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Fine particle iron oxide based aerogels for the partial oxidation of methanol

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Abstract

Fine particle pure and supported iron oxide materials have been prepared by the aerogel approach. These particles have diameters in the range 50–300 nm. They were evaluated as catalysts in the fixed bed reactors (gas phase and supercritical CO_2) for the partial oxidation of methanol. The products observed were dependent upon support and reactor temperature. For example, the pure iron oxide aerogel achieved greater than 70% selectivity to dimethyl ether over a temperature range 220–275°C. If the reaction is carried out over 20% iron oxide on molybdenum oxide from 250°C to 330°C, the main product observed was formaldehyde. The results are related to the surface chemistry of the iron oxide aerogel, and are influenced by the surrounding support.

Keywords: Aerogel; Iron oxide; Methanol oxidation; Dimethyl ether; Formaldehyde; Mixed oxides

1. Introduction

Aerogels, originally discovered by Kistler [1], have always had potential as catalysts. The ability to make high surface area, porous, materials that therefore allow molecules accessibility to active site is a characteristic that is unmatched by any other method of material synthesis. Renewed activity in using these materials as catalysts began with their reinvention by Nicolaon and Teichner [2]. Several reviews have been published in the field including those of Pajonk [3,4]. Some recent papers that have appeared about aerogels as catalysts include the work of Schneider and Baiker [5] and Ko and coworkers [6].

Another field growing in recent years are reactions conducted in supercritical fluids – especially supercritical CO_2. Recent reviews include the work of Johnston [7] and most recently the use of supercritical water for total oxidation has gained international interest [8]. The application of catalysts within a supercritical fluid system is relatively new. Published work about hydrogenation has appeared from the group of Poliakoff at the University of Nottingham [9]. The work discussed below is one of the first to look at catalytic oxidation conducted in supercritical CO_2. Our original goal was total oxidation of organics in supercritical CO_2 at temperatures lower than that used for total oxidation in supercritical water. Methanol was selected because it has served as a model reaction for supercritical water oxidation [10]. However, as the work evolved we found partial oxidation dominated in the temperature and residence time

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ranges we were working in. Thus, we elected to focus on these reactions.

The reactions determined to be significant in this work are:

- Partial oxidation of methanol to formaldehyde:

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O \quad (1)$$

- Partial oxidation of methanol to methyl formate:

$$2CH_3OH + O_2 \rightarrow CH_3OOCH + 2H_2O \quad (2)$$

- Dehydration of methanol to dimethyl ether:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (3)$$

- Total oxidation of methanol to carbon dioxide:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \quad (4)$$

The resultant selectivities to various partial oxidation products were quite encouraging as the work below will show.

2. Experimental

The aerogels prepared for use in this work were based around iron oxide (Fe_2O_3). The methods are not too dissimilar from those originally described in Teichner et al. [11]. For example, the pure Fe_2O_3 aerogel was formed by combining iron(III) acetylacetonate (Aldrich 99%) in methanol and adding a small amount of water for hydrolysis (1.2 times the stoichiometric amount required). No gel was formed before the solution was placed into the autoclave. The solution within the autoclave had enough solvent to reach the critical conditions of methanol (240°C and 76 bar). After sealing the autoclave, heating commenced until the temperature and pressure reached supercritical points (270°C, 100 bar is typical). Depressurization followed at constant temperature. When the pressure reached ambient, heating was discontinued, and the autoclave was allowed to cool overnight with a gentle purge flow of N_2. The material removed were reddish black particles that were easily broken up by lightly grinding in a coffee grinder. The aerogels were then post treated by carefully heating in air beginning with ambient temperature and slowly bringing the oven to 500°C where it was held for 2 h to burn off surface methoxy groups.

The aerogels were compressed to reduce macro volume by about 50% for reaction evaluations done under supercritical fluid (SCF) conditions. They were then placed inside a tubular ($\frac{3}{8}$ in. o.d., 0.035 in. wall thickness, 316 SS) vertical reactor that was heated by a Lindberg tubular furnace. The reactor system had the ability to feed CO_2 (the carrier) at high pressure (91 bar absolute). Liquid methanol (fed by a high pressure metering pump) and high pressure oxygen were added to the CO_2 flow before a static mixer. Typical feed concentrations in CO_2 were 1.1 wt% methanol and 1.8 wt% oxygen. Space velocity (W/F) for this system based on a reactant stream flow rate 432 g/h and 1.5 g of Fe_2O_3 aerogel is 288 h^{-1}. Contact time is approximated to be about 0.85 s based on catalyst volume and volumetric flow rate within the reactor. An oxidative pretreatment was done before each run that consisted of passing an air stream at 475°C for 2 h across the catalyst bed.

