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Preparation of nanostructured $NiFe_2O_4$ catalysts by combustion reaction

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Abstract Nanosize nickel ferrite powders ($NiFe_2O_4$) have been prepared by combustion reaction using nitrates and urea as fuel. The resulting powders were characterized by X-ray diffraction (XRD), nitrogen physical adsorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and catalytic activity. The results showed nanosize nickel ferrite powders with high specific surface area (55.21 m^2/g). The powders showed extensive XRD line broadening and the crystallite size calculated from the XRD line broadening was 18.0 nm. The nickel ferrite powder presented significant activity as catalyst for the water gas shift reaction, over the temperature range of 250–450 °C.

Introduction

Nanostructured materials exhibit unusual physical and chemical properties, significantly different from those of conventional bulk materials, due to their extremely small size or large specific surface area [1–3]. Nanosized spinel ferrite particles have attracted considerable attention and continued efforts to investigate them for their technological importance to the microwave industries, high speed digital tap or disk recording, repulsive suspension for use in levitated railway systems, ferrofluids, catalysis and magnetic refrigeration systems [4–6]. For example, nickel zinc spinel ferrites as catalysts have well-established catalytic properties for alkylation of aniline [7].

High specific surface areas of particles are extremely important for heterogeneous catalytic processes. Ferrite materials obtained by conventional ceramic method often have very low surface areas corresponding to that of sintered solids, due to sinterization upon treatment/calcinations at high temperatures, and this is a disadvantage for heterogeneous catalysis. The preparation of materials by the classical solid-state reactions requires high calcinations temperature and hence induces the sintering and aggregation of particles [8]. To produce nanosized ferrite particles, some techniques such as chemical coprecipitation [9], hydrothermal synthesis [10, 11], hydrolysis of metal carboxylate in organic solvent [12], sol–gel [13], freeze drying [10], spray drying [14], citrate precursor [15] and aerosolization [16] have been developed. In particular, the synthesis by combustion reaction technique has been shown to have great potential in the preparation of ferrites [17–19]. The process is quite simple since multiple steps are not involved. It is employed in the field of propellants and explosives, and involves an exothermic and self-sustaining chemical reaction between the desired metal salts and a

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suitable organic fuel, usually urea [20, 21]. The resulting product is usually a product that is dry, crystalline, has high chemical homogeneity and purity, is inexpensive and is agglomerated into highly fluffy foam [22, 23].

Metal doped magnetite is a proven industrial catalyst for the water gas shift reaction (WGSR), an important step in the ammonia synthesis process. More recently, this reaction has also attracted much attention as a means for hydrogen purification for fuel cell devices:

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \qquad (1)$$

Thus, an active WGSR catalyst should present adequate redox properties besides high hydrothermal and textural stabilities [24–26].

This work reports the prepared and characterization structural, morphologic and catalyst of nickel ferrite nanoparticles ($NiFe_2O_4$) by a single step solution combustion reaction using nitrates and urea as fuel. The obtained nickel ferrite powder was further evaluated and as compared to a commercial catalyst for the water gas shift reaction.

Experimental

Nanosize particle oxides of nickel ferrite with nominal composition $NiFe_2O_4$ was prepared by combustion reaction using urea as fuel. The starting materials were iron nitrate, nickel nitrate and urea. Stoichiometric compositions of metal nitrate and urea were calculated using the total oxidizing and reducing valences of the components which serve as the numerical coefficients for the stoichiometric balance so that the equivalence ratio Φ_c is unity and the energy released is maximum [27]. The batches were placed in a vitreous silica basin, homogenized and directly heated up in the hot plate to temperature around 480 °C until the ignition took place, producing a nickel ferrite in a foam form. The ignition temperature was determined by an infrared pyrometer (Raytek, model MA2SC) and the ignition flame time was measured with a digital chronometer (Condor, model S1000). The powders were characterized by X-ray diffraction (Kristaloflex D5000, Cukα with a Ni filter, and scanning rate of 2° 2θ/min, in a 2θ range of 20–60°). The average crystallite sizes calculated from X-ray line broadening (d_{311}) using Scherrer's equation [28]. The specific surface area and the average particle size were determined in a Gemini—2370 Micromeritics apparatus. Specific surface area was calculated from the N_2 physisorption data using the equation by Brunauer, Emmett and Teller (BET) [25]. The powder density was determined using a helium pycnometer (Pycnometer Micromeritics, ACCUPYC 1330). The lattice parameters were calculated from the X-ray diffraction patterns. The morphology of the powder was analyzed by using a scanning electron microscopy (Philips XL30 FEG)—SEM. The morphology and size of the particles were observed using transmission electron microscopy (TEM). For the TEM studies the powders were supported on carbon-coated copper TEM grids and analyzed using a Philips EM420 transmission electron microscope at an accelerating voltage of 120 kV. Bright-field and dark-field imaging was performed to reveal the size and morphology of the nanopowders. Structure information was obtained using selected area diffraction patterns.

