

Effect of the preparation method on the properties of hematite-based catalysts with lanthanum for styrene production

Manuela de S. Santos^a, Sérgio G. Marchetti^b, Alberto Albornoz^c, Maria do Carmo Rangel^a

^aGECCAT-Universidade Federal da Bahia, Instituto de Química, Campus Universitário de Ondina, 40155-290, Salvador, Bahia, Brazil. e-mail: mcarmov@ufba.br

^bCINDECA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900, 47 y 115, La Plata, Argentina

^cInstituto Venezolano de Investigaciones Científicas, Apartado 21 827, Caracas 1920-A Venezuela

Abstract

The influence of the preparation method on the properties of lanthanum-doped hematite prepared with potassium carbonate was studied aiming to get catalysts for styrene production from ethylbenzene dehydrogenation. The most active catalyst was obtained by adding the reactants on water. This solid has the highest intrinsic activity, the highest resistance against reduction and the lowest conversion drop. These properties were related to the presence of potassium compounds on the surface and to the presence of Fe⁺³ species (active phase) stabilized in lanthanum oxide lattice.

Keywords: lanthanum, iron oxide, potassium carbonate, styrene, ethylbenzene.

1. Introduction

The main commercial route to produce styrene, a high-value chemical, is the ethylbenzene dehydrogenation in steam presence. The industrial catalysts are hematite doped with potassium and chromium oxides, which have low price and are active and selective. However, they quickly deactivate with time [1, 2] and there is a need for investigating new systems, concerning formulation and textural and catalytic properties, the last ones closely related to the preparation methods. In previous works [3, 4] we have found that hematite with lanthanum, obtained with ammonium hydroxide, sodium carbonate and sodium hydroxide, is promising to ethylbenzene dehydrogenation. Ammonium hydroxide produced the best catalysts, but its use in industry is not allowed due to the environment and human health restrictions. Therefore, in the present work, we continue this investigation by studying the effect of the order of mixing the reactants on the properties of hematite with lanthanum, using potassium carbonate as precipitant.

2. Experimental

Samples were prepared by the sol-gel method by hydrolysis of iron and lanthanum nitrate with a potassium carbonate solution (6 mol.L⁻¹) to get solids

with lanthanum to iron molar ratio of 0.1. The solids were then calcined under nitrogen flow at 600 °C, for 2 h. The sample named CK was obtained by the addition of the reactants solutions on a beaker with water, under stirring. Other two samples were prepared by changing the order of mixing the reactants: the first one (CKM sample) was obtained by adding the precipitant on the solution of iron and lanthanum nitrate and the second one (MCK) by the inverse procedure. A reference sample was also prepared using ammonium hydroxide instead of potassium carbonate (LF sample).

The X-ray diffraction (XRD) experiments were performed with a Shimadzu model XD3A instrument using CuK α radiation generated at 30 kV and 20 mA, using a nickel filter. The specific surface areas were measured in a Micromeritics model ASAP 2020C equipment on samples previously heated under nitrogen (150 °C, 2 h). The temperature programmed reduction (TPR) was performed in a Micromeritics model TPD/TPO 2900 equipment, using a 5% H₂/N₂ mixture. X-ray photoelectron spectra (XPS) were obtained with a VG ESCALAB 220i-XL spectrometer with a MgK α X-ray radiation source (hv= 1253.6 eV) and a hemispherical electron analyzer, at 400 W. The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ⁵⁷Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 6 μ m-thick α -Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard.

The catalysts were evaluated in a fixed-bed microreactor at 530 °C and 1 atm, using a steam to ethylbenzene molar ratio of 10. The gaseous effluent was collected in a condenser and the organic phase was analyzed by a CG-35 chromatograph. The spent catalysts were characterized by XRD, specific surface area measurements and Mössbauer spectroscopy. The coke amount in spent catalysts was measured in a CS-200 LECO model equipment.

3. Results and discussion

The use of potassium carbonate instead of ammonium hydroxide led to the production of different solids. While the sample prepared with ammonium hydroxide showed only hematite, those obtained with potassium carbonate showed several phases, whose identification by XRD was complicated by the coincidence of the peaks of the different phases. The catalyst prepared by adding the reactants on water (CK) was made off hematite and lanthanum oxide (La₂O₃) but the presence of a mixed oxide (FeLaO₃), potassium ferrite (KFeO₂) and potassium oxide (K₂O) could not be discarded. On the other hand, La₂O₃ and KFeO₂ were found in CKM sample and hematite and KFeO₂ were detected in MCK sample; the other phases could not be confirmed. During ethylbenzene dehydrogenation, a phase transition occurs and magnetite was produced; however, it was not possible to distinguish the presence of the other phases.

