



# Nanocluster iron oxide-silica aerogel catalysts for methanol partial oxidation

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## Abstract

Nanostructured pure and silica-supported iron oxide materials have been prepared by the aerogel approach. Pure iron oxide powder derived from sol-gel ferric acetylacetonate formed agglomerates of 5–30 nm small crystallites of hematite and maghemite according to TEM identification of crystal faces. Depositing ferric species to mesoporous silica aerogels generated 1–5 nm particles in the amorphous matrix. They were evaluated for methanol oxidation in an ambient fixed-bed flow reactor from 225 to 300 °C. Product selectivity and oxidation activity were dependent upon iron dispersion and reactor operation. The formation of dimethyl ether was mainly related to the bulk phase and Lewis acidity of iron oxide. Active catalysts that were selective to formaldehyde and methyl formate required appropriate iron dispersion on the silica surface, including a strong electronic interaction. Methoxy transformation to formaldehyde and formate species was found to be a function of surface temperature based on a Fourier transform infrared (FT-IR) analysis. Low to moderate reactor temperature and short catalyst contact time favored methanol conversion to formaldehyde. The formation of methyl formate was found to compete with that of formaldehyde. The dependence of response time on oxygen feed attenuation suggests that mobile lattice oxide ions participate in the surface reaction and that oxygen molecules help to maintain surface iron sites highly oxidized for Lewis chemisorption and redox electron transfer. A good correlation between microstructures and reaction characteristics is proposed.

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## 1. Introduction

Aerogels, nanomaterials normally prepared by sol-gel polymerization and supercritical drying, have had great potential for use in molecular recognition and chemical conversion, such as sensors, adsorbents and catalysts [1–3]. Silica aerogels are highly porous and consist of mesopores supported by a nanoparticle cross-linking framework. High porosity and surface area are attractive properties for catalytic chemisorption and favor accessibility for reaction molecules to active centers. In the NO<sub>x</sub> reduction with propane reaction, catalytic activity of aerogels is higher than that of their homologues xerogels because of the higher

effective diffusivity of reaction gas that is attributed to the high porosity and larger pore size [4,5]. Kim et al. [6] found that alumina-supported nickel aerogels showed a remarkably lower coking rate in methane reforming due to highly dispersed nickel particles than the rates for similar catalysts prepared by an impregnation method. High thermal stability makes aerogels, such as zirconia-silica [7], suitable for the destruction of volatile organic compounds. Recently, aerogels as catalysts have been successfully expanded into high-pressure flow reactors as well [8].

Partial oxidation of methanol has many commercial applications such as pathways to formaldehyde, methyl formate, and dimethyl ether. Production of formaldehyde over iron-molybdenum oxide catalysts is of particular industrial importance [9]. Dimethyl ether has been recognized as a promising clean alternative fuel in the next generation due to its perspective value for low

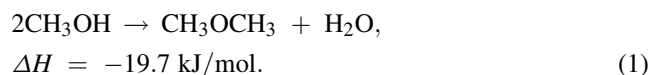
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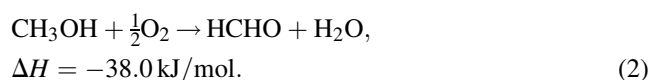
pollutant emission and its non-toxic character [10]. Steam reforming with this ether provides a useful hydrogen source for fuel cells [11]. Further, methanol oxidation is also an excellent probe reaction to characterize oxidation catalysts using flow reactor data. The selectivity pattern and the formation rates of the reaction products provide information on the surface nature and dispersion of active sites at the molecular level [12]. Strong Lewis acidity helps to promote dehydration of methanol to dimethyl ether over metal oxide catalysts, such as niobia or alumina [13]. The high basic character of oxide catalysts tends to oxidize methanol to adsorbed formate species, followed by further decomposition to carbon oxides [12]. If redox sites are present on an oxide surface, such as molybdena, vanadia or zirconia, then formaldehyde or methyl formate is mainly produced [13–15]. However, when metal oxides generally considered as acidic types are deposited on silica, redox active sites then prevail on the catalyst surface during methanol oxidation [16]. Therefore, mixed oxides have been of great interest for use as catalysts because of the opportunity to adjust the variation in surface acidity.

