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PHYSICO-CHEMICAL CHARACTERISTICS OF SOME MIXED OXIDES OF NICKEL AND IRON

S.K. Mazumdar*, A.S. Brar
Department of Chemistry
Indian Institute of Technology
New Delhi-110016, India.

ABSTRACT

A series of mixed oxides of iron and nickel as well as nickel ferrite was prepared by calcination of ferrous oxalate and nickel hydroxycarbonate at 300,500,700 and 900°C respectively for 6 hours in air, fixing the atomic ratio of iron and nickel in the process as 1:0.75. The samples were analysed for different species using X-ray diffraction and infrared spectroscopy. The decomposition products were also established with the aid of thermal gravimetric and differential thermal analyses. The percentage composition of different species formed at 300°C were also calculated by analysing the Mössbauer spectrum of the sample. The surface area for these samples were measured through conventional N_2 adsorption BET experiments carried out at liquid air temperature. The decomposition of hydrogen peroxide on these samples was also studied to establish the catalytic activity of these catalysts.

INTRODUCTION

The main class of reactions that lead to the formation of active oxide catalysts is essentially thermal decomposition of suitable compounds(1). The chemical composition of the starting materials and the methods of preparation play an effective role in altering the properties of the final products(2). Nickel ferrites and mixed oxides have been reported to act as active catalysts(3-5) and hence, an attempt was made to prepare mixed oxides of nickel and iron at different temperatures and characterize the products thus formed.

EXPERIMENTAL DETAILS

Stiochiometric amounts of ferrous oxalate dihydrate (Reidal, Germany) and nickel hydroxycarbonate tetrahydrate (Sarabhai Chemicals, India) containing iron and nickel in atomic ratio 1:0.75 were subjected to calcination at 300,500,700 and 900 ± 5°C for 6 hours each in air at an heating rate of 5°C/min. The samples were labelled as I,II,III and IV respectively.

The TGA and DTA of pure components of the starting material

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were studied in the temperature range 0-1000°C on Shimadzu Thermal Analysis Instrument (Japan).

The Mössbauer spectrum was recorded on a Canberra Mössbauer spectrometer using a $^{57}Co(Pd)$ source. The details of the other experimental measurements and instrumentation techniques appear elsewhere$^{(2)}$.

RESULTS AND DISCUSSION

The TGA of ferrous oxalate indicates complete dehydration at 220°C with an experimental weight loss of 19.3% (theoretical 20%) corresponding to which, an endothermic peak appears in the DTA. The compound is fully decomposed at 280°C with an apparent weight loss of 53.5% (theoretical 55.5%) corresponding to which, a strong exothermic peak appears in the DTA, the reason for the exothermic nature lying in the formation of the oxidation product Fe_2O_3. The thermogram of nickel hydroxycarbonate indicates the loss of water molecules in its TGA by virtue of an apparent weight loss of 20% (theoretical 19.1%) followed by the formation of NiO as indicated by the weight loss of 38% (theoretical 40.25%). An endothermic peak in DTA at 320°C corresponds to the total loss. The thermogram of the starting material appeared as a rough overlap of the thermograms of the two individual components.

The representative X-ray diffractograms of samples I,II,and III are shown in fig 1. The bulk of the species formed at 300°C comprises of α-Fe_2O_3, which is shown by the presence of peaks with d values 3.60(012), 2.65(104), 2.49(110), 1.84(024) and 1.48(214) A°. The XRD of samples II and III show, in addition, peaks with d values 2.36(222), 2.05(400) and 2.01(331) A° respectively corresponding to the formation of $Ni_xFe_{3-x}O_4$. In a different X-ray diffractogram of sample IV, not shown in the fig, $Ni_xFe_{3-x}O_4$ was found to be the bulk phase present, along with the presence of α-Fe_2O_3.

The infrared spectra of the samples II,III and IV show the presence of two peaks at 680 and 540 cm^{-1} due to $Ni^{2+}O_4^{2-}$ and $Fe^{3+}O_4^{2-}$ polyhedron oscillations respectively thereby indicating the formation of $Ni_x^{II}Fe_{3-x}^{III}O_4$. The strong peaks at 480 and 320 cm^{-1} along with a shoulder at 380 cm^{-1} correspond to the presence of α-Fe_2O_3 in the sample.

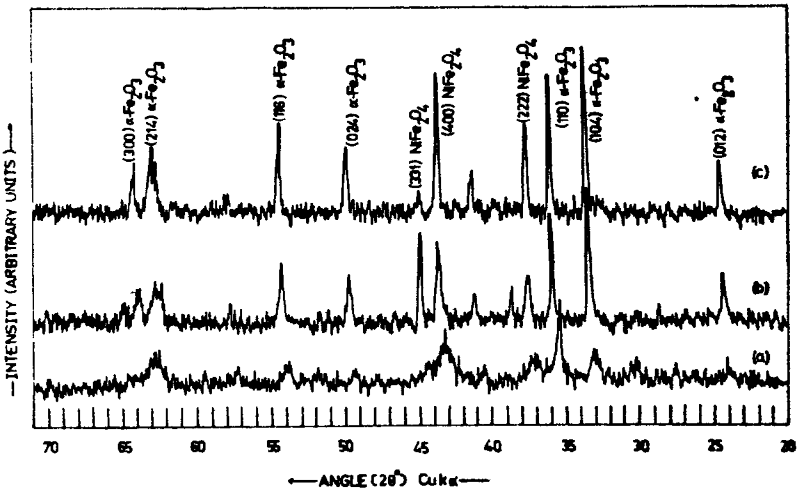

Fig 1 X-ray diffractograms of samples (a) I (b) II (c) III

The Mössbauer spectrum of the sample I heated at 300°C, indicates a six line hyperfine split spectrum, owing to the presence of α-Fe_2O_3, with isomer shift and quadrupole splitting values 0.57 and 0.46 ± 0.04 mms^{-1} respectively. A magnetic field of the order of 501 ± 5 KOe arises due to the interaction of the nuclear dipole moment with the magnetic field in the antiferromagnetic specimen of α-Fe_2O_3(6). The spectrum also shows the presence of an additional doublet with isomer shift and quadrupole splitting values 0.25 and 0.46 ± 0.04 mms^{-1} respectively. Since the values are quite lower than those for ferrous oxalate at room temperature, the appearance of this doublet may be attributed to the formation of $Fe_2^{III}(C_2O_4)_3$ in a very small amount.

The surface area for the catalysts were found to be 10.1 , 12.2, 8.9 and 6.6 m^2g^{-1} respectively. The rate constants k for the decomposition of hydrogen peroxide (0.5% w/v) over catalyst surfaces (I,II,III and IV) at 30 ± 0.1°C have been found to be 3.51, 3.22, 1.34 and 0.69 min^{-1} respectively. These values decrease with an increase in the temperature of decomposition of the samples due to fall in the total number of active centres as a result of sintering which is also reflected by a corresponding decrease in the surface areas of the respective samples. The initial rate of reaction k' expressed per unit time (sec^{-1}) per unit weight per unit surface area (m^2/g) of the catalyst have been calculated to be .113 , .087

.050 and .035 respectively, which sheds an additional light on the formation of mixed oxides and their catalytic behaviour due to their inherent crystal defects. These specific rate constants do not follow a regular trend owing to a greater formation of $Ni_xFe_{3-x}O_4$ per unit area of the sample, with an increase in the temperature of preparation.

These results, thus, give an idea of the optimum experimental conditions for preparation of the active catalysts.

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