The use of potassium carbonate favored the production of solids with lower specific surface area, in comparison with that prepared with ammonium hydroxide (Table 1). The addition of the reactants to water (CK sample) led to the production of the solid with the lowest specific surface area while no

Table 1. Specific surface area before (Sg) and after reaction (Sg*), activity (a), intrinsic activity (a/Sg), conversion drop (ΔX), selectivity to styrene (S_S), benzene (S_B) and toluene (S_T) and coke deposited on the catalysts during ethylbenzene dehydrogenation.

| Samples | LF | CK | CKM | MCK | Commercial |
|--|------|------|------|------|------------|
| Sg (m ² .g ⁻¹) | 115 | 1.0 | 3.2 | 3.0 | -- |
| Sg* (m ² .g ⁻¹) | 10 | 4.0 | 4.0 | 4.3 | -- |
| a.10 ⁷ (mol.g ⁻¹ . s ⁻¹) | 8.9 | 11 | 6.1 | 5.2 | 6.4 |
| a/Sg.10 ⁸ (mol.s ⁻¹ .m ⁻²) | 8.9 | 27 | 15 | 12 | -- |
| ΔX (%) | 1.5 | 1.7 | 5.0 | 9.2 | 3.6 |
| S _S (%) | 96 | 100 | 100 | 100 | 97 |
| S _B (%) | 0.74 | -- | -- | -- | 0.8 |
| S _T (%) | 2.7 | -- | -- | -- | 1.8 |
| Coke (%) | 1.09 | 3.81 | 3.73 | 2.32 | 1.36 |

significant difference was found between the samples prepared by the other methods. After reaction, the solids showed higher values, indicating that the phase changes led to the formation of pores and/or particles of smaller sizes.

The order of mixing the reactants also changed the reducibility of lanthanum-doped hematite, as inferred by the TPR curves (not shown). The samples prepared by adding the metallic precursors on the precipitant (MCK) or by the inverse procedure (CKM) showed similar profiles, with several reduction peaks; the last sample was the most susceptible to reduction. The low temperature peaks, in the range of 360 to 563 °C, are related to the reduction of Fe³⁺ to Fe²⁺ species, as pointed out early [2-5]. In these samples, the multiplicity of peaks suggests the presence of Fe³⁺ species in different compounds, in accordance with the X-ray diffraction results. The two high temperature peaks occurred in the range of 600 to 850 °C and are associated to the reduction of Fe²⁺ to Fe⁰ species on the surface and in the bulk, respectively [2-5]. On the other hand, the sample prepared by adding the reactants on water (CK) showed the most resistance against reduction with a single peak at 683 °C with a shoulder at around 700 °C and another peak at 886 °C, showing that the Fe³⁺ species are stabilized in this solid. The first peak can be related to the reduction of Fe³⁺ species stabilized by lanthanum oxide La₂O₃, as inferred by Mössbauer spectroscopy. In fact, the spectrum of the CK sample showed two sextuplets, with hyperfine parameters typical of α -Fe₂O₃, the second one assigned to smaller particles. A central doublet was also noted, associated to superparamagnetic α -Fe₂O₃ and/or to paramagnetic ferric ions in La₂O₃ lattice. Taking into account the hyperfine parameters values, the presence of FeLaO₃ and KFeO₂ was discarded [6, 7].

The activity and selectivity of the catalysts were also affected by the order of mixing the reactants as well as by the presence of potassium. As shown in Table 1, potassium increased the activity and this can be related to an increase of the intrinsic activity (a/Sg). Also, the selectivity achieved 100 % due to potassium and no benzene and toluene were produced. However, they produced higher amounts of coke than the potassium-free sample, indicating that lanthanum is much more able to prevent coke in the absence of potassium which, in turn, is

less efficient than lanthanum. However, this coke seems not to be harmful to the catalysts, since there is no relationship between coke and the conversion drop. The catalyst prepared by adding the reactants on water (CK) was the most active one and this can be related to its highest intrinsic activity and also to its highest resistance against reduction, due to the stabilization of Fe^{3+} species, which are responsible for the activity of the catalysts in the reaction. The XPS spectra of this sample revealed the presence of lanthanum ($\text{La/Fe} = 0.884$) on the surface as well as a high concentration of potassium ($\text{K/Fe} = 12.229$), which can be associated to the production of potassium oxide, which is believed to increase the activity of iron in ethylbenzene dehydrogenation [1, 8]. This catalyst was more active and selective than a commercial one (Table 1) which makes it a candidate for industrial applications.

4. Conclusions

The addition of potassium increased the intrinsic activity of lanthanum-containing hematite, but its action depends on the preparation method. Concerning the order of mixing the reactants, the best method consists in adding the metallic precursor and potassium carbonate on water. The solid produced has the highest intrinsic activity, the highest resistance against reduction and the lowest conversion drop in ethylbenzene dehydrogenation to produce styrene. These properties were related to the presence of potassium compounds on the surface as well as to the stabilization of Fe^{3+} species, which are believed to be the active phase.

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