

The role of vanadium on the properties of iron based catalysts for the water gas shift reaction

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Abstract

The substitution of chromium by vanadium as dopant in the iron oxide based water gas shift (WGS) catalyst has been investigated. Catalysts prepared as magnetite with different amount of vanadium have been prepared and tested with different amounts of water in the gas feed. The results obtained showed that vanadium was a promising dopant leading to very active and stable catalysts. The vanadium-doped catalysts have been characterized by means of chemical analysis, X-ray diffraction, Fourier transform infrared spectroscopy, specific surface area measurements, temperature-programmed reduction, Mössbauer spectroscopy, X-ray photoelectron spectroscopy and high resolution transmission electron microscopy with electron diffraction. Vanadium has been shown to be present both as V(III) and V(IV) species at the surface and in the bulk near the surface of the magnetite structure. It increased the specific surface area of the catalysts and kept the particles apart on the surface delaying sintering. The vanadium doping has been shown to have also an effect on the Fe(III) content of the magnetite which increased favoring the successive oxidation and reduction cycles, during the reaction.

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1. Introduction

The demand for high-purity hydrogen for industrial application is today largely met by the water gas shift reaction (WGSR). In some applications, like the manufacture of ammonia or the production of synthesis gas, hydrogen is primarily obtained from the reforming of methane or higher hydrocarbons, a reaction that produces carbon monoxide and hydrogen as main products. However, the hydrogen concentration obtained is not sufficient for the applications cited above and the WGSR has to be used to maximize the hydrogen production. The reaction presents the advantage of simultaneously reducing the carbon oxides to a very low level and thus avoiding the poisoning of the ammonia-synthesis catalysts as well as of most of the metallic hydrogenation catalysts [1,2].

In order to achieve rates for commercial purposes, the WGSR is performed in two steps, successively at high temperature (623–723 K) and at low temperature (453–523 K) [1,3,4]. The first step involves an iron and chromium-based catalyst, which decreases the carbon monoxide concentration from ca. 10 mol% (for natural gas derived synthesis gas) to ca. 3 mol% in kinetic favorable conditions. In the second step, the carbon monoxide concentration is further decreased to ca. 0.3 mol%, using a copper zinc oxide based catalyst in thermodynamic favorable conditions [1,3].

The classical industrial high temperature shift (HTS) catalysts contain iron oxide as well as chromium oxide which is believed to act as a stabilizer, retarding sintering and avoiding the loss of specific surface area [1–3]. It contains 92% by weight of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and 8% by weight of chromium oxide (Cr_2O_3), whereby the components may be prepared by several routes separately or together [5]. Before the HTS catalysts can be used hematite must be converted to magnetite (Fe_3O_4), which is believed to be the active phase. This reduction is carried out with the

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process gas (a mixture with composition around 10% CO, 10% CO₂, 60% H₂ and 20% N₂) and is controlled to avoid the further reduction of magnetite to metallic iron, which would promote undesirable reactions like methanation and carbon monoxide disproportionation [1,2]. In order to ensure the magnetite stability in industrial processes, large amounts of steam are added to the gas feeds, which drastically increase the operational costs. There is thus the need to develop more stable catalysts that would not need too much water and that would be more difficult to reduce to metallic iron [2]. With that respect, the development of a catalyst directly in magnetite form may increase the process efficiency not only because of the energy saved but also due to the gain in life-time of the catalyst that could be expected. This work, which has been undertaken as a part of a general study of the development of such catalysts, deals with the use of several dopants instead of chromium in HTS catalysts produced directly as magnetite [6–10].

In previous works it has been noted that magnetite can be conveniently obtained by heating iron(III)hydroxoacetate (IHA) under nitrogen [6,10], providing an inexpensive and reliable route for this oxide for industrial applications. In the present work, the production of vanadium-doped magnetite by heating vanadium-doped IHA was described. Different vanadium containing catalysts have been prepared and characterized by means of chemical analysis, X-ray diffraction, Fourier transform infrared spectroscopy, specific surface area measurements, temperature-programmed reduction, Mössbauer spectroscopy, X-ray photoelectron spectroscopy and high resolution transmission electron microscopy with electron diffraction. The catalysts were tested in a microreactor in the HTS reaction.

