



Iron-oxide aerogel and xerogel catalyst formulations: Characterization by ^{57}Fe Mössbauer and XAFS spectroscopies

Frank E. Huggins^{a,*}, Sumit Bali^b, Gerald P. Huffman^a, Edward M. Eyring^b

^a CFFS, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

^b Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

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ABSTRACT

Iron in various iron-oxide aerogel and xerogel catalyst formulations ($\geq 85\% \text{Fe}_2\text{O}_3$; $\leq 10\% \text{K, Co, Cu, or Pd}$) developed for possible use in Fischer–Tropsch synthesis (FTS) or the water–gas–shift (WGS) reaction has been examined by ^{57}Fe Mössbauer spectroscopy. The seventeen samples consisted of both as-prepared and calcined aerogels and xerogels and their products after use as catalysts for FTS or the WGS reaction. Complementary XAFS spectra were obtained on the occurrence of the secondary elements in some of the same materials. A broad, slightly asymmetric, two-peak Mössbauer spectrum was obtained from the different as-prepared and calcined catalyst formulations in the majority of cases. Such spectra could only be satisfactorily fit with three quadrupole doublet components, but no systematic trends in the isomer shift and quadrupole splitting parameters and area ratios of the individual components could be discerned that reflected variations in the composition or preparation of the aerogel or xerogel materials. However, significant reductions were noted in the Mössbauer effective thickness (recoilless absorption effect per unit mass of iron) parameter, χ_{eff}/g , determined at room temperature, for aerogels and xerogels compared to bulk iron oxides, reflecting the openness and lack of rigidity of the aerogel and xerogel structures. Mössbauer measurements for two aerogels over the range from 15 to 292 K confirmed the greatly diminished nature of this parameter at room temperature. Major increases in the effective thickness parameter were observed when the open structure of the aerogel or xerogel collapsed during calcination resulting in the formation of iron oxides (hematite, spinel ferrite). Similar structural changes were indicated by increases in this parameter after use of iron-oxide aerogels as catalysts for FTS or the WGS reaction, during which the iron-oxide aerogel was converted to a mixture of nonstoichiometric magnetite and the Hägg carbide, $\chi\text{-Fe}_5\text{C}_2$, or nonstoichiometric magnetite, respectively.

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1. Introduction

In Fischer–Tropsch synthesis (FTS) and the water–gas–shift (WGS) reaction, unsupported and supported iron oxides, usually promoted by potassium and other elements, are known to have significant catalytic activity and to be the basis for commercial catalysts, especially for higher temperature applications [1]. Typically, such iron oxides are originally small-particle hematite ($\alpha\text{-Fe}_2\text{O}_3$) with moderate to high surface areas and are reduced to mixtures of principally iron carbides and nonstoichiometric magnetite ($\text{Fe}_{3-x}\text{O}_4$, where $0 < x < 0.33$) during FTS [2–4] or to magnetite during the WGS reaction [5,6]. Recently, non-crystalline iron-oxide aerogels and xerogels, substituted by minor amounts of other ele-

ments (K, Co, Cu, and Pd), have been examined as potential catalysts for both FTS [7] and the WGS reaction [8]. Iron aerogels and xerogels are low-density solids derived from iron-oxide gels in which the liquid component of the gel has been replaced by a gas, either by extracting the liquid supercritically (aerogel) or by slow evaporation (xerogel). The resulting aerogels and xerogels exhibit several remarkable properties, including high thermal insulation and very large surface areas and it is this latter property that makes them suited for catalytic applications. Here, we summarize data obtained by iron Mössbauer spectroscopy on seventeen different iron aerogel and xerogel catalyst formulations, including those that have been described in previous investigations of their catalytic activity for FTS and the WGS reactions [7,8]. The samples consist of both as-prepared and calcined aerogel and xerogels, as well as their products after use as catalysts for FTS or the WGS reaction.

In addition, observations made with XAFS spectroscopy are summarized on the occurrence of minor elements (K, Co, Cu, and Pd) in some of the same iron-oxide aerogel and xerogel catalyst formulations. These studies, although not as comprehensive in scope

* Corresponding author at: CFFS, Department of Chemical and Materials Engineering, University of Kentucky, 533 S. Limestone St., 103 Whalen Building, Lexington, KY 40506 0043, USA. Tel.: +1 859 257 4045; fax: +1 859 257 7215.

E-mail address: fhuggins@engr.uky.edu (F.E. Huggins).

as the Mössbauer investigation of iron, supply insights on these minor elements that complement those obtained for iron. These elements were specifically chosen to be included in the catalyst formulations because of their well-established roles as promoter elements in iron-based catalysis of FTS and the WGS reaction [9]. Previous studies of potassium and other alkali promotion of iron-based FTS catalysts have revealed that such elements may affect the rate of FTS, as well as the selectivity and isomerization of the products [10,11]. Both copper and palladium are known to promote iron-based FTS catalysts [9,12], whereas cobalt is known to be an effective alternative to iron for catalysis of FTS. Although XAFS spectroscopy can reveal how elements are combined in iron-based catalysts, there have been relatively few XAFS studies of promoter elements such as K, Cu [13], or Pd in catalyst formulations for FTS or the WGS reaction, which is surprising given the large number of XAFS investigations of Fe and Co-based catalysts that have been reported for these applications.

