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Investigation of Hydrogen Reactivity and Its Use as a Surface Probe on High Surface Area Copper–Chromium–Silver Impregnated Charcoal

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ASC whetlerite is a copper/chromium/silver impregnated, activated charcoal which is used effectively to remove and hydrolyze vapor contaminants from gas streams. Its catalytic activity is known to decrease as the chromium oxidation state is reduced from +6 to +3. A thermal treatment process was used to systematically reduce the Cr(+6) species to Cr(+3)-containing species and a pulse technique was developed to nondestructively quantify this reduction using hydrogen. The data illustrated that hydrogen uptake can be correlated with the oxidation state(s) of the chromium metal impregnant. In addition, total uptake of hydrogen was determined in a static adsorption system. These data showed that total hydrogen uptake was independent of the oxidation state of chromium on the charcoal surface and was much greater than a one-to-one relationship between metal atoms and hydrogen atoms. These results suggested that hydrogen molecules are adsorbed and dissociated by the Cr(+3)-containing species and then diffuse away from the "Cr(+3) centers" to the activated charcoal support. Finally, the hydrogen pulse results together with ESCA data indicated that the deactivation of whetlerite involves not only the reduction of chromium, but most likely also the separation of the chromium/copper impregnants.

INTRODUCTION

Charcoals impregnated with copper, chromium, and silver salts (e.g., "whetlerites") have been used quite effectively in air purification systems. These high surface area charcoals adsorb both light as well as heavy vapors. The impregnants act to both react with, and catalytically hydrolyze many vapors to less toxic gases. These adsorbant/reactant/catalytic systems are very difficult to quantitatively analyze. However, it is known that these materials become less catalytically effective when the oxidation state of the chromium is reduced from +6 to +3. The deactivation occurs under a number of conditions: exposure to high temperatures, exposure to high humidities, or over periods of extended use. This investigation was undertaken to develop a rapid, nondestructive method to quantify deactivation due to extremes in temperature, and in the process to obtain a better understanding of the deactivation mechanism.

EXPERIMENTAL

Steam-activated, impregnated charcoal (ASC whetlerite) was supplied by Calgon Corporation. It was prepared by the impregnation of CWS grade charcoal with ammoniacal carbonate solutions of copper (Cu(II)), chromium (Cr(VI)), and some silver salts (*1*). The percentages by weight of the metal constituents reported in (*1*) and measured by wet-chemistry techniques were as follows: copper = 8%, chromium = 2.8%, and silver = 0.2%. The charcoal granule size was 12 to 30 mesh (U.S. Standard Sieve) and the BET surface area as determined using a nitrogen adsorbate was 650 m^2/g.

(*a*) *Whetlerite Characterization*

Conventional wet-chemistry techniques

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were used for the bulk analysis of copper and chromium ions contained on ASC whetlerite charcoal. A series of extractions with either acidic and/or basic solvents were used to bring Cu(+2), Cu(+1,0), Cr(+6), and Cr(+3) ions into solution. Ammonium hydroxide was used first to bring Cu(+2) and Cr(+6) species into solution. The residue from this extraction was then treated with a 1:1 mixture of perchloric and nitric acid. The acid mixture brought the lower oxidation state species (i.e., Cr(+3) and Cu(+1,0)) into solution by oxidizing them to Cr(+6) and Cu(+2) compounds. All solutions were then analyzed quantitatively by atomic absorption spectrophotometry. Since the absorbance of the chromate ion was shown to be a function of solution pH (*2*), a sodium acetate–acetic acid buffer was used to keep the solutions at pH 3. Details of this procedure have been presented in (*3*).

Electron spectroscopy for chemical analysis (ESCA) was used to monitor the concentrations and oxidation states of copper and chromium species at the charcoal surface (i.e., 20–40 Å probe depth). The ESCA work was done at the Institute of Materials Science of the University of Connecticut. The samples were prepared by pressing powders (<180 μm) into indium foil for introduction into the instrument. The Cu $2p_{3/2}$/Cu L3VV peaks were used to monitor the chemical state of the copper species. The Cr L3M23 Auger peak, generally used for determining the chemical state of chromium, was obscured by interferences from O KL23L23, Fe $2p$, and In $3p_{1/2}$ peaks. Thus, a higher resolution setting on the spectrometer was used to collect data on the Cr L3M23M23 Auger and on the Cr $2p_{1/2}$, $2p_{3/2}$ peaks. A least-squares fitting of Gaussian/Lorentzian peaks to a fresh whetlerite sample and a sample thermally treated at 490 K (maximum pretreatment temperature) was completed.

A JEOL 100 C transmission electron microscope was used to observe the nature of the metal impregnants on the charcoal support. The bright field image of all samples was observed in the conventional TEM mode (100 kV excitation). Whetlerite samples were prepared for microscopy by first grinding with a mortar and pestle to a fine powder (<50 μm), drying for 1 h at 378 K, then sprinkling the powder onto holey carbon support grids.

