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Styrene oxidation by H_2O_2 using Ni–Gd ferrites prepared by co-precipitation method

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Abstract

Gadolinium substituted nickel ferrites were prepared by co-precipitation method using NaOH at pH 14 at room temperature. Spinel phase formation was identified by taking the XRD pattern. DRIFT, TG, BET surface area and pore volume measurements, SEM and EDAX were the other characterization techniques used. Mössbauer analysis was performed to find out the site distribution of iron. Under optimized conditions, the prepared spinels were selectively forming benzaldehyde by the oxidation of styrene. Hydrogen peroxide was used as the oxidant. Effect of reaction temperature, reaction time, styrene to hydrogen peroxide molar ratio and effect of solvent medium were also studied.

Keywords: Spinel; Co-precipitation; Styrene oxidation; Cation distribution of spinels

1. Introduction

Mixed metal oxides possessing spinel structure exhibit interesting structural, electrical and magnetic properties [1,2]. These properties depend on the nature of ions, their charge and their distribution among tetrahedral and octahedral sites. Ternary oxides crystallizing with spinel structure were found to exhibit interesting solid state and catalytic properties [3]. Mixed metal oxide materials are good alternatives to both zeolites and aluminium phenolate for many alkylation reactions [4]. Among various oxides, transition metal oxides based on iron oxide in combination with other metal oxides are found to be the most active and selective for *ortho* alkylation reactions [5,6]. Spinel ferrites are found to be highly active towards many aromatic alkylation reactions such as methylation of phenol, aniline, pyridine, phenol *tert*-butylation etc. [7–9]. The catalytic effectiveness of these systems is due to the ability of the metallic ions to migrate between the sub lattices without altering the structure, which makes the catalyst efficient for many organic transformation reactions.

Diverse properties of the spinel compounds are derived from the possibility of synthesis of multicomponent spinel by partial substitution of cations in positions A and B of spinel structure. In these compounds the properties are controlled by the nature of ions, their charge and site distribution among O_h and T_d sites. In ternary ferrite systems, Fe^{+3} ions can be easily replaced between O_h and T_d sites by stoichiometrically varying the concentration of other ions. This peculiar structural feature enables ferrospinels to withstand even extremely reducing atmospheres [10].

Catalytic oxidation is widely employed in the manufacture of bulk chemicals from aromatics and more recently, as an environmentally attractive method for the production of fine chemicals. The use of hydrogen peroxides in the oxidation of organic molecules is a major goal, both in academic and in industry, because of the environmental acceptability of this oxidant, which depends mainly on the nature of its by-product, water. In heterogeneous catalysis, over nanosize spinel-type $Mg_xFe_{3-x}O_4$ or Nb (Co)-MCM-41, the major reaction was oxidative C=C cleavage into benzaldehyde

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[11,12]. Guin et al. [13] have studied styrene oxidation using hydrogen peroxide catalyzed by nickel and zinc ferrites and obtained benzaldehyde as the major product (C=C cleavage). By-products such as phenyl acetaldehyde and styrene oxide were formed in negligible amount (less than 1%).

In this article, preparation and physico-chemical properties of gadolinium incorporated nickel ferrites prepared by co-precipitation method has been discussed. The catalytic performance of these materials in the selective oxidation of styrene with H_2O_2 as oxidant to form benzaldehyde, targeting the fine chemical industry, has also been addressed. An attempt has been made to correlate the catalytic activity with the distribution of cations at O_h and T_d sites.

2. Experimental

2.1. Catalyst synthesis

Different compositions of ferrospinel series viz, $NiFe_2O_4$ (NF), $NiFe_{1.6}Gd_{.4}O_4$ (NGF1), $NiFe_{1.2}Gd_{.8}O_4$ (NGF2), $NiFe_{.8}Gd_{1.2}O_4$ (NGF3), $NiFe_{.4}Gd_{1.6}O_4$ (NGF4), $NiGd_2O_4$ (NG) were prepared by a low temperature co-precipitation method reported by Date and co-workers [14], using aqueous solutions of ferric nitrate (2.6 M), gadolinium nitrate (3.4 M), nickel nitrate (3.4 M) and NaOH (5.3 M). The stoichiometric amounts of the premixed nitrate solutions were rapidly added to the NaOH solution at room temperature. After aging overnight, the precipitate was washed free of nitrate ions. The precipitate was then initially dried in air at 110 °C for 24 h. The materials were powdered and calcined.