The catalytic activity of the prepared $NiFe_2O_4$ (NiF) sample (100 mg) was examined as a function of the reaction temperature (250–450 °C), at atmospheric pressure, using a gas flow of $CO:N_2:H_2O$ = 1:4:3 in a fixed-bed flow reactor coupled to a gas chromatograph. The commercial Fe_2O_3–Cr_2O_3 (FeCr) water gas shift catalyst was tested under identical conditions. Prior to the activity evaluation, the catalysts were reduced under a flow of 30%H_2 in N_2 (v/v), for 1h at 400 °C.

Results and discussion

The combustion flame time and temperature of the synthesis by combustion reaction exerts an important effect on the final characteristics of powders. These parameters depend, mainly of the intrinsic characteristics of each system. For the system $NiFe_2O_4$ the combustion flame time and temperature of reaction reached during the synthesis, whose obtained experimental values were 11.0 s and 622 °C (±2 °C), respectively. This show that the system led the lower temperature and lower combustion time, avoided, this way, the pre-sintering and/or growth of particles. Table 1 shows the characteristics of the $NiFe_2O_4$ powder (specific surface area, particle size, average agglomerate size, crystallite size, powders density and lattice parameters) prepared by combustion reaction. The average agglomerated size, specific surface area (BET) and the nanoparticle size calculated from the physisorption data were 8.13 μm, 55.21 m^2/g and 20.2 nm, respectively. Comparing this last value to that calculated using the Scherrer's equation (18.0 nm), it was observed that the values were close, indicating the efficiency of the synthesis process. The density of the powder was 4.99 g/cm^3 (92.9% of the theoretical density—TD). These results can be attributed, mainly, to the combustion flame time and temperature of reaction during the synthesis.

The X-ray diffraction pattern of the $NiFe_2O_4$ nanopowder after synthesis is showed in Fig. 1. Through the diffractograms obtained for the powder, it was observed that the combustion flame temperature controlled during

Table 1 Powder characteristics of $NiFe_2O_4$ prepared by combustion reaction

Specific superficial area (BET) (m^2/g)	Particle size* (nm)	Average agglomerated size 50% (μm)	Crystallite size** (nm)	Powder density Experimental (g/cm^3) (%TD)
55.21	20.20	8.13	18.00	4.99 (92.9)

*Calculated from specific surface area

**Calculated from Scherrer's equation [28]

***Theoretical density 5.37 g/cm^3

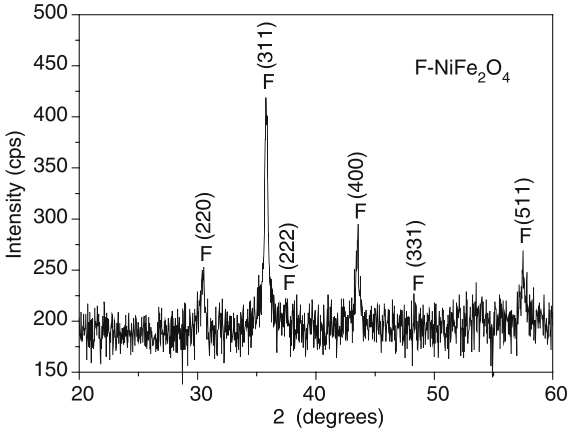

Fig. 1 X-ray diffractogram patterns of $NiFe_2O_4$ powder as prepared by combustion reaction

the combustion reaction (622 °C) was sufficiently high to the complete formation of the crystalline phase of nickel ferrite with cubic spinel structure. The XRD pattern for the powder shows considerable line broadening, indicating the nanosize particle nature of nickel ferrite prepared by combustion reaction. The crystallite size calculated from X-ray line $d_{(311)}$ broadening using Scherrer's equation [28] was at 18.0 nm.

