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High Temperature Water Gas Shift Catalysts with Alumina

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Abstract

Alumina (Al_2O_3) was added as a component of conventional iron oxide based high temperature water gas shift (WGS) catalysts. The catalysts contained Fe-Al-Cr-Cu-O and were synthesized by coprecipitation. A series of catalysts were prepared with 5 to 50 wt% Al_2O_3 , 8 wt% Cr_2O_3 , 4 wt% CuO, and the balance Fe_2O_3 . One catalyst was prepared in which the chromia was replaced by alumina. All of the catalysts were compared to a reference WGS catalyst (88 wt% FeO_x , 8 wt% Cr_2O_3 , and 4 wt% CuO) with no alumina. The catalysts were characterized using temperature programmed reduction (TPR), surface area analysis using nitrogen physisorption, and scanning electron microscopy (SEM) with compositional analysis. The catalysts were also tested kinetically under WGS conditions.

Addition of 10 to 15 wt% alumina increased the catalyst activity and thermal stability, with approximately 15 wt% alumina addition being optimum, as this catalyst produced a reaction rate (normalized per mass) 74% higher than the reference catalyst. The effect of alumina addition was greater than the surface area increase alone, which suggests that alumina alters the activity of the iron oxide domains, likely through an increase in reducibility, as shown by the TPR results. This synergistic effect was only observed when both alumina and chromia were present. Alumina alone (as a replacement for chromia) was not as an effective stabilizer as chromia. Although both the alumina-containing catalyst (without chromia) and the reference with chromia had similar initial surface areas ($\sim 160 \text{ m}^2/\text{g}$), the alumina-containing catalyst retained only 74% as much surface area after reaction. Results from the catalysts with 50 wt% alumina suggest that the loss of catalytic activity is due also to the formation of aluminates.

Keywords: Alumina, thermal stability, HT water gas shift catalyst

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1. Introduction

The water gas shift (WGS) reaction is one of the main industrial methods for the production of hydrogen. Typically, the carbon monoxide (CO) reactant is derived from the synthesis gas (syngas) obtained from various carbonaceous materials [1].



As shown above, WGS is a moderately exothermic, reversible reaction. Thus, the equilibrium constant increases at lower reaction temperatures, which is the reason the industrial reaction is operated in two stages. The initial stage involves high temperature (HT) conversion (300-500°C) with an iron oxide/chromia spinel catalyst [1, 2, 3, 4], which reduces the exit CO concentration to about 3 vol% [1, 9]. Conversion of the majority of the remaining CO is carried out in a second low temperature (LT) process stage (210-250°C) using a high activity Cu/ZnO/Al₂O₃ catalyst [1, 3, 4, 5].

Iron oxide based WGS catalysts were discovered in 1909 by BASF researchers [1]. The active component of the catalyst is magnetite (Fe₃O₄) [1, 6, 7, 8]. However, the thermal stability of magnetite is low, resulting in rapid sintering at the 300-500°C reaction temperature. Therefore, a refractory oxide (Cr₂O₃) was added to increase the thermal stability by slowing the rate of sintering. Although catalysts with 14 wt% Cr₂O₃ were more resistant to sintering, 8 wt% Cr₂O₃ produced a more active catalyst [8]. The mechanism of chromia's effect was a matter of debate: whether chromia prevents sintering as crystals that physically block the movement of iron [7] or by entering the magnetite structure as solid solution that modifies the characteristics of the material [8]. Using physical characterization techniques, the latter hypothesis was demonstrated

because crystalline chromia is not observed below 14 wt% Cr_2O_3 [8]. Copper was later incorporated into the industrial catalyst formulations because its addition as CuO increases the catalytic activity. Current industrial WGS catalysts include 2-4 wt% CuO. During reduction to activate the catalysts, metallic Cu leaches from the structure and forms individual crystallites on the surface of magnetite, which sinter into larger crystals if the initial CuO content is increased above 4 wt% and also increases the overall sintering of the catalysts [1, 9, 10]. Again, copper's role in HT-WGS is still the subject of debate. Some researchers propose that the effective component is metallic Cu, which acts in the same way as in the Cu/ZnO/ Al_2O_3 LT-WGS catalyst [1], while others suggest that Cu in the magnetite structure modifies the electronic properties of the standard $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$ catalyst [6].

