Catalytic properties of nanocomposites based on cobalt ferrites dispersed in sol–gel silica

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Abstract

In this work, composites based on cobalt ferrite ($CoFe_2O_4$) dispersed in a porous silica matrix have been prepared via sol–gel method using tetraethylorthosilicate (TEOS) as a silica precursor, and iron and cobalt nitrates as precursors. In this process, Co and Fe ions dispersed in a sol–gel matrix reacted upon thermal treatment to form Co–Fe crystallites with nanometric dimensions. The structural, morphological, and textural changes of the composites treated at various temperatures were studied by X-ray diffraction, electronic microprobe, and gas adsorption. The treated composites had surface areas in the range 263–359 $m^2 g^{-1}$ with mesopore contribution. These materials were active as catalysts in the total oxidation of chlorobenzene in air. The most active catalyst was the composite treated at 500 °C, which was stable at a temperature as high as 600 °C for 72 h.
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1. Introduction

In the recent years, the catalytic properties of ferrite have been studied due to their activity and their stability in reducing or oxidizing conditions [1–4]. Ferrite catalytic properties depend on cation distribution in tetrahedral and octahedral sites. Its catalytic activity is due to the position of the octahedral sites, which are more external than tetrahedral sites in the crystallites structure. Therefore, the tetrahedral sites are inactive and do not contribute to this activity [5]. Ferrites are important in catalysis [3], however their powders can agglomerate, reducing the exposed specific surface area, and consequently its catalytic activity. The dispersion of ferrites in an inert matrix by sol–gel process can produce a porous material with catalytic activity.

At present, structured catalytic materials have been developed, and consequently the utilization of the sol–gel process has gained an impulse [6,7] because it makes it possible to prepare catalysts with greater stability. The use of supports such as SiO_2 or Al_2O_3 avoids the formation of particle agglomerates and affords control of particle size [7]. It is known [8] that the catalytic efficiency of metals and oxides increases with decreasing particle size and the consequent increase in surface area. The catalytic properties of supported metallic oxides is affected by the support, the dispersion, and concentration of the metal ion in the matrix, the microstructural characteristics, and the surface changes occurring during catalytic reaction and redox cycles.

In this work, nanocomposites formed with cobalt ferrite particles dispersed in a silica matrix were prepared via sol–gel method. In this route, Co, Fe and Si precursors are dispersed in an alcoholic solution and left to rest for gelation. Upon thermal treatment, the Co and Fe ions reacted to form $CoFe_2O_4$ particles in the silica matrix.

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Hereon, we describe the study of the effect of thermal treatment on structural, morphological, and catalytic properties of $CoFe_2O_4/SiO_2$ composites for the total oxidation of a model contaminant, chlorobenzene. Organochloro contaminants were chosen due to their toxicity and stability in natural environments [9,10]. These compounds are destroyed by incineration, but it is an expensive process as it requires temperatures over 1000 °C and corrosion resistant incinerators, and is fuel consuming. In contrast, catalytic oxidation can be carried out in much milder reaction conditions [11–15] without fuel consumption. Ferrites are potential catalysts for this reaction due to their redox activity and their stability under oxidative conditions [15–17].

2. Experimental

SiO_2 xerogels were obtained with the mixture of tetraethylorthosilicate (TEOS), ethyl alcohol, water and nitric acid. $CoFe_2O_4/SiO_2$ xerogels [18] were obtained adding 30 wt% of cobalt ferrites to the matrix solution in the form of nitrates ($Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, Merck). Next, the solutions were stirred for 1 h for homogenization and left to rest for gelation. The wet gels were aged at 60 °C for 24 h, dried at 110 °C for 12 h, and thermally treated at 300, 500, 700, 900 and 1100 °C for 2 h. The samples were identified in agreement with the treatment temperature (Table 1).