2. Experimental

Reagents used were analytical grade. In sample preparation a 0.25 M nitric acid aqueous solution was slowly added to an ammonium metavanadate one (0.025 M) at room temperature. The subsequent addition of a concentrated ammonium hydroxide (25%) led to an orange solution indicating the presence of the VO₄³⁻ ion. The resulting solution was mixed with an iron nitrate solution (1 M) and kept under stirring for 1 h at room temperature. The final pH was 10. The sol was centrifuged, washed with a 5% (w/v) ammonium acetate solution and centrifuged again. This procedure was repeated until no nitrate ion was detected anymore. The qualitative analysis of nitrate was performed by adding about 1 ml of concentrated sulfuric acid to 10 ml of supernatant, after each centrifugation [11]. The gel was dried in an oven at 393 K, sieved in 100 mesh and then heated at 673 K for 2 h, under nitrogen (100 ml/min). This procedure produced the V10 sample (V/Fe (molar) = 0.1). The method described was repeated using a 0.008 M solution of ammonium metavanadate to get a

sample with a V/Fe = 0.03 (V3 sample). A sample without vanadium was also prepared by the same method (I sample). The solids thus obtained were characterized by several techniques and without any pretreatment.

In order to determine their iron content, the solids were dissolved in concentrated hydrochloric acid, under reflux for 10 min in a carbon dioxide atmosphere. After reduction of the Fe(III) to Fe(II) with stannous chloride, the solution was titrated with potassium dichromate [11]. The analysis of the Fe(II) content was carried out on fresh and on spent catalysts to follow the magnetite formation and its stability under the reaction atmosphere. The amount of vanadium in the solids was determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES), using an ARL model 3410 equipment. Carbon analyses were carried out using a LECO model 761-100 apparatus.

Fourier transform infrared spectroscopy (FTIR) was used to confirm the presence of acetate species in solids. The experiments were carried out by means of a Jasco model Valor-III equipment in a range of 400–4000 cm⁻¹ using KBr discs. X-ray diffractograms were taken at room temperature in a Rigaku Miniflex model instrument using Cu K α radiation.

The specific surface areas were measured by using the BET nitrogen adsorption method. The catalyst (0.20 g) was heated for 1 h under flowing nitrogen at 423 K and then analyzed in a Micromeritics TPD/TPO 2900 model equipment, using a 30% N₂/He mixture. The TPR profiles were recorded in the same equipment, using 0.35 g of the sample and following the hydrogen consumption from a 5% H₂/N₂ mixture in the range of 298–1273 K.

The Mössbauer spectra were recorded at room temperature, using a 2 GBq ⁵⁷Co/Rh source and a conventional constant acceleration spectrometer, operating in triangular mode. The samples were diluted into alumina in order to avoid a too high Mössbauer absorption, and pressed into pellets. The isomer shifts (δ) were given with respect to α -Fe and were calculated, as the quadrupole splittings (Δ), with a precision of about 0.03 mm s⁻¹. The validity of the computed fits was judged on the basis of both χ^2 values and convergences of the fitting processes. All the fits have been achieved using sextuplets without fixing any parameters. The relative ratio of the magnetite sites (A and B) has been calculated using the relative spectral surface areas and considering a f_a/f_b ratio determined by Häggström et al. equal to 1.25 [12].

The recording of the high resolution transmission electron micrographs (HRTEM) and electron diffractograms were carried out using a JEOL 2010 equipment operating at 200 kV with a high resolution pole piece and an energy dispersive x-ray spectrometer (EDS) (Link Isis from Oxford Instruments). The samples were dispersed in ethanol using a sonicator and a drop of the suspension was dripped onto a carbon film supported on a copper grid and then ethanol was quickly evaporated. EDS study was carried out using a probe size of 15 nm to analyze borders and centers of the particles

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