For comparison, a gas phase atmospheric reactor system was also built. We elected to keep the catalyst residence time similar for this study. Thus, we used a reactant stream flow rate of 7.7 g/h and 1 g of Fe_2O_3 aerogel (compressed powder). Because the density of the gas phase is significantly less, the contact time was approximately 0.6 s. Further details about the reactor system and design can be found in Wang [12].

3. Results

Fig. 1 is a scanning electron micrograph of Fe_2O_3 aerogel (pure iron oxide only). This micrograph shows the fine particle nature of the aerogel with particle diameters in the range 50–200 nm. The particle is actually an agglomerate of primary particles in the range 8–30 nm as determined by XRD [13]. This small particle size has advantages in that molecules can access the surface easily and thus internal diffusional resistances are minimal. A major experimental challenge was keeping these particles in place in the reactor. By compressing beforehand and using a $\frac{1}{2}$ micron sintered metal filter as a support, these particles remained stationary in the reactor bed for the duration of catalytic runs completed.

Fig. 2 shows methanol conversion and product selectivities for passing 432 g/h of a 1.1 wt% metha-

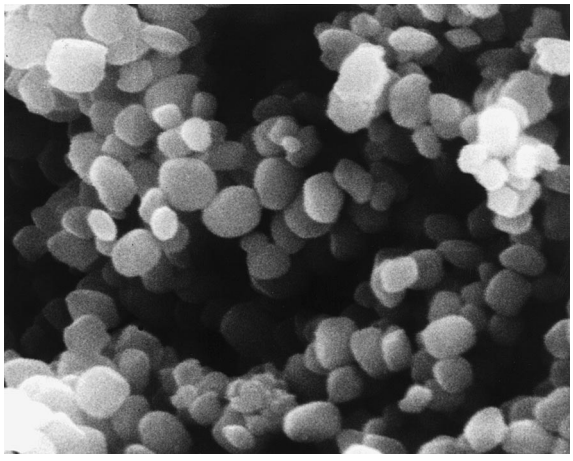

Fig. 1. Scanning electron micrograph of Fe_2O_3 aerogel after compression but before insertion into the reactor.

nol and 1.8 wt% oxygen in CO_2 over 1.5 g of Fe_2O_3. The pressure for this run was 91 bar absolute. Thus, the combination of pressure and temperature places the mixture in the supercritical fluid region.

The most dominant product at temperatures below 300°C is dimethyl ether. Also observed are small amounts of formaldehyde and methyl formate (selectivities are below 10%). Selectivity in this work is defined as follows:

$$\text{Selectivity } (\%) = \text{moles of product } P \text{ produced} / \text{moles of methanol converted} \times 100 \times \text{SF}.$$

where SF is the stoichiometric factor (moles of methanol/moles of P) as given by reactions (1)–(4).

Conversion and selectivity are a function of residence time. An evaluation of residence time was conducted at 275°C. The conversion of methanol increased from 18% to 45% with increasing the catalyst residence time from 0.53 to 1.26 s. The selectivity to dimethyl ether increased, reaching a broad maximum, and then decreased with increasing residence time. Highest selectivity observed (about 70%) was reached at residence times between 0.71 and 1.09 s. This behavior indicates that the catalytic maximum yield for the dehydration of methanol to dimethyl ether has been approached in this residence time range in which the adsorbed surface methyl species (CH_3) would preferably form dimethyl ether. Shorter residence times favored the formation of formaldehyde. Longer residence times favored the formation of methyl formate.

Conversion of methanol dropped substantially and the selectivity to dimethyl ether is also lowered when the reaction is done without oxygen present (reaction was done with the 20 wt% Fe_2O_3–SiO_2 aerogel [12]). Thus, another finding of this work relevant to iron oxide was that the reaction to dimethyl ether is

