

Studies on Reduction of Iron-Nickel Mixed Oxides System

G C MAITI

Physical Research Wing, Projects and Development India Ltd,
Sindri, Dhanbad (Bihar)

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Structural changes in mixed composite consisting of iron and nickel oxides during calcination and reduction have been studied. X-ray and IR spectroscopic studies indicate that oven-dried composite consists of mixed oxide hydrate and nickel hydroxide phase. On heat treatment above 500°C, the mixed oxide hydrate is transformed into NiFe_2O_4 spinel. Reduction of calcined samples under H_2 atmosphere leads to a single face-centred cubic γ -NiFe phase. The presence of NiO makes the reduction of iron oxide easier, which is complete around 300°C. Elemental nickel is formed at the first step of reduction, which favours the building up of γ -NiFe lattice on subsequent reduction.

One of the most significant advances in catalysis in the recent years is the development of bimetallic systems for the control of catalytic properties¹⁻³. Bimetallic Fe-Ni and Fe-Co catalysts have been reported for the selective hydrogenation of carbon monoxide^{4,5}. Bimetallic catalysts are generally obtained by co-precipitation of hydroxides, followed by thermal treatment of the composite^{6,7}. The nature of precipitate formed during the formation of Fe_2O_3 -NiO system and the characterisation of compounds obtained during thermal treatment of Fe_2O_3 -NiO are still not well-defined. Therefore, it seems necessary to undertake thermochemical studies on Fe_2O_3 -NiO system with a view to evaluating pretreatment conditions for the preparation of Fe-Ni bimetallic catalyst.

The composite Fe_2O_3 -NiO system was prepared by continuous co-precipitation method from aqueous solutions of mixed metal nitrates (0.15 M) by the addition of ammonium hydroxide (0.1 M). The pH was maintained at 7.6 ± 0.2 . The precipitate was washed with distilled water and dried at 120°C *in vacuo* for 15 hr. The oven-dried sample was used for thermoanalytical studies. The Fe:Ni ratio in the sample was found to be 2:3.

All the chemicals used were of AR grade. The details of method of preparation have been given elsewhere⁸. Differential thermal analysis (DTA) and thermogravimetric (TG) measurements were performed with a thermal analyser (Mettler) in air. The sample (200 mg) and $\alpha\text{-Al}_2\text{O}_3$ used as a standard were placed in two different Pt-caps. DTA under controlled atmosphere (in argon and H_2) was done using a Dupont instrument

(DTA-990). A sample of about 15 mg was used in each experiment.

X-ray powder photographs of the oven-dried, calcined and reduced samples were taken with a standard Guinier camera using crystal reflected monochromatic FeK_{α_1} radiation.

The crystallite size of the sample was measured using Scherer formula⁹. The lattice parameters were determined using a suitable computer program (ACTIVE 1). Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer using samples (3 mg each) admixed with KBr (300 mg).

The thermal behaviour of co-precipitated composite was followed employing differential thermoanalytical techniques in air and argon atmospheres. DTA curve of the oven-dried sample in air shows three endothermic peaks at 115°, 210° and 260°C. The corresponding total mass loss upto 260°C amounts to 8.62% during the calcination process. There is no further mass loss above 300°C. The nature of DTA curve in argon is similar to that obtained in air. The peak temperatures lie at 90°, 205° and 255°C. DTA curve in argon, in addition, shows an exothermic peak at 520°C. This peak is very broad in the DTA in air. DTG curve also indicates three maxima. X-ray diffraction pattern of the oven-dried sample shows that it is poorly crystalline and does not contain any free hydroxide phase.