The mechanism of the HT-WGS catalyst is regenerative, with electron exchange between Fe^{2+} and Fe^{3+} from the octahedral sites of the magnetite inverse spinel structure, as shown by Mossbauer spectroscopy [11], which ensures the redox coupling required by the regenerative mechanism [12, 13].

Although HT-WGS catalysts can function 10 years [8] by increasing the initial quantity of the catalyst in industrial reactors, typical iron based WGS catalysts are used for 2-5 years. The loss of catalytic activity is largely due to sintering [1, 8], as opposed to other causes of deactivation (from poisoning, coking, etc.). Therefore, a method to increase the resistance to sintering is desirable. Most of the loss in catalytic activity occurs in the first 150 h of operation, followed by a much lower rate of deactivation over extended periods of several years [1, 8].

The catalysts prepared in this study include alumina because alumina has been reported to enhance thermal stability [9, 14]. The effects on thermal stability and reaction rate with by alumina addition to iron oxide based HT-WGS catalysts will be described in this paper.

2. Experimental

2.1. Catalyst preparation

Appropriate amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>98.5%, Fisher Scientific) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>98.5%, Sigma-Aldrich) were dissolved in deionized water and stirred for about 30 minutes. Sodium hydroxide (97.6%, Fisher Scientific) or ammonium hydroxide (30% NH_4OH , J. T. Baker Chemical) solution was used to increase the pH from acidic (2-3) to basic to form a precipitate in a procedure described by Rhodes [1].

As shown in Table 1, which lists the solubility product constants of the precursor metal hydroxides, the solubilities vary by many orders of magnitude, with iron(III) having the lowest solubility product constant and Cu(II) the highest. In order to minimize segregation of these precipitates during titration, a precalculated quantity of sodium hydroxide (97.6%, Fisher Scientific) or ammonium hydroxide (30% NH_4OH , J. T. Baker Chemical) in solution was added in less than 5 seconds to the solution of nitrates to reach a pH of approximately 8. During and after titration, the solution was stirred (Corning stirrer/hot plate). The pH was monitored using a microprocessor pH meter (Hanna Instruments pH 211). The catalysts titrated with NH_4OH required copper addition during a separate aqueous incipient wetness impregnation step because the

copper cations form ammonium complexes that do not precipitate with the rest of the precursors.

Because the precipitate was difficult to filter if left at this intermediate pH value, the pH was increased to 11 in less than 1 minute by titration. After titration, the catalyst was aged for 1 h with stirring (870 rpm). The brown precipitate was then vacuum filtered and rinsed several times with deionized water to remove soluble anions and cations.

The material was dried for 16 h (overnight) in an oven at 90°C and then calcined in air using an electronic oven (Applied Test Systems 3210 furnace) at 300°C for 5 h to decompose the hydroxides to oxides.

These catalysts were named as function of their weight percentage of oxide content (Fe_2O_3 , Cr_2O_3 , CuO , Al_2O_3) expected after calcination, based on the nominal amounts of precursors used in their preparation. For example, 73Fe-15Al-8Cr-4Cu was prepared to contain 73 wt% Fe_2O_3 , 15 wt% Al_2O_3 , 8 wt% Cr_2O_3 and 4 wt% CuO after calcination in air.

After calcination, the catalysts were crushed and sieved to retain particles with sizes between 125-250 μm . Finer particles were pelletized at 34 MPa (using a Carver press) in a 13 mm evacuable pellet die, crushed, and sieved again until all catalysts were in the desired size range.

The following catalysts were synthesized based on this procedure:

- 88Fe-8Cr-4Cu, used as a reference, prepared using NaOH as precipitation agent;
- 88Fe-8Cr-4Cu, using NH_4OH as precipitation agent;
- 88Fe-8Al-4Cu, where chromia in the reference catalyst was replaced by alumina, prepared using NaOH as precipitation agent;

- 88Fe-8Al-4Cu, prepared using NH_4OH as precipitation agent;
- catalysts with increasing amounts of alumina, designated as 83Fe-5Al-8Cr-4Cu, 78Fe-10Al-8Cr-4Cu, 73Fe-15Al-8Cr-4Cu, and 68Fe-20Al-8Cr-4Cu, prepared using NaOH as precipitation agent;
- 43Fe-50Al-5Cr-2Cu, prepared using NaOH as precipitation agent;
- 43Fe-50Al-5Cr-2Cu(m), obtained by mechanical mixture of the 73Fe-15Al-8Cr-4Cu catalyst with high surface area γ -alumina (Alfa-Aesar, 99.9%, $\sim 220 \text{ m}^2/\text{g}$) to produce a physical mixture with a total of 50 wt% Al_2O_3 .