Cobalt ferrite ceramic powder was synthesized [19] from stoichiometric amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (Merck) dissolved in water, and destabilized by NH_4OH in a quantity sufficient to maintain the stoichiometry and to avoid the formation of complexes [19]. The precipitate was washed with deionized water to remove impurities and with ethanol to avoid the formation of agglomerates [15]. The powder was dried at 80 °C for 24 h and calcined at 500 °C for 2 h.

All samples were analyzed by X-ray diffractometry (Rigaku, Geigerflex 3034) with CuKα radiation [20]. Crystallite average size was estimated by Scherrer equation [21] using silicon as a standard. The standard deviation of the crystallite size was determined from ten X-ray measurement of the same sample. Samples were

examined in a scanning electron microscope (Jeol JXA, model 8900RL) equipped with energy dispersive spectroscopy (EDS), and by X-ray fluorescence spectrometry (Rigaku, Geigerflex 2037) to evaluate the composition and the impurity of the composites. Density measures were obtained with a helium picnometer (Quantachrome). Sample specific surface area and porosity were measured through nitrogen adsorption (Autosorb, Quantachrome Nova 1200) at liquid nitrogen temperature and the application of the Brunauer–Emmett–Teller (BET) equation [22] and the BJH method [22]. Samples were outgassed for 3 h at 300 °C before each analysis. Adsorption experiments were made in triplicate.

The catalytic reactions were carried out in a fixed-bed reactor [23] with 25 mg of composite. Chlorobenzene 0.1% at 0 °C was introduced into the air stream (30 ml min^{-1}) by a saturator. The reaction products were analyzed by gas chromatography (Shimadzu/GC 17A) with a flame ionization detector (FID) and a capillary column (Alltech Econo-Cap SE) (30 mm × 0.32 mm × 0.25 μm).

3. Results and discussion

The composites prepared in monolithic shape had a greenish color and were X-ray amorphous after heating to 300 °C. EDS mapping and backscattered electron images (Fig. 1) showed that the Fe ions were homogeneously dispersed at the nm scale throughout the matrix, and that the Co ions were agglomerated in spherical regions (Fig. 1(a)). Treatment in the temperature range 300–900 °C produced a brown material with the formation of crystalline cubic spinel $CoFe_2O_4$ (Fig. 2) with average crystallite size increasing from 10 ± 1 to 39 ± 4 nm, as revealed by XRD measurements (Table 1). Upon thermal treatment, the agglomerated Co and dispersed Fe ions moved within the matrix to react and form the crystallites (Fig. 1b). X-ray diffractogram did not revealed traces of quartz, crystobalite or intermediate products, during the formation of the $CoFe_2O_4$ crystals even at temperatures as high as 1100 °C.

Table 1
Textural characteristics of $CoFe_2O_4/SiO_2$ xerogels thermally treated at various temperatures and $CoFe_2O_4$ powder treated at 500 °C

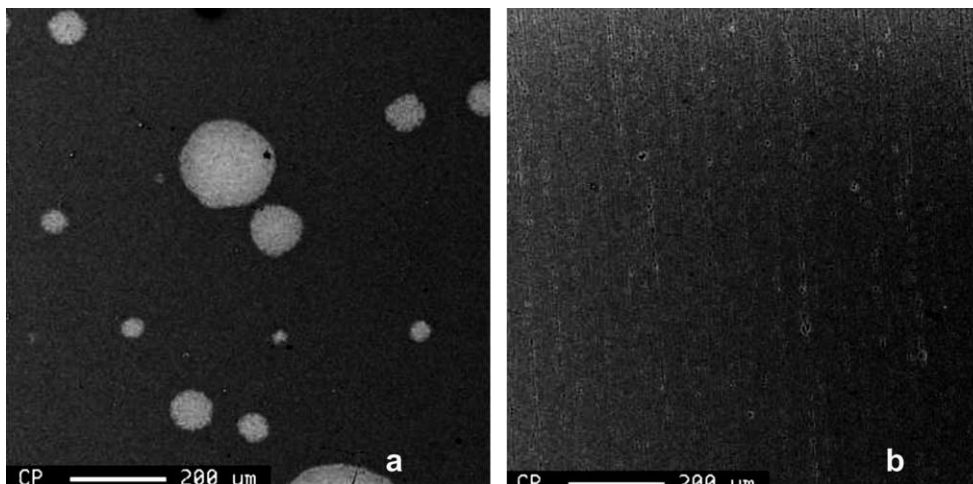| Sample	Calcination temperature (°C)	Specific surface area (m^{2}g^{-1})	Average crystallite size (nm)	Porosity (%)	Average pore size (nm)	Density (gcm^{-3})
Xero110	110	221 ± 11	–	25	6.0 ± 0.3	1.9 ± 0.1
Xero300	300	359 ± 18	<10	65	4.8 ± 0.2	2.1 ± 0.1
Xero500	500	307 ± 15	16 ± 2	62	6.8 ± 0.3	2.2 ± 0.1
Xero700	700	286 ± 14	31 ± 3	61	6.0 ± 0.3	2.3 ± 0.1
Xero900	900	263 ± 13	39 ± 4	48	5.8 ± 0.3	2.4 ± 0.1
Xero1100	1100	10 ± 1	92 ± 9	3	0.5 ± 0.1	2.6 ± 0.1
Ferrite	500	25 ± 2	37 ± 4	2	4.6 ± 0.2	3.1 ± 0.1