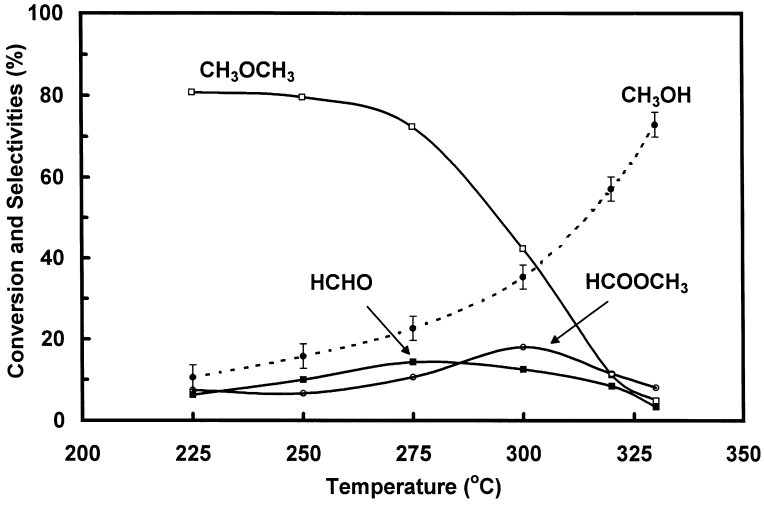

Fig. 2. Effect of reaction temperature on methanol conversion and product selectivities for the catalytic oxidation of methanol in supercritical (SCF) carbon dioxide over Fe_2O_3 aerogel (reactor pressure=91 bar absolute).

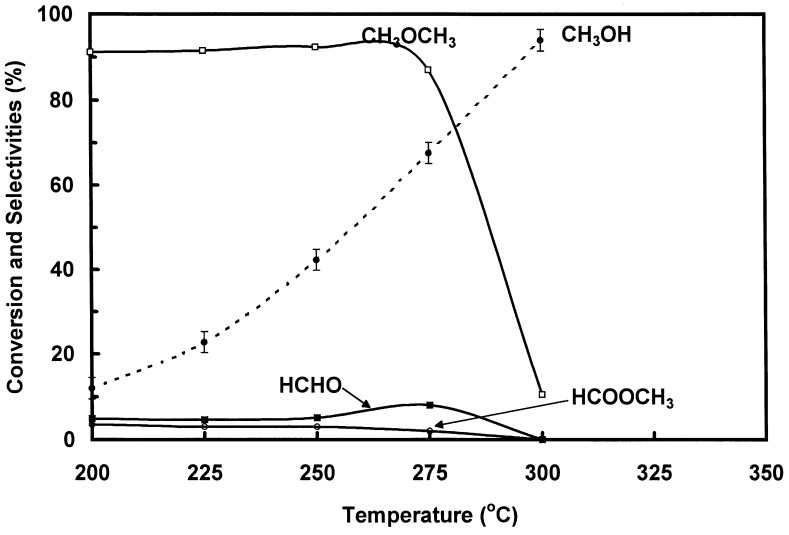

Fig. 3. Effect of reaction temperature on methanol conversion and product selectivities for the catalytic oxidation of methanol in gas phase carbon dioxide over Fe_2O_3 aerogel (reactor pressure 1 bar absolute).

promoted in the presence of a small amount of oxygen. As temperature increased above 300°C, selectivities dropped for all of the partial oxidation products. Yet, methanol conversion continued to rise. This is because CO_2 is forming from the total oxidation reaction.

Fig. 3 shows methanol conversion and product selectivities for the same reaction done over the same catalyst. The difference was that the carrier gas, CO_2, is at atmospheric pressure. Compared to the SCF run, higher selectivity to dimethyl ether is noted (selectivities are above 90% for temperatures between 200°C and 250°C). Similar runs were also completed with a N_2 carrier in place of CO_2 [12]. Conversion of methanol was similar compared to the CO_2 gas phase run; however, selectivities to dimethyl ether were slightly lower averaging 88% instead of 92% at temperatures below 250°C. A reason why selectivities are higher for the CO_2 carrier based runs may be related to the presence of excess CO_2 on and near the catalyst sites. This presence may hinder further oxidation to CO_2 on the catalyst surface.

Fig. 4 shows a comparison of production rates of dimethyl ether by the two major methods presented. The rates are normalized by the amount of catalyst used. An approximate 3- to 5-fold increase in production rate is noted for the SCF approach compared to the gas phase approach. This is a significant finding and should encourage further research in the field. Note that above 300°C the gas reaction production to dimethyl ether is nil. Production of the other by-products, formaldehyde and methyl formate, were 8 and 16 times greater, respectively, for the SCF approach compared to the gas phase approach [12]. A disadvantage; however, is the lower selectivity of DME in the SCF phase as compared to the gas phase for the pure iron oxide aerogel.