2.2. BET surface area

Nitrogen physisorption experiments to obtain BET surface area [5] measurements were performed (Micromeritics ASAP 2010).

2.3. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) studies were conducted in a flow microreactor using about 0.05 g (50 mg) catalyst for each sample. Before the TPR, the catalysts were dehydrated and oxidized for 1 h at 300°C in 20 sccm (standard cubic centimeter/minute) of flowing air (US Welding) and N_2 (Ultra High Purity, UHP, US Welding) mixtures with 5% O_2 . The temperature was then decreased to room temperature under flowing nitrogen to prevent moisture from reentering catalyst. Then, 5 vol % H_2 in N_2 , (total flow = 40 sccm), was used to reduce the catalyst. The temperature was increased from room temperature ($\sim 25^\circ\text{C}$) to 800°C at a rate of $10^\circ\text{C}/\text{min}$. The hydrogen concentration in the effluent gas was monitored in real time using a quadrupole mass spectrometer (MKS Cirrus 100).

2.4. EPMA/SEM

Scanning electron microscopy (SEM) with electron probe micro-analyzer (EPMA) were used to obtain chemical compositions of the samples. The EPMA measurements were performed on a JEOL, JXA-8900R WD/ED combined microanalyzer. All of the samples were screened to retain 125-250 μm diameter particles, as used for the kinetic experiments. The samples for EPMA were prepared as thin sections representative of the near surface of the catalysts.

2.5. Kinetic evaluation

The WGS kinetic experiments used the following gases: CO (UHP, Airgas), N₂ (99.998%, US Welding), H₂ (UHP, Messer MG Industries), He (UHP, US Welding), air (H.P., US Welding), and CO₂ (99.99%, US Welding).

The flow rate of each gas was controlled via a mass flow controller (Porter Instruments series 201). Water was supplied by a high pressure pump (Scientific Systems-Lab Alliance Series 1) and vaporized in a coil type vaporizer wrapped in heating tapes. The stainless steel tubing before and after the reactor was heat traced and included thermocouples to monitor the temperature. During all experiments, all heat-traced tubes were maintained at a temperature above the dew point of water to avoid water condensation. The reactor was a 7 mm internal diameter quartz U-tube with a porous frit to support the catalyst. The reactor pressure used for these experiments was atmospheric. Following the reactor, the water vapor was condensed in a water-cooled condenser. The remaining product gases were treated in a desiccant-filled water trap and analyzed by a gas chromatograph (Agilent 6890N) equipped with a packed column (Supelco Carboxen 1000) to separate the H₂, CO, N₂, and CO₂, and a thermal conductivity detector (TCD) to measure the concentrations of the gases.

The catalysts were reduced in situ for 2 h at 400°C in a 125 sccm flow of 20% hydrogen, 30% steam, and 50% N₂. Under these reduction conditions, Fe₃O₄ is the stable phase [2, 8].

Each catalyst (0.1 g) was tested kinetically under water gas shift conditions of 3:1 H₂O:CO volume ratio at a total molar flow rate (H₂O and CO) of 1.24 x 10⁻⁴ mol/s. All were tested for at least 24 h. Most were subjected to extended tests for 100 h at 400°C, followed immediately by 16 h at 500°C to accelerate sintering and to simulate a longer use. The temperature was decreased again to 400°C for comparison with the initial activity. A few experiments were conducted at lower H₂O:CO molar ratios of 2.

Experiments to determine activation energies were conducted at reaction temperatures between 350°C and 425°C. The method of initial rates was used to measure the apparent activation energy of the forward reaction. Reaction rates at four different flow rates (space times) were measured at each temperature. The data were extrapolated to zero space time to approach the limit of zero conversion at which the reverse reaction is negligible. These initial reaction rates were used to determine the apparent activation energy of the forward WGS reaction on these catalysts.

3. Results and Discussion

3.1. BET surface area

Table 2 shows the BET surface areas obtained by nitrogen physisorption of both the unreduced (fresh) catalysts and the used catalysts exposed to WGS reaction conditions for 100 h at 400°C, followed by 16 h at 500°C.

