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Synthesis of Barium Hexaferrite and Catalytic Behavior in the Combustion of Methane

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Abstract. Barium hexaferrite doped with iridium was synthesized by two methods: the citrate gel and the polyacrylamide gel methods. The nature of phases obtained and the specific surface area were determined after heat treatments in air at 700°C, 900°C and in air containing 10% humidity at 1200°C. The catalytic activity in the combustion of methane was measured after heat treatment at 900°C. These hexaferrites showed a good catalytic activity after treatment at 900°C. However this catalytic activity and the specific surface disappeared after heat treatment at 1200°C.

1. INTRODUCTION AND EXPERIMENTAL PROCEDURE

In a recent study, it was shown that $\text{BaAl}_{12}\text{O}_{19}$ doped with Fe or Mn presents interesting catalytic properties for the clean combustion of hydrocarbons [1]. In the present study, we focused on $\text{BaFe}_{12}\text{O}_{19}$ doped with Ir. Such materials were synthesized from barium acetate and hydrated ferric nitrate according to 2 methods. In the first method, gelation was achieved by evaporation at $\approx 70^\circ\text{C}$ and $\text{pH} \approx 7$ with NH_4OH , after complexation with 2 moles of citric acid per mole of cation. In the second method, only 1 mole citric acid per mole of + charge was used, and gelation was achieved by adding ≈ 12 g of acrylamide and 0.5 g of N,N'-methylene bisacrylamide to ≈ 200 mL of the solution. Polymerization of acrylamide was initiated by adding 50 mg of azo-bis-isobutyronitrile (AIBN) and ≈ 0.05 mL of N,N,N',N'-tetramethylethylenediamine (TEMED) dissolved in ≈ 4 mL ethanol. Gelation occurred at $\approx 90^\circ\text{C}$ in a few minutes. Samples containing 1% and 5% iridium were made by adding iridium acetylacetonate in acetone before gelation. However, at 5% iridium with the polyacrylamide, precipitation of Ir in the solution was obvious.

All gels were calcined at $\approx 500^\circ\text{C}$. Some samples were heated 3h in air at 700°C . Other samples were treated similarly at $T = 900^\circ\text{C}$. A third set of samples were treated at 1200°C for 24 hours, in air containing 10% humidity. After each thermal treatment, the specific surface of these materials was measured by the Brunauer, Emmett and Teller (BET) method and the nature of phases was determined by powder X-ray diffraction. Catalytic tests were achieved on fixed powder bed reactors containing ≈ 0.5 g of ferrite, crossed by a through flow of a gas mixture composed of 1% methane, an over-stoichiometric proportion of oxygen for the combustion of methane, and nitrogen. The total flow rate at room temperature under 1 bar was ≈ 6.4 L h^{-1} . The temperature was progressively increased by increments of 50°C , from 350°C up to 800°C . At each temperature, a holding time of 3 h was maintained, and the proportions of CH_4 , CO_2 and CO in the exit gas were analyzed in a chromatograph, at regular time intervals of 30 min.

2. EXPERIMENTAL RESULTS

The temperature where the hexaferrite phase was formed depended on the fabrication procedure. At 700°C in samples containing no Ir, the polyacrylamide route led to Fe_2O_3 as the major phase, while in the samples made by the citrate route Fe_2O_3 was a minor phase (Fig. 1). Also, the relative intensity at 700°C of the Fe_2O_3 diffraction peaks, with respect to the $\text{BaFe}_{12}\text{O}_{19}$ peaks, was roughly independent of the Ir content in samples made by the citrate method, while it drastically decreased as the Ir content increased in the samples made by the polyacrylamide method. After heat treatment at 900°C all samples showed the same X-Ray powder diffraction pattern where the only observable phase was $\text{BaFe}_{12}\text{O}_{19}$. The specific surface area is reported in Fig. 2. It was roughly independent of Ir content in samples made by the citrate technique, while it increased significantly with the Ir content in samples made by the polyacrylamide technique. After aging at 1200°C in the presence of humidity, all samples had lost their porosity.

The ferrites synthesized at 900°C in the present study showed a good catalytic activity, with 100% selectivity in CO_2 . For instance, as shown in Fig. 3, the T10 temperature (10% conversion temperature) was about 80°C lower for the best hexaferrite without Ir than for $\text{BaMn}_2\text{Al}_{10}\text{O}_{19}$ [2]. This catalytic activity was relatively independent of the Ir content in the citrate

samples, while it improved gradually with the Ir content in the polyacrylamide samples. After treatment at 1200°C in wet air, this activity virtually disappeared.