2.2. Structural analysis

The catalyst samples were analyzed by adopting various physico-chemical methods. The spinel phase formation was identified by taking XRD pattern using Philips diffractometer (PW 1710) with Ni filtered Cu Kα radiation. The IR spectra of the spinel samples were recorded by a diffuse reflectance (DR) method (Shimadzu, model 8300). The BET surface area was measured by N_2 adsorption in liquid N_2 temperature using a Micromeritics Gemini analyzer. SEM and EDAX analysis were done by using JSM-840 A scanning electron microscope. The thermal stability of the samples were checked by taking TG/DTG curves using Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer by heating the sample at a rate of 20 °C/min from room temperature to 1100 °C in nitrogen. A continuous flow cryostat was applied to record ^{57}Fe Mössbauer spectra at room temperature. The chemical isomer shifts are related to α-iron. The source of radiation used is commercial ^{57}Co/Rh-foil.

2.3. Catalytic reaction

The catalytic reaction was carried out in a 50 ml 2 neck RB flask, fitted with a water condenser, in an oil bath. Pre-activated catalyst was placed inside the RB and then styrene is added followed by H_2O_2 drop wise. The reaction was carried out by varying temperature, time, styrene to H_2O_2 molar ratio and using various solvents. Liquid products were analyzed by Chemito 1000 GC equipped with a FID detector and a capillary column. N_2 was used as the carrier gas. The identification of products was carried out by comparison of their retention times to the standards.

3. Results and discussion

3.1. Characterization of the catalysts

All the prepared catalysts were found to contain the spinel phase, which is identified from the XRD analysis. The samples show peaks due to spinel phase at characteristic 2θ values. The XRD patterns are shown in Fig. 1a. Crystallite size was calculated using the Scherrer equation from the peak width corresponding to (3 1 1) peak. The crystallite size is found to be in the nanometer range.

The DRIFT spectrum for NGF 3 is shown in Fig. 1b. The spectrum was taken in the range 400–1400 cm^{-1}. Spinles typically show two strong bands v_1 and v_2 at around 700 cm^{-1} and 500 cm^{-1}, respectively. According to Waldron et al. [15] and White et al. [16], the high frequency band at 700 cm^{-1} is due to the stretching vibration of the tetrahedral M–O bond and the low frequency band at around 500 cm^{-1} is due to the vibration of the octahedral M–O bond present in the spinel structure. The appearance of these two bands confirms the formation of spinel phase.

Thermal analysis of the as-prepared samples was done to know the possible changes occurring when they are subjected to heat treatment. The weight loss at around 100 °C and 350 °C is due to loss of water and nitrate ions. After this temperature, not much weight loss has been observed indicating the high thermal stability of the systems. Behavior of nickel ferrite and gadolinium substituted nickel ferrites towards heat treatment is almost same.

For mixed systems, both surface area and pore volume are increasing with increase in gadolinium content. The SEM photographs for NF, NGF3 and NG are shown in Fig. 2. In nickel ferrite, the particles exist as big clusters with well-defined edges whereas for gadolinium containing systems, the edges disappeared. Presence of gadolinium also leads to a uniform distribution of particles. The elemental compositions of the systems were checked by EDAX analysis and there is a good agreement between experimental and theoretical values. Structural parameters of the samples are shown in Table 1.

The Mössbauer spectra are shown in Fig. 3. At room temperature, the spectrum for nickel ferrite shows two signals corresponding to two sites, with both sites magnetically split showing sextets. Mössbauer spectra of gadolinium containing samples (except NGF4) show not only considerable doublets from the quadrupole splitting, but also detectable sextets from the magnetic splitting. The appearance of doublets from the quadruple splitting of