The surface areas of the catalysts dropped significantly after use due to sintering [1, 9, 10]. Comparing 88Fe-8Cr-4Cu with 88Fe-8Al-4Cu before reduction and use, they

have similar surface areas (around 160 m²/g), but after use, the Fe-Cr-Cu catalyst has ~33% higher surface area than Fe-Al-Cu (19.5 m²/g vs. 14.9 m²/g), showing that alumina-containing catalyst (with no chromia) has lower thermal stability. This is consistent with the result reported by Liu *et al.* [14] that alumina could enhance catalyst stability to some extent, but was not as efficient as chromia and is the reason commercial catalysts contain chromia instead of alumina for stability.

When alumina was combined with chromia, the surface area after use increased in the order 83Fe-5Al-8Cr-4Cu, 78Fe-10Al-8Cr-4Cu, 73Fe-15Al-8Cr-4Cu. After reaching maxima for 78Fe-10Al-8Cr-4Cu (fresh) and 73Fe-15Al-8Cr-4Cu (used), the surface area of both the used and unused catalyst 68Fe-20Al-8Cr-4Cu decreased significantly. A value of around 15 wt% alumina enhances the used catalyst surface areas apparently by interaction with the traditional stabilizing component, chromia, because this effect of alumina was not observed for the catalyst without chromia. Beyond ~15 wt% alumina addition, the catalysts have smaller surface areas (and lower activity), possibly because of structural collapse during drying [15, 16, 17].

3.2. TPR

Figure 1 shows the result of the TPR-H₂ experiments for the unreduced (fresh) alumina-containing catalysts, as well as for the reference catalyst that contains no alumina. The figure shows hydrogen consumption spectra for each catalyst in arbitrary units as a function of reduction temperature. The number shown above the first peak is the temperature at the maximum rate of reduction. This peak, near 320°C in each spectra, is attributed to the reduction of Fe₂O₃ (hematite) to Fe₃O₄ (magnetite) [9, 12, 18]. The broad, higher temperature peak centered around 600-700°C is attributed to further

reduction of Fe_3O_4 to FeO [12, 18, 19]. The peak attributed to the reduction of Cr^{6+} to Cr^{3+} (expected near 225°C) [18] and twin peaks associated with reduction of Cu^{2+} to Cu^0 (expected around 150°C) [18] were not observed, which suggests good dispersion of chromia and copper oxides in the structure [6] broadened the peaks and caused them to be below the detection limit of the apparatus. The low concentrations (4 wt%) of CuO in the calcined catalyst also contribute to the difficulty in detecting its reduction peak. The other possible explanation for the absence of these peaks, which is limited or no reduction of these compounds, is unlikely because CuO and Cr_2O_3 are known to reduce at these conditions [18].

In the series the catalysts containing both chromia and alumina, the low temperature reduction peak for the catalyst containing 10 wt% Al_2O_3 is closest to the temperature reported for conventional Fe-Cr-Cu-O catalysts (310°C vs 311°C) [18]. Although the other TPR maxima in this series of catalysts occur at higher temperatures compared to the reference catalyst, alumina addition to the catalysts with chromia produces a broad lower temperature shoulder leading up to the maxima. This shoulder is pronounced in the catalysts with 10 and 15 wt% alumina and indicates an increased quantity of material reducible below 311°C that favorably impacts WGS reaction rates because these two catalysts display the highest activity in this series of catalysts (see Section 3.4). The catalysts containing 10 and 15 wt% alumina also have the lowest peak maxima temperature of the catalysts containing both alumina and chromia.

3.3. EPMA/SEM results

EPMA/SEM was used to determine the chemical composition of the catalysts. The results are shown in Table 3. Previous research has shown that similar oxidized

catalysts contain Fe_2O_3 and Cr_2O_3 as the predominant oxides [2]. Generally, XRD has not been useful in identifying separate CuO and Al_2O_3 phases [9, 14], but the presence of these compounds, as well as Na_2O , have been assumed to interpret the EPMA data in Table 3. The first value in each column shows the target synthesis composition, while the number following in parentheses is the experimentally determined value from EPMA, after converting the measured atomic compositions to the proportional weight % of the corresponding oxides. The measured values for Fe, Cr, Al, and Cu are all slightly less than the target values because of some residual sodium content. The sodium oxide concentration in each catalyst prepared by NaOH titration ranged from ~2 to 4 wt%, despite triple-rinsing with deionized water during filtration to remove the dissolved ions. Quadro et al. [10] reported a similar amount of sodium in similar catalysts precipitated with NaOH. The sodium content did not appear to have a negative long-term effect on catalyst performance, as discussed later in Section 3.4.