Fig. 5 shows infrared spectra for CO adsorbed onto oxidized and reduced 20% Fe_2O_3–SiO_2 aerogels that were also prepared for the work done. The spectra show two bands: one at 2210 cm^{-1} that represents CO adsorbed onto oxidized iron oxide, and one at 2170 cm^{-1} that represents CO adsorbed onto reduced iron oxide. Similar adsorption studies were completed on pure SiO_2 aerogel [12]. No CO adsorption could be detected. Thus, the bands observed in Fig. 5 are due to surface iron in the +2 and +3 oxidation state. The ability of the iron site to change its oxidation state easily is part of the reason it has catalytic activity towards the partial oxidation of methanol. Additional work with ammonia adsorption showed that at room temperature Lewis and Brønsted acid sites exist as well as exposed oxygen anions. These sites do not have the same strength. Upon heating to 200°C, the ammonia remains only on the Lewis acid site (exposed Fe^{3+}). The activity for methanol condensation to dimethyl ether is related to these strong Lewis acid

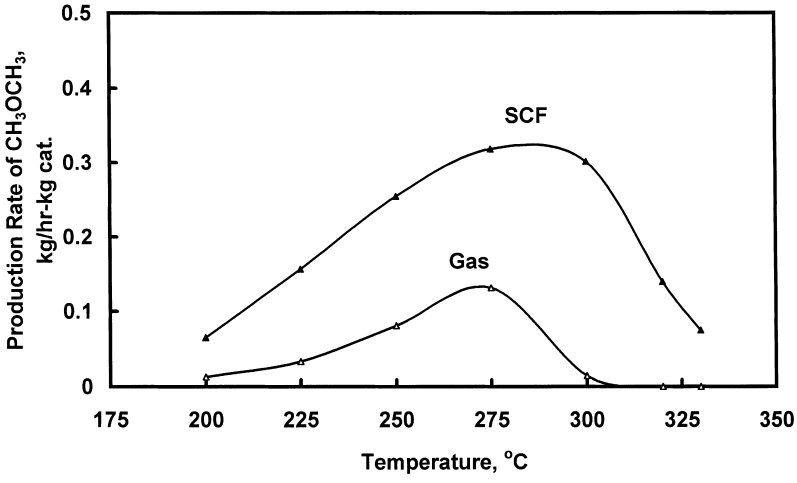

Fig. 4. Comparison of dimethyl ether production rates obtained from catalytic oxidation of methanol in supercritical (91 bar absolute) and gaseous carbon dioxide (1 bar absolute).

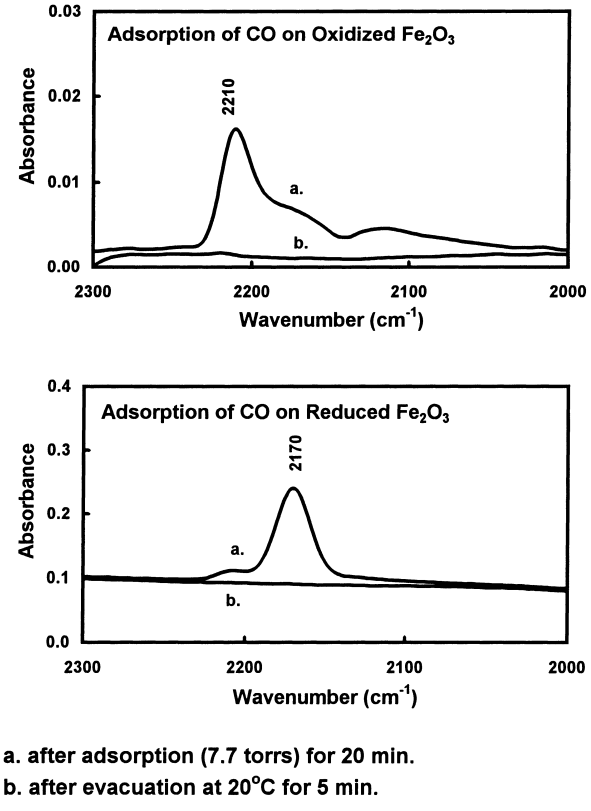

Fig. 5. Infrared spectra of CO adsorbed on oxidized and reduced 20% Fe_2O_3–SiO_2 aerogels.

sites and on pure iron oxide they are quite close to each other.