Iron oxide itself exhibits strong acidic and weak redox properties [17]. Most known iron oxide-silica catalysts were prepared with iron nitrate and with nitrogen-containing bases as gelation agents [18]. The present study aims to employ iron acetylacetonate simply with water in sol-gel synthesis at the molecular level, and to investigate the catalytic reactivity of silica coordinated and bulk iron oxide aerogels. Attempts have been made to demonstrate new data of aerogel structure comparable to those made from ferric salts. The methanol oxidation reaction is selected as the test probe to investigate the surface nature by aerogel evaluation in an ambient flow reactor. Detailed examination of reactor parameters, such as reaction temperature, catalyst contact time and oxygen feed, aids to determine a correlation between catalyst structure and product selectivity. Fourier transform infrared (FT-IR) and X-ray photoelectron (XPS) techniques were used to characterize surface intermediates and active iron oxide sites. The primary pathways under consideration and their gaseous standard heats of reaction (product basis) are as follows [19].

Dehydration of methanol to dimethyl ether:



Partial oxidation of methanol to formaldehyde:



Partial oxidation of methanol to methyl formate:



## 2. Experimental

### 2.1. Aerogel preparation

The iron and silicon oxides were synthesized with a typical two-stage sol-gel procedure. An example of preparation is described for the 20 wt.% (weight percent) iron oxide-silica aerogel. Ferric acetylacetonate (4.427 g, Fluka, 97%) and tetramethyl orthosilicate (10.138 g, Fluka, 98%) were mixed and dissolved in methanol (85 g, Tedia, 99.9%). Water triply deionized (6.564 g) was then added into the precursor solution for hydrolysis and condensation. An oxide wet gel solution formed, and complete mixing continued for another few hours. The final gel solution in a Pyrex glass liner was then placed inside a 316 S.S. autoclave reactor (American Engineering), and high temperature supercritical methanol drying followed. The overall aerogel yield per batch production is about 98 wt.%.

### 2.2. Catalytic evaluation

Catalytic reaction tests by methanol oxidation were carried out in a fixed-bed flow apparatus at ambient pressure. A feed mixture was prepared by flowing nitrogen gas through liquid methanol placed inside a temperature-controlled Pyrex glass saturator. Finally, an oxygen flow was injected into the reactor. The feed stream normally at 0.7 g/min contains 2.2 mol% methanol, 5.2 mol% oxygen, and nitrogen for the balance. After being grounded into very fine powder, 0.5 g of aerogel was packed inside a tubular Pyrex glass tube (20 mm i.d.) placed in a temperature PID controlled oven. Contact time was estimated based on specific packing density and volumetric flow rate. The hydrocarbon species in the reactor inlet and effluent (methanol, dimethyl ether, formaldehyde, and methyl formate) were nicely separated with a Cowax 10 capillary column (Supelco, 60 m × 0.53 mm × 2.0 μm film thickness) and analyzed on a gas chromatograph (China Chromatography, Model 9800) with a flame ionization detector (Varian) in series with a thermal conductivity detector (Varian). Formic acid was never detected. In order to completely avoid total oxidation to carbon oxides, we maintained a low conversion of below 25%. The reaction temperature was incrementally raised from 225 to 300 °C, and for each step a 45-min interval was allowed for taking conversion and selectivity data at steady state.

### 2.3. Structural characterization

BET surface areas of aerogels were determined by 77 K nitrogen gas adsorption measurements (Micromeritics, Model ASAP 2010). Transmission electron micrographs (TEM) were taken on a JEOL 2000SX instrument. Surface morphology was examined by taking field emission scanning electron micrographs (FE-SEM, JEOL, and

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