Figures 2(a) to 2(d) show the SEM images obtained during the EPMA analysis on the 73Fe-15Al-8Cr-4Cu sample. These representative figures respectively highlight the Fe, Al, Cr, and Cu distribution in the unreduced and unused (fresh) 73Fe-15Al-8Cr-4Cu catalyst after calcination. The images show that Fe, Al, Cr, and Cu are distributed fairly evenly in the catalyst particles, although the Cu shows some agglomeration, as indicated by the bright islands visible in some areas of the particles.

3.4. Kinetic results

3.4.1 Impact of alumina addition

One catalyst in which alumina completely replaced chromia was synthesized to investigate the relative effects of these two components in the magnetite-based high

temperature WGS catalysts. The catalyst without chromia was compared with a typical high temperature WGS catalyst prepared with 88 wt% Fe_2O_3 -8 wt% Cr_2O_3 -4 wt% CuO (88Fe-8Cr-4Cu). This fresh catalyst had a slightly smaller initial surface area ($158 \text{ m}^2/\text{g}$ vs. $166 \text{ m}^2/\text{g}$) and a significantly smaller final surface area after use ($14.9 \text{ m}^2/\text{g}$ vs $19.5 \text{ m}^2/\text{g}$) compared with chromia-containing catalyst. The rates of both catalysts under WGS conditions during an extended 120 h experiment are shown in Figure 3. The y axis is the specific reaction rate (rate of CO converted (mol/s) per gram of catalyst), while the x axis is the runtime of the experiment.

This experiment confirmed the previous result of Araujo and Carmo Rangel [9] that alumina cannot effectively replace chromia in these magnetite-based catalysts. Therefore alumina was included in addition to a base amount of chromia in a series of catalysts (i.e., the alumina was added at the expense of the iron content in the catalyst in 5 wt% increments up to 20 wt% alumina). Each catalyst was tested under the same conditions as described for Figure 3.

The activity results for these catalysts are shown in Figure 4, along with the reference catalyst that contained no alumina. The catalyst with 5 wt% alumina (the triangular data points in Figure 4) produced slightly higher rates relative to the catalyst with only alumina (shown in Figure 3), but was worse than the reference catalyst with chromia but no added alumina (the diamond data points in Figure 4). Although the 5 wt% alumina catalyst initial surface area was $140 \text{ m}^2/\text{g}$ compared with $166 \text{ m}^2/\text{g}$ for the catalyst with no alumina, the surface area of the used catalyst, tested under the same conditions, was $22.5 \text{ m}^2/\text{g}$ compared with $19.5 \text{ m}^2/\text{g}$, which shows that alumina provides

higher thermal stability through increased resistance to sintering [9, 14]. The rate at the end of the experiment was similar for both catalysts.

In Figure 4, the WGS rate of the catalysts decreased in the order: 73Fe-15Al-8Cr-4Cu > 78Fe-10Al-8Cr-4Cu > 88Fe-8Cr-4Cu > 83Fe-5Al-8Cr-4Cu > 88Fe-8Al-4Cu > 68Fe-20Al-8Cr-4Cu, which is approximately in the order of their surface area (see Table 2). High temperature WGS reaction occurs on the surfaces of iron oxide (magnetite) domains [1]. Therefore, higher surface areas make more active sites available for the water gas shift reaction, which produces higher catalytic activity. At the end of the experiment, the catalyst that produced the highest rates and had the highest thermal stability, as determined by its surface area after use, contained 15 wt% alumina.

Up to a value of approximately 15 wt% alumina addition at the expense of the active iron compound, alumina enhances the used catalyst surface areas apparently by interaction with the traditional stabilizing component, chromia. Beyond 15 wt% alumina addition, the catalysts have smaller surface areas, possibly because of structural collapse due to higher aluminum hydroxide content that might increase the fragility of the three dimensional structures generated during drying [15, 16, 17]. Another factor in the decreased activity is the reduction in iron oxide content, which is the active phase [1, 2]. However, this loss of iron content is counterbalanced by the synergetic activity of the added alumina for the catalysts containing 10 and 15 wt%, since the rate for both of these catalysts increases relative to the other catalysts that contain more iron. This effect is not merely a simple increase in surface area, as the rate increases exceed the proportional increase in surface area. This observation clearly shows that the loss of iron is not by itself responsible for the poor performance of the catalyst with 20 wt% alumina. The

formation of aluminate compounds with the other catalyst components [20] that appear to be inactive for WGS reactions is also a possible explanation for the observed decrease in activity for the 20 wt% alumina catalyst.