(*b*) *Pulse Reactor and Static Adsorption Studies*

Hydrogen has been reported to adsorb (*4–8*) and in some cases dissociate (*9–12*) on chromium-impregnated catalysts. It has been hypothesized by several investigators (*9, 10, 12, 13*) that chromium in the +3 oxidation state is the adsorption/dissociation site. Thus, it was proposed that small pulses of hydrogen injected into a whetlerite bed could quantify the degree of Cr(+6) to Cr(+3) conversion (deactivation). That is, to use small pulses of hydrogen to quantify the number of Cr(+3) sites.

Typically, 2.2 g whetlerite was packed into each of several stainless-steel tubes (20 cm long, 18 cm packed; 0.508 cm i.d.). These packed tubes were connected in a gas chromatograph oven as chromatographic columns and were heat-treated for 6 h in an inert nitrogen carrier gas stream (flow rate: 30 ml/min, NTP). Thermal treatment temperatures from 303 to 490 K were used to attain desired levels of Cr(+6) to Cr(+3) conversion; above this temperature oxidation of the charcoal support became more severe (i.e., only 3% weight loss at 490 K versus 10% weight loss at 580 K). Following the thermal treatment process, the whetlerite was analyzed for changes in copper and chromium oxidation states, variations in impregnant size and morphology, and hydrogen uptake in both a pulse reactor system and a static adsorption apparatus.

The hydrogen uptake by whetlerite in the pulse reactor system (Perkin–Elmer Sigma 1) was determined using 20-cm whetlerite-packed stainless-steel tubes (Fig. 1). A van Deemter analysis (*14*) on fresh, nonreactive

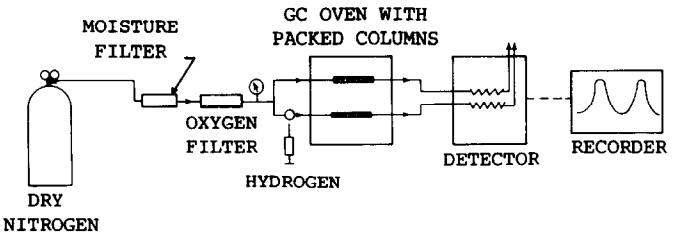


FIG. 1. Experimental apparatus for pulse reactor studies.

whetlerite indicated a carrier gas flow rate of between 10 and 20 ml/min (NTP) was optimum. A value of 10 ml/min (NTP) was generally used and 0.1-ml (NTP) hydrogen pulses were injected every 4 min. The area response was monitored by a hot-wire detector. For most experiments, the hydrogen uptake was monitored at 303 K. However, uptake data were also collected at 323, 343, and 363 K so that the activation energy for the interaction between hydrogen and the whetlerite could be determined.

Total hydrogen uptake by ASC whetlerite was determined gravimetrically in a constant volume and pressure system. The experimental procedure is a standard one and is reported by Wu *et al.* (*15*). Each adsorption/uptake run was repeated three times to ensure reproducibility of the data. In addition, each sample following hydrogen exposure was reevacuated at 378 K for 2 h and the adsorption run was repeated such that the extent of reversibility could be determined.

RESULTS

The results of the heat treatment process are shown in Figs. 2 and 3. Figure 2 illustrates the behavior of the Cr(+6)/Cr(+3) ratio in whetlerite (determined by wet-chemistry techniques) as a function of thermal treatment temperature. There is a sharp decrease in this ratio as the treatment temperature is increased indicating that the hexavalent chromium species is reduced. The fresh, untreated whetlerite has a Cr(+6)/Cr(+3) ratio of about 48; however, this ratio decreases to a value of about 7 for whetlerite thermally treated at 490 K. This represents a sevenfold increase in Cr(+3) content. The data of Fig. 3 show that the Cu(+2)/Cu(+1,0) ratio in the whetlerite assumes values between 5.5 and 6.0 and does

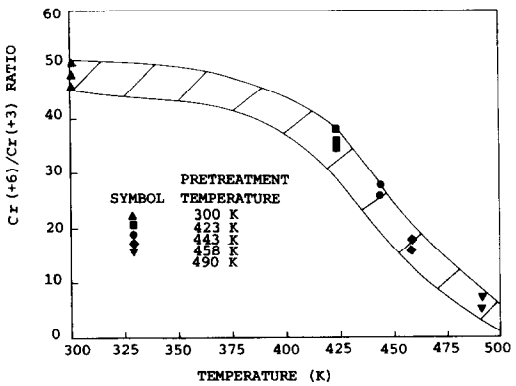


FIG. 2. Cr(+6)/Cr(+3) ratio versus thermal pretreatment temperature.