Fig. 1. SEM images (backscattered electrons) of composites treated at different temperatures, where the light grey spherical regions are agglomeration of Co ions: (a) 300 °C and (b) 900 °C.
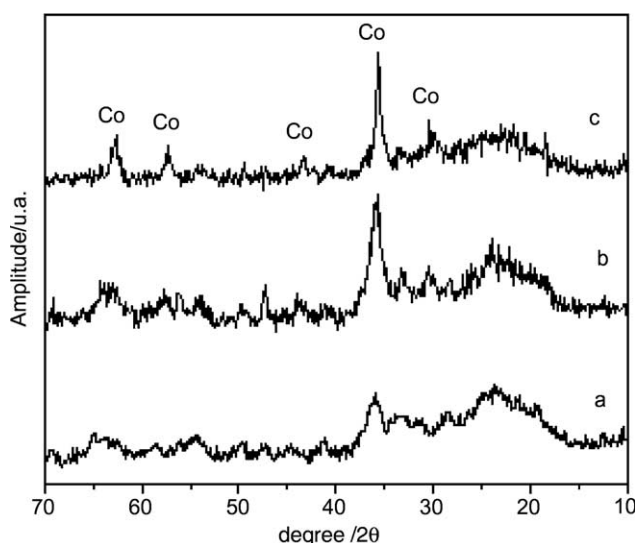

Fig. 2. XRD reflections of CoFe$_2$O$_4$/SiO$_2$ xerogels, treated at 300 °C (a), (b) treated at 500 °C before of catalytic tests and (c) treated at 500 °C after of catalytic tests. (Co) CoFe$_2$O$_4$.

Crystal surface area increased with thermal treatment due to the liberation of organic residues and water up to 300 °C, and then decreased to 900 °C (Table 1). The composite isotherms indicate the formation of mesoporous materials (type IV isotherm by BDDT[21] classification) [22]. Over 900 °C, there was a decrease in surface area and porosity due to the densification process (Table 1) [23].

The composites were tested as catalysts for the oxidation of chlorobenzene with air. No organic byproducts were observed by gas chromatography, which, we suggest, indicates total oxidation under our reaction conditions:

$$C_6H_5Cl + 7O_2 \rightarrow 6CO_2 + 2H_2O + HCl \qquad (1)$$

Fig. 3 shows the steady state conversions of chlorobenzene at different temperatures in the presence of the samples. We observed that Xero500 (Table 1) is the most active catalyst, converting chlorobenzene at temperatures as low as 150 °C. In contrast, the other catalysts were active only at temperatures higher than 300 °C. An SiO$_2$ powder sample showed no activity for chlorobenzene conversion, even at high temperatures (Fig. 3). A decrease in catalytic activity was observed for the composite treated at 1100 °C. This could be related to the densification of the silica matrix (Table 1), and the encapsulation [18] of the ferrite particles. This encapsulation, also observed in previous works [23,24], hinders the access of the gas phase molecules to the ferrite surface and inhibits the catalytic process.