This sharp decrease in rate for the catalyst with 20 wt% alumina was investigated through two experiments with catalysts containing larger amounts (50 wt%) of alumina with nominal compositions of 43Fe-50Al-5Cr-2Cu. One was prepared as a mechanical mixture of the most active catalyst (73Fe-15Al-8Cr-4Cu) with sufficient γ -alumina to produce a physical mixture with 50 total wt% Al_2O_3 , identified as 43Fe-50Al-5Cr-2Cu(m). The other was prepared by coprecipitation with a nominal composition of 50 wt% alumina (43Fe-50Al-5Cr-2Cu).

Both catalysts were tested kinetically under the same water gas shift conditions as the other catalysts. The results of these two experiments are illustrated in Figure 5, along with the 73Fe-15Al-8Cr-4Cu catalyst for comparison. Although the catalyst prepared by coprecipitation (triangles, Figure 5) has higher initial activity compared to the physical mixture catalyst (filled circles, Figure 5), it exhibits low thermal stability and rapid deactivation, possibly due to formation of $\text{FeO-Al}_2\text{O}_3$ iron aluminate [20]. Compared to the 73Fe-15Al-8Cr-4Cu catalyst (open circles, Figure 5) used to make the physical mixture, the rate produced by the physical mixture is roughly 40% lower, consistent with the amount of inert alumina added, as experiments with pure alumina produced no detectable reaction. The physical mixture has higher activity and thermal stability than the the co-precipitated catalyst with 50 wt% alumina, which suggests that an iron aluminate compound only forms to an appreciable extent when the components are in atomic proximity, as expected during the coprecipitation synthesis. The catalysts appear

to be stable during simple interfacial contact with alumina, but not under mixing at an atomic or very small crystallite scales.

Although XRD and SEM data on these catalyst samples were desirable, unfortunately they are unavailable (see endnote), but literature results can be used to interpret the data. The effect of alumina addition to iron oxide-chromia based catalysts can be interpreted based on surface and bulk diffusion of atoms and ions in solids, correlated to the Tammann and Huttig temperatures [8]. The Tammann temperature (T_T) is conventionally defined as $0.5T_m$, where T_m is the absolute melting point of the material. At T_T , ions within the bulk of the solid are generally considered to be sufficiently mobile for bulk diffusion. The Huttig temperature (T_H) is conventionally defined as $0.3T_m$, at which surface species have sufficient mobility to begin to agglomerate and sinter.

The Tammann temperatures for the pure oxides [8, 20] are ~ 1302 K (1029°C) for Cr_2O_3 , ~ 935 K (662°C) for Fe_3O_4 , and ~ 1152 K (879°C) for Al_2O_3 , which are all above the reaction temperature of 350 - 500°C . This likely explains why the mechanically mixed catalyst showed good thermal stability, as no bulk diffusion is expected.

The Huttig temperatures for the same oxides [8, 20] are ~ 868 K (595°C) for Cr_2O_3 , ~ 623 K (350°C) for Fe_3O_4 , and ~ 768 K (495°C) for Al_2O_3 . Therefore, iron will be the most mobile surface species at the reaction temperatures of this study (350 - 500°C). Thus, for oxides mixed at an atomic or very small crystallite scales, the catalyst is expected to be less thermally stable compared with the mechanical mixed one. This analysis is complicated by the possibility of solid solution formation [3, 8, 9, 20] because the ionic radii of Cr^{3+} (0.0755 nm) and Al^{3+} (0.0675 nm [3]) are close to Fe^{3+} (0.069 nm) [3]. Examination of the ternary phase diagram for FeO - Fe_2O_3 - Al_2O_3 [20] suggests the

possibility of formation of FeO-Al₂O₃ iron aluminate spinel (hercynite), which is stable below 2053 K (1780°C).

Alumina and the possible formation of aluminates apparently act as a physical barrier for the movement of iron, thus reducing the loss of surface area which in the magnetite based catalysts has been shown to occur by sintering [1, 9, 10]. However, alumina contents greater than ~15 wt% appear to react with the other catalyst components to form compounds that are inactive for WGS.

