



Spin conversion of hydrogen using supported iron catalysts at cryogenic temperature



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ABSTRACT

Alumina-supported iron oxides have been prepared by incipient wetness impregnation method and employed for orthohydrogen to parahydrogen spin conversion at cryogenic temperature. These materials were characterized using a series of characterization techniques such as SEM, XRD, Raman and *in situ* FTIR spectroscopy. The spin conversion was investigated at low temperature by a batch mode of operation. The *in situ* FTIR spectra were collected in a transmission mode to obtain the spin conversion. While the iron oxide was highly dispersed over alumina support at low loading percent, a rodlike crystallite of iron oxide was formed at high loading percent. The 10 and 20 wt% iron oxides on alumina were proved to be the most active catalysts. The spin conversion process was very slow and time-dependent. It was concluded that the spin conversion was a function of various factors including the iron oxide loading percent, calcination temperature, and different supports.

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1. Introduction

Dihydrogen is present in two different forms: ortho and para states of hydrogen. The ortho state of hydrogen is populated more at room temperature. The parahydrogen fraction gradually increases with decreasing temperature. The exothermic process of conversion is very slow in the absence of catalysts. The parahydrogen has polarization property which is absent for orthohydrogen, and the spin converted parahydrogen can be stored in a storage vessel with proper insulation for longer time [1–4]. The polarization property of parahydrogen has been used for various scientific applications such as sensitivity enhancement in liquid state NMR [4], biomedical research and medical diagnostics [5,6], angiography or MRI (Magnetic Resonance Image) [7–13], PHIP (Para hydrogen induced polarization), DNP (dynamic nuclear polarization) study to elucidate the mechanism of various catalytic hydrogenation reactions [4–7,14–19]. Moreover, the NMR images

of hyperpolarized ¹³C nucleus (pyruvate or lactate) are used for *in vivo* measurement of nanomolar amounts of inter-cellular metabolites and metabolic reaction rates in seconds with enhanced signal strength [8]. One of the major usages of hydrogen is alight fuel for car, space shuttle, and supersonic aircraft [20–23]. Spin converted parahydrogen has been stored in large vessels for mobile applications, however, there are some difficulties while stored in smaller vessels. It is known that hydrogen is explosive when contaminated with air in storage vessel [6]. Thus, the boil-off of normal hydrogen during storage in smaller vessels is another major challenge and practical issue at cryogenic temperature [24,25]. The boil-off of hydrogen inside the storage tank is due to internal heat liberation of ortho–para spin conversion and an external heat leakage from the improper insulation of storage tank. Several materials have been studied and developed as catalysts to overcome these problems for the safe storage of liquid parahydrogen at cryogenic temperature [26]. Moreover, various modifications have been also made on liquid hydrogen storage tank to short out the boil-off problems [27].

The adsorption of hydrogen has been investigated using different micro-porous materials. The materials studied for liquid

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hydrogen storage are MOFs and zeolites [26,28,29–31], clathrates [31], metal hydrides [2,32], activated carbon [32,33], carbon nanofiber, carbon nanotube [34], ZnO [35], and various sodium compounds [36]. A series of catalysts have been reported to convert orthohydrogen to parahydrogen such as activated charcoal, $\text{LaFeO}_3/\text{Al}_2\text{O}_3$, Cr_2O_3 , $\text{FeCl}_3/\text{SiO}_2$, Fe_2O_3 , chromium–nickel, FeOOH , $\text{Fe}(\text{OH})_3$ [3,6,37–43]. An external magnetic field which accelerates the rate of spin conversion was also examined [44,45].

The nature of adsorption and spin conversion of hydrogen over materials has been studied at cryogenic temperature using several characterization techniques. These techniques are FTIR [26,29–31,46–60], Raman spectra [47,55,58,61], thermal conductance [33], solid hydrogen impurity spectroscopy [33], matrix isolation spectroscopy [48], and NMR [62–66]. Other techniques to understand the properties of iron catalysts are XRD [67,68], Mossbauer [67], SEM [68]. However, there are a limited number of investigations reported for the ortho–parahydrogen spin conversion over iron catalysts using *in situ* FTIR spectroscopy [13,42,46,47].

The present study was aimed at synthesizing various kinds of iron oxide materials using different metal loading percents and supports, and attempting to find out the most active catalyst for spin conversion reaction from orthohydrogen to parahydrogen at cryogenic temperature. In pursuing this purpose, we have realized that there were several factors to influence the activity of iron oxide catalysts, such as time dependent spin conversion, role of support, metal loading percent, and calcination temperatures. To investigate the physical and chemical properties, a series of characterization techniques including SEM, X-ray diffraction, Raman and FTIR spectroscopy was utilized. In particular, the data of adsorption and spin conversion were monitored by *in situ* FTIR spectroscopy. Based on these results, it was concluded that we have finally developed one of the promising catalysts, which is a novel supported iron oxide catalyst for ortho–parahydrogen spin conversion at cryogenic temperature.