Pure iron-oxide aerogels and xerogels, prepared by methods similar to those employed in the current study, have been examined previously with Mössbauer spectroscopy by at least two other groups. An iron-oxide xerogel was examined by Durães et al. [14] by various analytical methods, including Mössbauer spectroscopy. A broad quadrupole doublet was observed in the room temperature Mössbauer spectrum of the iron xerogel that was attributed to superparamagnetic hematite (α -Fe₂O₃) or goethite (α -FeOOH) or possibly Fe(OH)₃. Carpenter et al. [15] reported TEM observations and SQUID magnetometry and Mössbauer results for two as-prepared aerogels and for aerogels heated to 260 °C in argon and air. They concluded that the as-prepared iron aerogels were amorphous or poorly crystalline and exhibited Mössbauer spectra similar to that of ferrihydrite. These aerogels became nonstoichiometric, partially oxidized magnetite (Fe_{3-x}O₄) when heated in argon at 260 °C before becoming fully oxidized as maghemite (γ -Fe₂O₃) when subsequently heated in air. However, neither of these earlier Mössbauer studies investigated iron-oxide aerogels or xerogels in which minor elements such as K, Co, Cu and Pd were substituted at levels up to 10 wt%. Furthermore, we present data for an additional parameter, the Mössbauer effective thickness that was not explicitly discussed in these two previous studies. This parameter provides added insight into the changes in the structure of the aerogel or xerogel brought about by thermal treatments and reaction during catalysis.

2. Experimental

2.1. Aerogel and xerogel preparation

The preparation of the iron aerogels and xerogels is described in detail elsewhere [7,8]. Basically, an iron-oxide wet gel is first synthesized by a modification of the reported procedure [16,17] using propylene oxide as the proton scavenger for the initiation of hydrolysis and polycondensation. FeCl₃·6H₂O is used as the Fe(III) source for the 100% iron aerogel and xerogel; the same compound is mixed with appropriate amounts of K, Co, or Cu, in the form of potassium carbonate, cobalt chloride hexahydrate (CoCl₂·6H₂O), or copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), respectively, for the synthesis of substituted iron aerogels and xerogels. A typical synthesis begins with dissolution of FeCl₃·6H₂O and the appropriate amount(s) of additive element precursor(s) in anhydrous ethanol mixed with water. Propylene oxide is then added to the resulting solution with stirring. After stirring for about 5 min the solution is transferred to a 15 mL plastic cylindrical tube, which is then sealed. Dark red colored monoliths of iron-oxide gel are normally obtained within 10 min. The wet gels are allowed to age for 24 h under ambient conditions, after which they are subjected to supercritical drying

Table 1

List of aerogel and xerogel samples investigated by Mössbauer spectroscopy.

Aerogel/xerogel	As-prep/Calc./React.	Nominal composition (wt%)				
		Fe ₂ O ₃	CoO	K ₂ O	CuO	PdO
Aero-1A	A	85	10	5		
Aero-1C	C	85	10	5		
Aero-2A	A	98				2
Aero-2R	C, R: WGS	98				2
Aero-3C	C	100				
Aero-3R	C, R: FTS	100				
Aero-4C	C	95		5		
Aero-4R	C, R: FTS	95		5		
Aero-5C	C	90	10			
Aero-5R	C, R: FTS	90	10			
Xero-1A	A	98			2	
Xero-2A	A	95		5		
Xero-2C	C	95		5		
Xero-3A	A	93		5	2	
Xero-4A	A	85	10	5		
Xero-4C	C	85	10	5		
Xero-5C	C	100				

A: as-prepared; C: calcined at 300 °C; R: reacted; FTS: Fischer–Tropsch synthesis; WGS: water-gas-shift reaction.

or evaporation to form aerogels or xerogels, respectively. Details of the supercritical CO₂ drying procedures of the wet gels to produce aerogels are described elsewhere [7]. Xerogels are produced by evaporative drying under ambient conditions in a fume hood for 10 days. Both drying processes result in the formation of dark red iron aerogels or xerogels that retain the shape of the wet gels.

Palladium was incorporated into the iron aerogel using the gas phase incorporation technique described previously [8]. An appropriate amount of palladium precursor, (η^3 -allyl)(η^5 -cyclopentadienyl)Pd, a red solid, was mixed with the iron aerogel under nitrogen. The gradual disappearance of the Pd precursor was not easily visible because of the similar color of the gel. Hence, the mixture was allowed to stand overnight to ensure homogeneity and complete incorporation of Pd into the aerogel.

2.2. Samples

A variety of aerogels and xerogels samples were examined, including 100% Fe aerogel and xerogel, and various substituted iron aerogels, in which one or two of K, Co, Cu, and Pd had been added to the basic formulation in minor (≤ 10 wt%) amounts. In addition, selected aerogels and xerogels were examined as-prepared, after calcination in air at 300 °C for 2–4 h, and after FTS or the WGS reactions. A list of samples and their nominal compositions are given in Table 1. Descriptions of the reactors and conditions for performing FTS and the WGS reaction with these materials have been previously published [7,8].

2.3. Mössbauer spectroscopy

The phases of iron present in the aerogel materials investigated in this study were determined by iron Mössbauer spectroscopy. The Mössbauer spectra were obtained using a conventional constant-acceleration spectrometer consisting of a Halder, GmbH, Mössbauer drive and control unit interfaced to a personal computer by means of PHA/MCS boards from Canberra Nuclear. The γ -ray source at each end of the drive consisted of radioactive ⁵⁷Co doped into a thin foil of rhodium. The Mössbauer spectra were collected in symmetric mirror-image mode over 1024 channels and the data were then folded to provide a 512-channel spectrum of enhanced signal/noise ratio. A spectrum of metallic iron in thin foil form was collected at the opposite end of the Mössbauer drive simultaneously to the data collection for the unknown

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