3.4.2 Impact of synthesis method on kinetic performance

Some of the catalysts in this study were prepared by co-precipitation using either NaOH or NH₄OH as the titrating agent. The target and actual (determined by EPMA) compositions of the reference catalyst and the catalyst without chromia prepared by the two methods are shown in Table 3. The catalysts prepared by different methods have nearly the same chemical composition, with the exception of the small amount of sodium in the catalysts prepared using NaOH titration. However, the activity and stability are significantly different.

Catalysts prepared by with NH₄OH titrations that required Cu addition during a subsequent incipient wetness impregnation step showed high initial activity, but their deactivation during operation was larger than for the catalysts prepared in a single step by NaOH titration. For example, the initial rate produced by the 88Fe-8Cr-4Cu catalyst was more than double that of the similar catalyst prepared by NaOH titration (results presented later in Table 8). However, after 100 h of operation at 400°C and 16 h at 500°C, the catalyst prepared with NH₄OH produced only 71% of the rate of the one prepared with NaOH. By the two-step synthesis when the copper is added in a second

step, copper is further concentrated near the surface of the catalysts, as shown by the larger amount measured by EPMA (4.5 wt% versus 3.7 wt% CuO for the 88Fe-8Cr-4Cu catalysts prepared by NH_4OH and NaOH titration, respectively, in Table 3). The 88Fe-8Cr-4Cu catalyst prepared by NH_4OH titration shows high initial activity, but it is prone to sintering during operation. With sintering of the copper, the catalysts lose activity. The copper concentration from EPMA after WGS operation for the 88Fe-8Cr-4Cu catalysts at 9 different points on the surface is shown in Table 4. Consistent with the EMPA data in Table 3, the multiple-location data in Table 4 show that the average copper concentrations are 22% larger in the NH_4OH titrated catalysts than the NaOH titrated catalysts, which suggests that formation of larger copper crystallites with proportionally fewer accessible surface atoms are responsible for the rapid rate decline on the NaOH titrated catalysts.

The data in Table 4 also show that the copper in the catalysts prepared by NH_4OH titration is not evenly distributed after use, which further suggests that the copper particles have agglomerated into large crystallites. The standard deviations of the copper compositions (0.20 for the catalyst prepared with NaOH versus 0.93 for the catalyst prepared with NH_4OH) indicate that there is much larger variability among the copper concentrations for the catalyst prepared with NH_4OH , which is consistent with sintering to form some large copper particles at the expense of other areas of the surface. Thus, some areas of the surface have high concentrations of large copper crystallites, while other areas of the surface are depleted in copper. A catalyst with less exposed copper surface area, due to agglomeration into larger copper particles, is expected to produce lower WGS reaction rates, which is consistent with the observed results.

3.5. Reaction temperature sensitivity: activation energies

WGS conversions for the series of alumina-containing catalysts (with 20 wt% or less alumina) at 350°C, 375°C, 400°C, and 425°C are shown in Table 5 and in Figure 6. Also shown in Figure 6 is the calculated value of the equilibrium conversion at the reaction conditions. The rates of all catalysts increased with increasing temperature, consistent with an Arrhenius-type dependence. Cinchen et al. [21] measured 8.5 mm diameter HT-WGS industrial pellets and observed diffusion limitations which influenced the measurements. For smaller particles, Rhodes and Hutchings [6] found that activation energy was independent of particle size for particles between 100 μm and 1000 μm , suggesting that mass transfer and diffusion are not limiting for these small particles at reaction conditions similar to those applied in the experiments presented here. Consistent with these reported results, diffusional limitations were not observed for particles with diameters of 125-250 μm used in the present study, which permitted the measurement of apparent activation energies. Arrhenius plots for the HT water gas shift catalysts are shown in Figure 7, which contains data for initial WGS reaction rates at zero space time. The activation energies determined from the data in Figure 7 are summarized in Table 6. All catalysts with alumina have lower apparent activation energies values compared with the value of 90.5 kJ/mol obtained for the reference catalyst, 88Fe-8Cr-4Cu. The decrease in the value of activation energies with increasing alumina addition suggests that alumina plays more than merely as a textural support that increases surface area, but is actually involved in the catalysis. The modification of the catalysis could be due to an electronic modification of the iron domains, making them more reducible, as suggested by the TPR results (see Figure 1), and consistent with some reports that have suggested that the WGS