IR spectra for the oven-dried sample and of samples thermally treated at 300° and 600°C are shown in Fig. 1. IR spectrum for the oven-dried sample exhibits a very broad stretching band in the region 3660-3300 cm^{-1} . Three other bands at 640, 495 and 340 cm^{-1} also appear in the region of OH bending mode of vibration. The IR spectrum of the sample calcined at 300°C displays two bands at 630 and 420 cm^{-1} and the

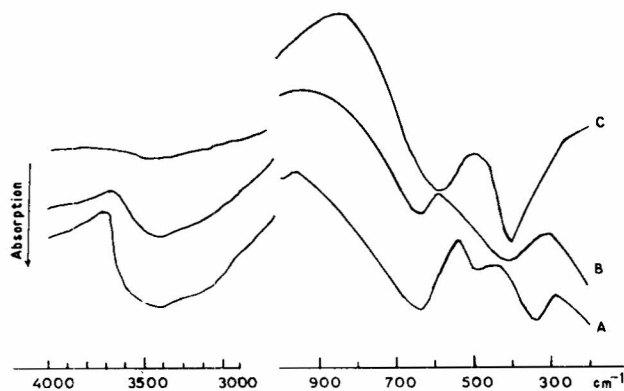


Fig. 1—Infrared spectra of the composite calcined at 120° (A), 330° (B) and 600°C (C)

band positions are changed further on heat treatment at 600°C (Fig. 1).

DTA results indicate that dehydration of composite occurs in three different steps. On complete dehydration, NiO and NiFe_2O_4 phases are formed. However NiFe_2O_4 phase remains in poorly crystalline state below 500°C. The results indicate that oven-dried sample consists of mixed oxide hydrate of iron and nickel instead of free metallic hydroxides. Thermogravimetric measurements show only a mass loss of 8.62%, which also supports the formation of a mixed oxide hydrate as a major constituent in co-precipitated composite. Broad band in the stretching region 3660-3300 cm^{-1} can be due to the formation of mixed oxide hydrate. The exothermic peak at 520°C can be assigned to crystallization of NiFe_2O_4 phase. Measured lattice parameter ($a_0 = 8.336 \text{ \AA}$) is very close to that of reported¹⁰ ASTM data of NiFe_2O_4 . Formation of NiO at 300°C and crystalline NiFe_2O_4 phase above 500°C, has also been indicated by the IR spectra (Fig. 1).

After calcining the samples at 300, 450 and 600°C in the DTA cell under argon atmosphere, the samples were subjected to heat treatment again under H_2 atmosphere in order to follow the nature of reduction process. DTA curves under H_2 atmosphere (Fig. 2) show three endothermic maxima and two exothermic maxima for samples precalcined at 300 and 450°C and only a single broad endothermic peak for the sample precalcined at 600°C. Thermogravimetric measurements indicate that reduction starts above 270°C and is complete at 320°C. Total mass loss amounts to 25.9% during reduction. The details of TG results are given elsewhere¹¹.

X-ray diffraction patterns show the formation of a single γ -NiFe phase in all the cases. Formation of no separate elemental iron or pure nickel phase has been detected.

DTA studies indicate that reduction process does not occur in a single step if the sample is precalcined only at 450°C; this is possibly related to the presence of distorted NiFe_2O_4 phase. The overall reduction leads

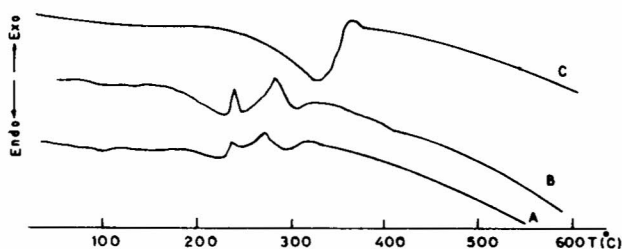


Fig. 2 --DTA curves of the calcined samples under H_2 atmosphere (A, 300°C; B, 450°C; and C, 600°C)

to the formation of a single phase consisting of mixed lattice of γ -NiFe. DTA curve becomes simpler, consisting of a single broad endothermic peak with a maximum at 335°C for sample precalcined at 600°C. The reduction of NiO is weakly exothermic. But as the reduction of NiFe_2O_4 is more endothermic, an overall endothermic peak is noticed. γ -NiFe phase is also formed as a residual product of reduction in this pretreatment process. The measured lattice parameter value of the reduced phase ($a = 3.58 \text{ \AA}$) is in good agreement with the formation of an alloy consisting of 60% Ni (see ref. 12). The results indicate that elemental nickel formed by the reduction of NiO is easily assimilated in γ -NiFe lattice, which is formed by the reduction of NiFe_2O_4 phase.

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