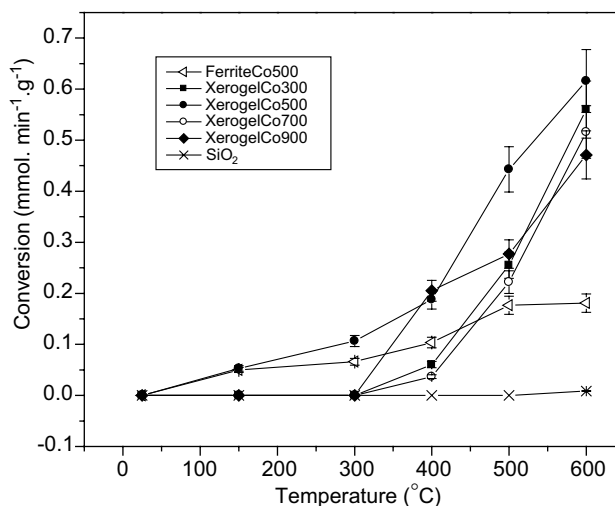The greater activity observed for Xero500 may be due to the following effects associated to the catalytic

Fig. 3. Catalytic oxidation of chlorobenzene in the presence of CoFe$_2$O$_4$/SiO$_2$ xerogels thermally treated at various temperatures.

reaction: (i) formation and (ii) dispersion of the ferrite $CoFe_2O_4$ phase, and (iii) the specific surface area of the $CoFe_2O_4/SiO_2$.

In the X-ray diffractogram of the composite treated at 300 °C (Fig. 2(a)), we observe that the $CoFe_2O_4$ phase was not completely formed. At this temperature, the Co ions are agglomerated in spherical regions in accordance with EDS mapping. These results and the low catalytic activity indicate that Co and Fe ions dispersed in the matrix are probably less active when compared to the $CoFe_2O_4$ phase. Upon treatment at 500 °C, the cobalt ferrite formed crystallites dispersed in the matrix. This dispersion results in a more active surface area, which leads to a greater catalytic activity. In contrast, higher treatment temperatures increase ferrite crystallite size and reduce composite surface area, as shown in Table 1, which probably cause a decrease in the catalytic activity.

Another spinel oxide that might be formed in the material is magnetite, Fe_3O_4. However, under the present reaction conditions, this phase would be easily oxidized by O_2 even at temperatures as low as 150 °C to form Fe_2O_3, which is poorly active for oxidation reactions [25]. As the composite obtained presented greater catalytic activity than that of Fe_3O_4, the formation of magnetite is discarded.

It is also interesting to observe in Fig. 3 that all the xerogel catalysts are more active than the pure $CoFe_2O_4$ ferrite. The powder ferrite treated at 500 °C had a surface area of $25 m^2/g$ (Table 1).

The stability of the catalyst Xero500 during the oxidation of chlorobenzene was studied at 600 °C. No measurable decrease in catalytic activity was observed during reaction for 72 h. XRD analysis of the catalyst after reaction showed no change in either the phase present or the crystallinity of the material (Fig. 2(c)).

4. Conclusion

Composites based on $CoFe_2O_4$ dispersed in a silica matrix can be prepared via the sol–gel method with Co and Fe precursors dispersed in a sol–gel matrix. These species react upon thermal treatment to form ferrite spinel crystallites with nanometric dimensions. These materials are mainly mesoporous with surface area in the range 263–359 m^2/g, with contribution of mesopores (average diameter between 2.4 and 3.4 nm).

These composites are active catalysts for the total oxidation of chlorobenzene. Thermal treatment affects catalytic activity, with the best results observed for catalyst Xero500. The catalytic activity does not decrease even upon reaction at 600 °C for 72 h.

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