mechanism on iron-based catalysts proceeds via an oxidation-reduction cycle [1, 11, 14]. The lowest absolute value of activation energy ($E_A = 65.9$ kJ/mol) obtained for 68Fe-20Al-8Cr-4Cu appears to be offset by the lower iron oxide concentration, by the presumed loss of some magnetite to formation of inactive compounds such as iron aluminates, and by the significant loss of surface area during reaction (as only ~ 10 m²/g remained after use, see Table 2). The most active catalyst, 78Fe-15Al-8Cr-4Cu, has a comparable activation energy ($E_A = 68.6$ kJ/mol), a larger iron content, and the highest surface area (38 m²/g) after use.

The activation energy measurements, which involved varying the reaction temperature in the range 350-425°C, were performed after 50 h of WGS reaction at 400°C. After these experiments, the rate was again measured at 400°C and compared with the rate at 400°C after 50 h. No significant decrease in catalytic activity was observed over the time scale of the activation energy experiments. Therefore, the presented activation energy results were not significantly influenced by deactivation.

3.6. Catalyst stability

3.6.1 Resistance to over-reduction

The catalytic activity of the series of alumina-containing catalysts (with 20 wt% or less alumina) at H₂O:CO of 2 is given in Table 7. The same trends are observed as described previously for the catalysts at H₂O:CO of 3. The GC column used in these experiments is capable of methane separation. No methane was detected during any experiment. Therefore, no detectable methanation reaction (which is catalyzed by metallic iron [1]) occurred, which indicates these catalysts are not susceptible to over-reduction to metallic iron.

3.6.2 Thermal stability

The catalysts were tested for 100 h at 400°C, followed by a 16 h period at 500°C to simulate a longer use, followed by a final reaction period at 400°C to compare with the rates at 400°C. When exposed to the 500°C reaction temperature, the catalysts deactivated rapidly as shown in Figures 4 and 5 and quantified in Table 8, which shows these relative rates for the series of alumina-containing catalysts.

The data in Table 8 confirm that 73Fe-15Al-8Cr-4Cu catalyst produced the highest final rate, indicating that it had the highest thermal stability after 16 hours of operation at 500°C, retaining approximately 70% of the activity it had at 100 h. This compares to less than 67% the next most stable catalyst (83Fe-5Al-8Cr-4Cu). Also, this rate is nearly 2 times higher than the reference catalyst (88Fe-8Cr-4Cu) prepared by NaOH titration, which highlights the thermal stability provided by addition of small amounts of alumina.

4. Conclusions

Alumina addition to conventional high temperature water gas shift catalysts at concentrations of approximately 15 wt% increases CO conversion rates and increases thermal stability. If the alumina replaces the chromia content of the catalyst, the surface area after use is only 74% of the surface area of the comparable Fe-Cr-Cu catalyst. Hence, alumina alone cannot effectively stabilize Fe₃O₄.

When alumina is combined with chromia, varying effects were observed on the HT water gas shift catalysts. For the fresh unreduced catalysts, catalysts with both chromia and 10-15 wt% alumina have high fresh surface areas (over 200 m²/g) that are 20-30% higher than the catalyst without alumina. The surface area increase is larger than

the proportional effect expected for the small amounts of alumina added. This suggests that the added alumina has an added structural effect on the other catalyst components. After use, these two catalysts retain higher surface areas (33.4 m²/g and 38.4 m²/g) compared to the other catalysts. Even the catalyst with the least amount of alumina, 83Fe-5Al-8Cr-4Cu, retained a surface area of 22.5 m²/g after use, which is higher than the reference Fe-Cr-Cu catalyst at 19.5 m²/g. Thus, alumina in Fe-Al-Cr-Cu catalysts significantly increase surface areas, especially for the used catalysts, indicating that thermal stability is also improved.

In the series of alumina-containing HT-WGS catalysts in this study, the optimum quantity of alumina addition is ~15 wt% (73Fe-15Al-8Cr-4Cu). This catalyst produced a CO conversion rate that was 73.8 % larger than the reference catalyst with no alumina (88Fe-8Cr-4Cu) at similar reaction conditions.

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Endnote

During a laboratory move, all catalyst samples, both fresh and used, were inadvertently discarded by a third party before desired additional XRD and SEM characterizations could be performed.

5. References

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