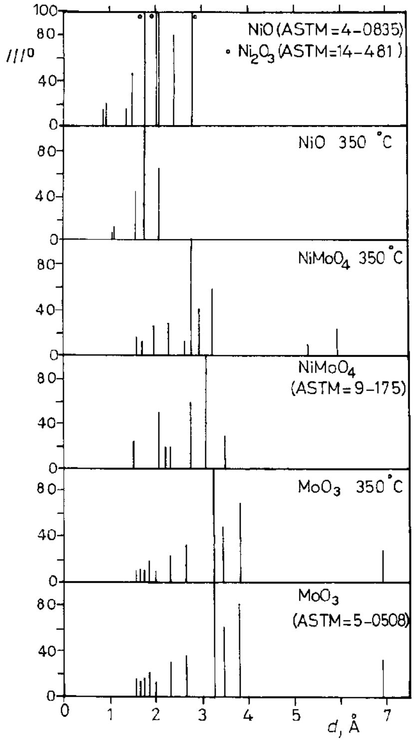

FIG. 6
XRD patterns of MoO_3, NiO and MoO_3–NiO 50 mole % mixture heated in air at 350 °C for 6 h

The X-ray diffraction pattern of MoO_3–NiO 50 mole % mixture, heated at 350 °C, also, have some features of the diffraction lines of $NiMoO_4$ (ASTM card no. 9-175), with the presence of some diffraction lines of MoO_3 at d = 3.22, 2.62 and 1.95 Å, and one diffraction line at d = 1.57 Å belonging to NiO.

The cumulative data for the texture characterization of the sintered samples of AM, $Ni(OH)_2$ and MoO_3–NiO 50 mole % mixture, heated for 6 h in air at different temperatures, are calculated and presented in Table II.

The maximum surface area obtained for AM heated in air at 250 °C for 6 h can be correlated to the removal of water of hydration as well as the thermal decomposition of AM, creating a pore system of the produced oxide. Increasing the heating temperature leads to a continuous decrease in S_{BET}, and a slight increase in density values of the samples. This can be related to a process of densification going parallel with a process of sintering, both processes will lead to a decrease in surface area.

When $Ni(OH)_2$ is heated at temperatures close to its thermal decomposition temperature, the chemisorbed water as well as the hydroxyl groups start to interact with each other through their protons. The removal of the chemisorbed water will accompanied by the creation of cation vacancies[2],

TABLE II
Cumulative data for ammonium molybdate, nickel hydroxide and MoO_3–NiO 50 mole % mixture sintered in air for 6 h at different temperatures

Sample	Heating temp. °C	S_{BET} m^2/g	Density g/cm^3	V_p ml/g	Degree of decomp.[a]
Ammonium molybdate	250	8.74	2.70	0.37	52.26
	300	5.98	2.86	0.35	71.68
	350	4.22	2.94	0.34	76.66
	400	2.61	3.35	0.30	79.61
$Ni(OH)_2$	200	29.94	3.10	0.32	14.69
	250	137.45	4.04	0.25	18.89
	300	107.13	4.54	0.22	51.43
	350	80.06	5.05	0.20	88.36
MoO_3–NiO 50 mole % mixture	200	16.49	2.44	0.41	31.68
	250	14.19	3.05	0.33	41.43
	300	5.89	3.63	0.28	54.90
	350	17.92	4.81	0.21	68.13

[a] Calculated from the total volatile materials.

$$Ni^{2+} + O^{2-} + H_2O \longrightarrow Ni^{2+} + 2\,OH^- + [Ni]'' , \qquad (1)$$

where [Ni]″ indicates a cation vacancy.

On further heating at higher temperatures, a decrease in S_{BET} is obtained. This is due to the formation of anion vancancies[17], which will facilitate lattice diffusion as follows:

$$NiO \longrightarrow [O]^{\bullet\bullet} + 1/2\,O_2 + Ni[Ni]'' , \qquad (2)$$

where $[O]^{\bullet\bullet}$ represents oxygen anion vacancy and Ni[Ni]″ indicates nickel atom that replaces nickel ion with two positive charges.

This is clearly observed from the data shown in Table II. The S_{BET} has its maximum value at 250 °C, then it decreased gradually with increasing the heating temperature.

The reduction in S_{BET} of $Ni(OH)_2$ with increasing heating time and temperature, also, can be resulted by chemical interaction through the production of hydrogen during the heating course.

The production of H_2 gas has been determined in the decomposition process elsewhere[18], and is identified practically in the present work, using gas chromatograph model Shimadzu GC-14 and the H_2 gas is sensed by TCD detector, during the thermal decomposition of $Ni(OH)_2$ using pure dry N_2 as a carrier.

The evolution of H_2 molecule will cause the formation of two O^- ions as follows:

$$2\,OH^- \longrightarrow 2\,O^- + H_2 \ \ (gas) \qquad (3)$$

This gas evolution will take place through [Ni]″ vacancies, as indicated for $Mg(OH)_2$ by Derouane et al.[19], and this in turn will lead to diminution of S_{BET} at higher temperatures and longer heating times.

The S_{BET} values of MoO_3–NiO 50 mole % mixture samples show a different behaviour, since the surface area decreased with increasing the heating temperature till a minimum value at 300 °C, then it increased again at 350 °C. This can be related to the replacement of MoO_3 into NiO lattice, and the evolution of O_2, which leads to the formation of more oxygen anion vacancies into the lattice[17], that causes a reduction in the S_{BET} as follows:

$$4\,[e]^{\bullet} + MoO_3 \longrightarrow Mo[Ni]^{\bullet\bullet\bullet\bullet} + NiO + O_2 \qquad (4)$$

and this is indicated in the XRD pattern of MoO_3–NiO 50 mole % mixture, heated at 350 °C, where some diffraction lines of MoO_3 have appeared. The S_{BET} value then increased at 350 °C, and this can be correlated to the saturation of the oxygen anion vacancies, that previously formed, at higher temperature as follows:

$$2\,[O]^{\bullet\bullet} + MoO_3 \longrightarrow Mo[Ni]^{\bullet\bullet\bullet\bullet} + NiO\,. \tag{5}$$

The differences in density values of the solid samples, produced at different heating temperatures for 6 h, set up a strain in the crystal lattice which produces a break up of the particles into new products, leading to different V_p values, see Table II.

The activation energy (E_a, kJ/mol) for the sintering process was calculated as 24.83, 35.56 and 37.04 kJ/mol for ammonium molybdate, nickel hydroxide and MoO_3–NiO 50 mole % mixture, respectively (see Table I).

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