Table 1 gives a summary of methanol conversion and product selectivities found with other iron oxide based aerogels investigated in the SCF reactor system at conditions as outlined in Section 2. The temperature selected for comparison is 275°C. This temperature is near the optimum temperature for the partial oxidation products formed. As iron oxide content increases on silica, methanol conversion decreases with one exception – a 20% Fe_2O_3–SiO_2 aerogel (giving total oxidation to CO_2). Selectivity to dimethyl ether is highest for pure iron oxide, and methyl formate forms when substantial SiO_2 is present. Another material evaluated was a 20% iron oxide on molybdenum oxide aerogel. This aerogel was extremely selective for the partial oxidation of methanol to formaldehyde.

4. Discussion of results

Novakova et al. [14] reported on methanol oxidation over iron oxide that had a surface area of 7.8 m^2/g. The temperature investigated was 220°C. Their products were CO, CO_2, and H_2O and no other partial oxidation products. This is in contrast to our results for iron oxide (surface area of 10 m^2/g) and temperature range 225–330°C. We did not detect CO within the

Table 1
Summary of aerogels investigated for partial oxidation of methanol in supercritical CO_2

Aerogel	Conversion at 275°C	Selectivity (%)			
		Dimethyl ether	Formaldehyde	Methyl formate	CO_2[a]
SiO_2	99	0	0	24	76
1% Fe_2O_3 on SiO_2	71	2	6	65	27
5% Fe_2O_3 on SiO_2	41	28	30	30	12
10% Fe_2O_3 on SiO_2	37	31	28	38	13
20% Fe_2O_3 on SiO_2	90	15	1	3	81
20% Fe_2O_3 on MoO_2	16	6	94	0	0
Pure Fe_2O_3	23	72	14	11	3

[a] Selectivity to CO_2 is based on difference ($100-\sum$selectivities to other products).

constraints of our instrumentation and our products were quite different. A portion of this discrepancy is related to the residence times and pressure. Novakova et al. [15] experiments were done in a batch reactor with contact times over 100 min and pressures at 0.5 mbar. As described above, our pressures were much higher (91 bar) and residence times much shorter (under 1 s).

The selective formation of dimethyl ether over the pure iron oxide aerogel is directly related to the surface acidity that this material has and this has been pointed out by others for other acidic materials [16–20]. The dilution effect by silica is profound on the dimethyl ether formation suggesting that the iron oxide surface atoms must be closely situated to promote the adsorption of two neighboring methanol groups as initially methoxy groups that subsequently combine to give dimethyl ether. The remaining surface hydrogen/hydroxyl groups (not necessarily from the same two methanol groups that paired to form dimethyl ether) combine to form water. The role of catalyst support (molybdenum oxide or silica) not only physically alter ability to have a dispersion of iron atoms together as near neighbors, but also change the acidic nature of iron oxide or mixed oxide. Further, the redox mechanisms (or electron transfer) across iron oxide are involved in formaldehyde formation, and this is enhanced by the presence of molybdenum oxide but not so much when silica is present. The influence of catalyst support effects on observed selectivities are interesting and must remain a focus of future research efforts.

Iron oxide on molybdenum oxide is a known oxidation catalyst used for the production of formaldehyde from methanol [21,22]. Our results confirm the ability of the 20% iron oxide–molybdenum oxide aerogel to selectively convert methanol to formaldehyde. What is further shown is the ability of this material to conduct partial oxidation reactions in supercritical fluids – especially in the presence of CO_2. CO_2 is the total oxidation product and at higher temperatures (above 350°C or so depending upon catalyst) is the predominant product. However, at lower temperatures its presence may help to retard complete oxidation reactions and hopefully future researchers will confirm this observation.

5. Conclusions

1. Fine particle iron oxide aerogels promote the conversion of methanol in the presence of oxygen to dimethyl ether, formaldehyde, or methyl formate at temperatures below 300°C. The selectivities to these products is a function of temperature and residence time.
2. Pure iron oxide aerogel favorably promotes the formation of dimethyl ether. This is true for gas and SCF CO_2 phase carriers.
3. Formaldehyde is favorably and selectively produced over iron oxide on molybdenum oxide aerogel.
4. Formation of methyl formate is favored when silica is used as the support and iron oxide is well dispersed with its content below 5%.
5. The selectivities observed are related to iron oxides ability to be reduced and reoxidized through each cycle of a reaction path. The pure iron oxide aerogel creates a Lewis acid that promotes for the formation of dimethyl ether. If a support is

present this acidity is altered and the iron oxide exhibits more redox capability.

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