2. Experimental

2.1. Material synthesis

A series of alumina-supported $\alpha\text{-Fe}_2\text{O}_3$ catalysts with different metal loading percents (5–30 wt%) has been prepared by incipient wetness impregnation (IWI) method [69,70]. The precursors used were iron (III) nitrate nanohydrate (98.5%, Samchun), cerium (III) nitrate hexahydrate (99%, Samchun), and citric acid (99.5%, Samchun). The supports used in this study were $\gamma\text{-Al}_2\text{O}_3$ (Sasol, surface area: $200\text{ m}^2/\text{g}$), TiO_2 (99.5%, Sigma–Aldrich, $160\text{--}190\text{ m}^2/\text{g}$) and CeO_2 ($\sim 35\text{ m}^2/\text{g}$). The CeO_2 support was prepared by a citrate method using cerium (III) nitrate hexahydrate precursor with appropriate amount of citric acid solution [71]. In the IWI method, the alumina support was pre-treated with the distilled water, and followed by drying, and finally calcined at 773 K for 6 h. A known amount of iron (III) nitrate nanohydrate was dissolved in a beaker with incipient wetness volume of water to form a solution. This precursor solution was added drop wise to the pre-treated support and mixed thoroughly. The iron impregnated support was kept in a desiccator for 12 h. The sample in desiccator was dried again at 383 K for 6 h, and followed by a stepwise calcination to a final temperature of 773 K for 6 h. A series of the alumina-supported iron oxides was denoted as $x\text{FeAl}$, where $x = 5, 10, 20,$ and $30\text{ wt}\%$. Similarly, the 10FeTi and 10FeCe samples were also prepared by using titania and ceria as support. A set of 10FeAl samples were synthesized using different calcination temperatures of 473, 573, 673, 773 and 873 K. A bulk $\alpha\text{-Fe}_2\text{O}_3$ catalyst was also synthesized by the above mentioned procedure.

2.2. Characterization

The surface morphology of the prepared materials was obtained using Field-Emission Scanning Electron Microscopy (FE-SEM, HITACHI-S4200). The SEM images were magnified by 50,000 times. The crystallite phase and size were determined by X-ray diffraction (Bruker D8 Advance) using the $\text{Cu K}\alpha$ irradiation with two theta value of $20\text{--}70^\circ$ with a scan rate of 2 degree per minute. The Raman spectra were obtained under ambient conditioned using a Renishaw Raman microscope equipped with a confocal microscope, 2400 l/mm (Vis) grating. The samples were excited with a 532 nm (Visible) Nd: Yag laser. All spectra were collected in the scan range of $100\text{--}1400\text{ cm}^{-1}$ using the WiRe software.

The normal hydrogen adsorption and *in situ* ortho–parahydrogen spin conversion in presence of materials were obtained by using FTIR spectrometer (Thermo-Scientific, Nicolet iS10) in transmission mode attached with cold head of a closed-cycle refrigerator (CCR) cryostat. The IR beam was passed through the materials before and after the quartz windows of the cold head of CCR cryostat. All of the spectra were collected in the range of $4000\text{--}5500\text{ cm}^{-1}$ with a resolution rate of 4 cm^{-1} .

2.3. Liquid phase hydrogen (LH_2)-in situ FTIR study

The details of FTIR experiments (Scientific Instrument Engineering, SciEnTech) are given below. A 20/5 W, He CCR Cryostat (Austin Scientific, Oxford Instruments) which has a cold head coupled with a spin conversion chamber made of copper tube (inner diameter 16 mm, length 170 mm) was used. The helium compressor was connected with cold water to maintain the compressor temperature. The orthohydrogen to parahydrogen spin conversion experiments were performed at 17 K. Two thermocouples were placed to maintain a constant temperature: one was located at the bottom of the cold head (cryostat) and the other was placed at the outer surface of the spin conversion chamber. The outer periphery of the chamber and the cold head were covered by a stainless steel metal container to maintain a vacuum insulation throughout the operation. The vacuum insulation of the outer periphery and inside of the chamber was maintained by using a rotary vacuum pump (W2V20, 4 kW, WooSung Auto Co. Ltd) and a turbo compound molecular pump (Osaka vacuum, Ltd) with rotation speed of 48,000 rpm. The vacuum insulation pressure was maintained throughout the operation at 5×10^{-5} torr. Based on the experiments, the catalyst was loaded inside of the spin conversion chamber before the vacuum operation. When the vacuum was created, the chamber temperature was slowly downed to reach at 17 K. The hydrogen gas (99.99%, DEO) at the temperature of 300 K was charged inside of the spin conversion chamber. The vacuum pressure of the chamber was maintained at 0.075 MPa by a compound pressure gauge during charging the hydrogen. Once the hydrogen gas was charged inside of the chamber, IR spectra were collected. The details of experimental setup and FTIR spectra acquisition were represented in Scheme 1.

2.3.1. Hydrogen at low temperature and its adsorption study

The different phases (gas, liquid, and solid) of normal hydrogen were obtained by varying the temperature from 24 K to 13.8 K without putting any catalysts inside of the spin conversion chamber. The hydrogen adsorption studies were carried out at 17 K over alumina support. A 150 mg of powder sample was made into pellet (10 mm of diameter and 1 mm of thickness) using a pelletizer (Carver Lab. Press), and the pelletized sample was placed inside the spin conversion chamber. An inlet flow rate of normal hydrogen gas was maintained at 200 ml/min by mass flow controller (Fujikin, T1000L). Various pulse volume of hydrogen are 1000,

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