Figure 2 presents the size, morphology and electron diffraction patterns of as-synthesized nickel ferrite particles observed by TEM micrograph. The powders appeared to be agglomerated. The electron diffraction clearly shows in both cases the rings belonging to the nickel ferrite phase and also the rings corresponding to spacing of around 2.97 Å and 1.62 Å of the nickel ferrite. The selected area aperture used in this study was enough to reveal all the

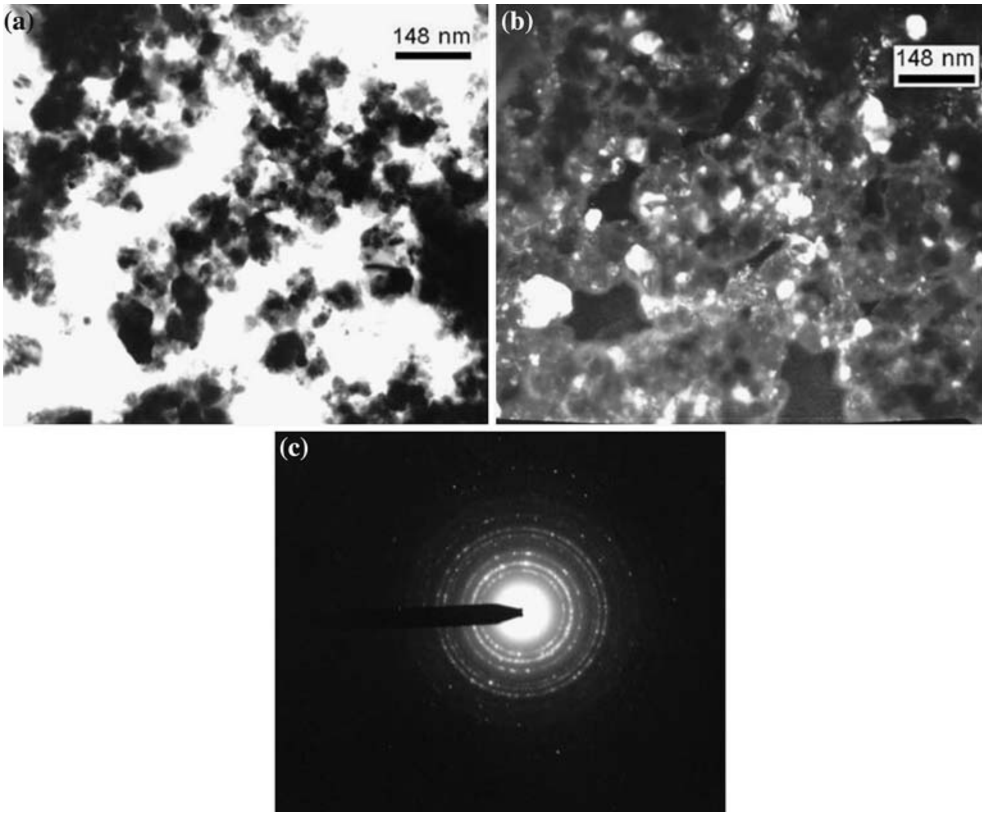

Fig. 2 Transmission electron micrographs of $NiFe_2O_4$ powder prepared by combustion reaction: (**a**) (BF) bright field image (**b**) (CDF) centered dark field image and (**c**) diffraction patterns (SADPs) showing rings that match d-spacing for the spinel structure

corresponding rings for the spinel structure. The TEM results showed that the particles did not have a narrow size distribution. Thus it can be inferred that the nucleation occurred as a single event, and this resulted in a size distribution of nuclei. The particle size calculated by TEM micrograph was in the range of 22–29 nm. This value of particle size for $NiFe_2O_4$ obtained by combustion reaction is in range of the values calculated by TEM micrograph and reported by Chen [13] nanoparticles (5–30 nm) prepared by the sol–gel method.

