Chapter 8

Case Study: Effect of Zirconium on the Textural and Catalytic Properties of Magnetite

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ABSTRACT

The effect of zirconium on the textural and catalytic properties of magnetite for the water gas shift reaction (WGSR) at high temperatures was studied in this chapter. The reaction is an important step in the industrial production of pure hydrogen. Samples with different amounts of zirconium (Zr/Fe (molar)= 0.1; 0.2; 0.3; 0.4 and 0.5) were prepared from the decomposition of iron(III)hydroxocetate doped with zirconium. It was found that zirconium increased the specific surface area of magnetite acting as spacer on the surface where it keeps the particles apart. Except for the zirconium-poorest solid, tetragonal zirconia was detected besides magnetite for all solids. Zirconium increased the intrinsic activity of the catalysts, stabilized the specific surface areas during reaction, and made the magnetite reduction to metallic iron more difficult. The zirconium-poorest is more active than magnetite and more resistant against deactivation by sintering and overreduction being attractive for WGSR.

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INTRODUCTION

Iron oxides are important industrial catalysts mainly because of the chemical properties and low cost. They have been commercially used for many years, in a large variety of reactions, including the water gas shift reaction (WGSR). By this reaction, the hydrogen production is maximized and the carbon monoxide level is decreased in streams coming from natural gas steam reforming (Newsome, 1980; Lloyd, Ridler & Twigg, 1996). In addition, the interest for this reaction has been increased even more in recent times because of its application in fuel cells (Grubert, Kolf, Baerns, Vauthey, Farrusseng, van Veen, Mirodatos, Stobbe, Cobden, 2006). Moreover, WGSR is expected to play an important role in biorefineries in the future, since the most promising routes to process biomass (pyrolysis and gasification) produce methane and carbon monoxide, which can be further processed to produce more hydrogen, by the reforming processes and the WGSR (Nikolaidis & Poullikkas, 2017).

The WGSR (Equation 1) is exothermic and reversible, being thus favored by low temperatures and steam excess. For industrial purposes, it is carried out in two stages, the first in the range of 320-450 °C (HTS, High Temperature Shift) while the other is performed at 200-250 °C (LTS, Low Temperature Shift) (Campbell & Young, 1970; Newsome, 1980).

\[ \text{CO} (g) + \text{H}_2\text{O} (g) \rightleftharpoons \text{CO}_2 (g) + \text{H}_2 (g) \quad \Delta H = -40.6 \text{ kJ mol}^{-1} \]

The LTS stage is performed in favorable thermodynamic conditions over copper-zinc oxide catalysts. However, the active phase (copper) is very susceptible to deactivation due to sintering and poisoning (Newsome, 1980). In last years, catalysts based on nickel were also proposed for the LTS stage in order to avoid deactivation (Fuentes, Faro Júnior, Silva, Assaf & Rangel, 2014).

The commercial catalysts used in the HTS stage are based on chromium-doped iron oxides that show high activity and selectivity, being resistant to sintering and to several poisons. They are commonly available as hematite (\(\alpha-\text{Fe}_2\text{O}_3\)) and are reduced in situ to produce magnetite (\(\text{Fe}_3\text{O}_4\)) using the process gas (a mixture of carbon dioxide and monoxide, hydrogen and methane). This reduction is highly exothermic and is controlled by adding excess steam to avoid hydrocarbons production (Newsome, 1980; Lloyd, Ridler & Twigg, 1996). However, these catalysts have the disadvantages of being toxic and of needing steam, which increase the operation costs. In addition, they have shown a decrease in activity with time, which has been assigned to the loss of specific surface area (Chinchen, Logan & Spencer, 1984). Moreover, it is needed to find catalysts that can be sold in active phase (magnetite) and then can be used without reduction saving energy. These drawbacks have motivated the search for new catalysts with improved properties such as high specific surface area, which can easily handled and discarded. With this goal in mind, the effect of zirconium on the textural and catalytic properties of magnetite was studied in this work. As found previously (Chinchen, 1982; Ladebeck & Kochloefl, 1995; Santos, Marchetti, Albornoz & Rangel, 2010), zirconium has been pointed out as an efficient textural promoter for hematite-based catalysts. However, it has also been found (Pereira, Berrocal, Marchetti, Albornoz, de Souza & Rangel, 2008; Ratnasamy & Wagner, 2009; Santos, Marchetti, Albornoz & Rangel, 2010; Rangel, Sassaki & Galemebeck, 1995) that the action of the dopants largely depends on the preparation method as well as on the phase of the final solid. As far as we know, there is no study about the effect of zirconium on the properties of magnetite for WGSR.