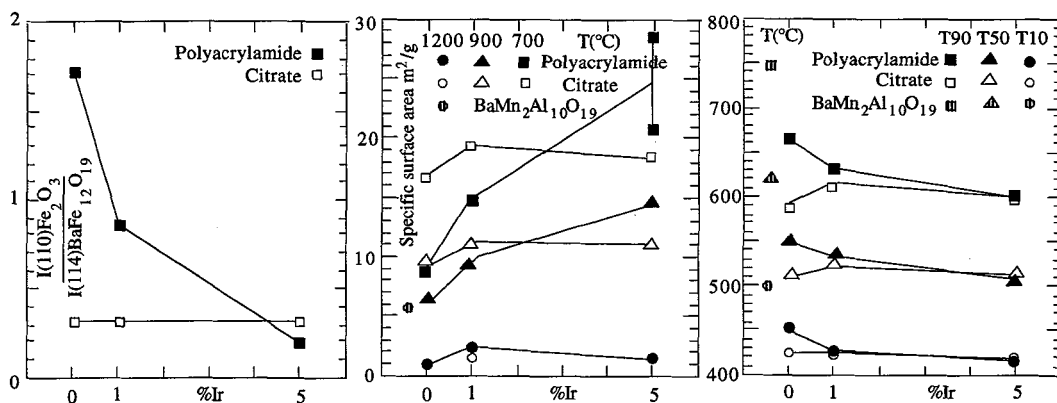


Figure 1: Intensity ratio of diffraction peaks (110) for Fe₂O₃ and (114) for BaFe₁₂O₁₉, at 700°C.

Figure 2: Specific surface area of ferrite samples (m²/g) and BaMn₂Al₁₀O₁₉ from [2]

Figure 3: Temperatures for 10% (T10), 50% (T50) and 90% conversion (T90), in the combustion of methane

3. DISCUSSION

The present study showed a drastic relation between the catalytic activity at 900°C, the specific surface area, and the proportion of barium hexaferrite formed at 700°C. In samples made by the citrate route, the phase transformation, specific surface area and catalytic activity were independent of the Ir content. On the other hand, in samples made by the polyacrylamide route, the formation, specific surface area and catalytic activity of barium hexaferrite improved as the Ir content increased. Using polyacrylamide was detrimental to the catalytic activity, but this was progressively balanced by addition of Ir. The polyacrylamide sample with 5% Ir, as well as all samples made by the citrate route, had roughly a similar and good catalytic activity.

The ionic radii of Fe³⁺ and Ir⁴⁺ are very similar to each other, respectively 0.0645 and 0.0625 nm [3]. For instance, Vincent et al. [4] synthesized similar M-type Zn and Co hexaferrites doped with Ir, where Ir mostly substituted for Fe. However, it is well known that the formation path of a complex phase is often influenced by the fabrication procedure. In the present study, the lower specific area and the higher Fe₂O₃ X-ray peaks intensity in the polyacrylamide sample containing no Ir at 700°C, by comparison with the citrate sample containing no Ir (Fig.1), suggests that relatively big hematite grains were formed when using polyacrylamide. Moreover, only when using the polyacrylamide route, precipitation of dark Ir crystals was observed upon addition of the Ir precursor in the solution. This was not observed in the citrate route. The fine precipitated Ir crystals in the polyacrylamide samples may possibly have hindered the growth of hematite grains. This resulted in a shorter diffusion path to form the hexaferrite phase more easily, and simultaneously increased the specific surface area. In the hexaferrite made via the citrate route, Ir may possibly have substituted for Fe.

Because one of the most active sample was made by the citrate route and contained no Ir, it appears that the catalytic activity which we observed was due to the hexaferrite phase. A comparison of Fig. 2 and Fig. 3 shows that this catalytic activity roughly increased with the specific area, so that it was independent of the Ir content in the citrate samples while it improved with the Ir content in the polyacrylamide samples. This observation is also consistent with the simultaneous collapse of the catalytic activity and specific surface area after treatment at 1200°C in humid air.

4. CONCLUSION

Barium hexaferrite is an active material to catalyze the combustion of methane. Its pore structure lacks thermal stability. However, adding Ir had a significant influence on the phase formation and specific surface area at 900°C in the polyacrylamide process. This suggests that other additives may be able to hinder the sintering of the hexaferrite at temperatures as high as 1200°C. Hence, the synthesis of a ferrite potentially as good as the hexaaluminate with respect to thermal stability and with a much better catalytic activity, appears to be possible.

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