The powder density was 4.99 g/cm^3 (92.9% of the theoretical value). The surface area of powder was 55.21 m^2/g and the particle size, calculated from of the surface area, was 18.0 nm. This result is in good agreement with the results obtained by TEM and Scherrer's equation (22–29 and 18.0 nm, respectively).

The Figure 3 presents the morphology of the powders obtained by scanning electron microscopy (SEM) of the resulting of $NiFe_2O_4$ powder. Through of the micrograph we can observe the formation of soft agglomerates (easy deagglomeration) with irregular morphology constituted of the quite fine particles.

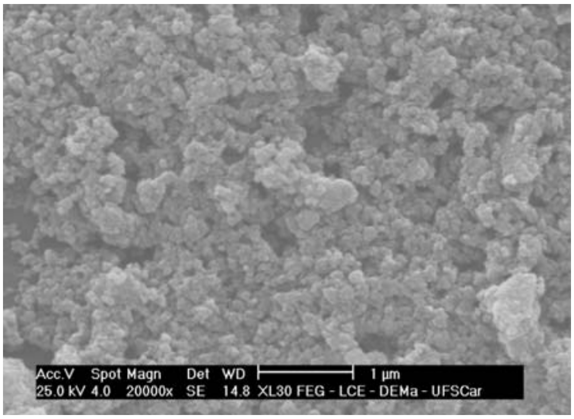

Fig. 3 Micrographs obtained by SEM showing the morphology of the of $NiFe_2O_4$ powder prepared by combustion reaction

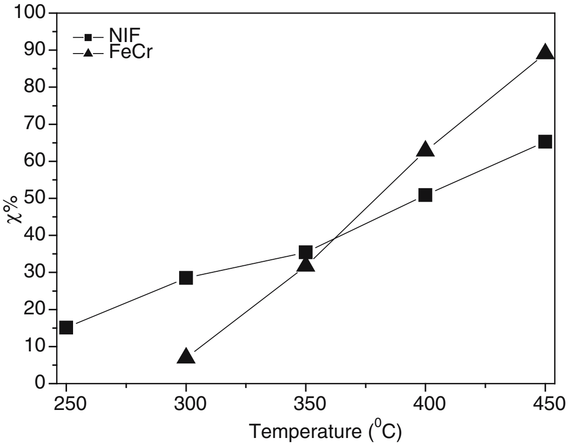

Fig. 4 CO conversion (%X) as a function of the reaction temperature, at atmospheric pressure. $CO:N_2:H_2O$ = 1:4:3, $W_{(catal)}$ = 100 mg, ▲ $NiFe_2O_4$, ■ FeCr (Fe_2O_3–Cr_2O_3, commercial catalyst)

Figure 4 shows the temperature dependence of CO conversion over the $NiFe_2O_4$ sample, under the water gas shift reaction. For comparison, the conversion plot for the commercial HTS catalyst (Fe_2O_3–Cr_2O_3) is also included. The $NiFe_2O_4$ (NiF) catalyst showed significant CO conversion over the investigated temperature range, namely, 250–450 °C, attaining nearly 70%, at 450 °C. As expected, the commercial HTS catalyst (FeCr) was active at temperatures higher than 300 °C and attained 90% conversion, at 450 °C. In spite of this, the results confirmed that the $NiFe_2O_4$ powder prepared by combustion reaction is active as catalyst for WGSR and may be useful for moderate temperature (<350 °C) processes.

Conclusion

The synthesis by combustion reaction was favorable to obtain crystalline powders with nanosize particles nickel ferrite. The X-ray lines broadening and TEM confirmed the nature of the nanosize particle of the powders that was 18.0 and 22–29 nm, respectively. The obtained powder may be useful as catalytic material for the water gas shift reaction.

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