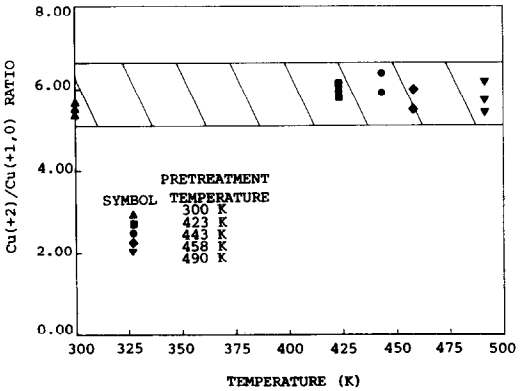


FIG. 3. Cu(+2)/Cu(+1,0) ratio versus thermal pretreatment temperature.

TABLE 1

ESCA Surface Content Data for ASC Whetlerite Samples

Sample	[Cu][a]	[Cr]	[O]	[C]	[Si][b]	[Fe][b]	[Ag][c]
Fresh whetlerite	7.73	2.71	17.07	100	1.92	0.51	—
443 K pretreatment	6.46	2.43	17.33	100	3.11	—	—
490 K pretreatment	4.65	2.49	19.73	100	2.86	1.11	—

[a] Contents are relative to 100 g carbon.
[b] Small amounts of SiO_2 and Fe_2O_3 are found on the charcoal support.
[c] Silver was not detected on these commercial whetlerites.

not vary with heat treatment. Thus, the copper species remains in the Cu(+2) form while the Cr(+6) species is being reduced by the thermal treatment.

The ESCA results are in excellent agreement with the data obtained by the wet-chemistry analysis. Relative ESCA surface contents are summarized in Table 1. The results are based on 100 g of carbon. The fresh whetlerite data confirm that the copper-to-chromium ratio at the surface is approximately 2.9 : 1. This value is the same as that determined for the bulk copper-to-chromium ratio (i.e., 8.0 : 2.8 or 2.9 : 1). There does appear to be a significant change in the surface copper-to-chromium ratio as the whetlerite treatment temperature is raised, however. The ratio decreases suggesting that the whetlerite surface either becomes depleted in copper or that large copper crystallites are forming.

An analysis of the Cu $2p_{3/2}$/Cu L3VV peaks suggests that the copper species exists in both the CuO and $CuCO_3$ forms for all whetlerite samples examined. This result supports our earlier finding that the copper species remains in the divalent oxidation state. The chemical state of chromium was more difficult to ascertain due to interferences from oxygen, iron, and the indium foil. A least-squares fitting of the Cr $2p_{3/2}$ peaks provided the data shown in Table 2. The Cr(+6)/Cr(+3) ratios exhibit the same behavior at the whetlerite surface as they do in the bulk. As seen from Fig. 2, the chromium ion ratio for fresh whetlerite compared to 490 K-treated whetlerite is about 48 : 7 or 6.9 : 1. The ESCA data confirm that this ratio is essentially the same (i.e., 6 : 1) at the surface of the whetlerite. Curve fitting was not done for the 443 K-treated sample. However, its Cr $2p$ peak envelope had a shape intermediate between that of the fresh sample and the 490 K-treated sample. This result suggested that the relative concentrations of Cr(+6) and Cr(+3) are intermediate also and in agreement with the data of Fig. 2.

(a) Pulse Reactor Studies

Typical hydrogen uptake data from the pulse reactor system are presented in Fig. 4. The gas chromatographic area response is plotted for a series of twenty 0.1-ml (NTP) hydrogen pulses injected into thermally treated whetlerite packed columns. Three experimental runs are depicted in Fig. 4. A complete set of data covering thermal treatment temperatures from 423 to 490 K using pulse temperatures between 303 and 363 K is listed in Table 3.

TABLE 2

Analysis of the Cr $2p_{3/2}$ Peaks in ASC Whetlerite Samples

Sample	Cr(+3) peak position (eV)	Cr(+6) peak position (eV)	Cr(+3) peak area	Cr(+6) peak area	[Cr(+6)]/[Cr(+3)]
Fresh whetlerite	576.05 (1.94)[a]	578.24 (2.94)[a]	27,598	111,417	4.04[b]
490 K pretreatment	576.02 (2.38)	578.04 (2.93)	70,682	47,620	0.67

[a] Full width of peak at half-maximum height (FWHM).
[b] Relative [Cr(+6)]/[Cr(+3)] ratios.

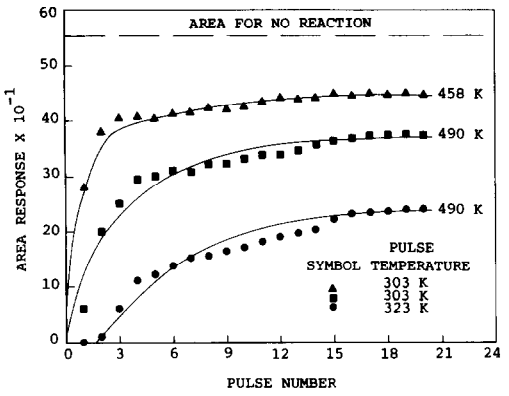


FIG. 4. Gas chromatographic area response versus pulse number.

The dashed line in Fig. 4 represents the area response for no hydrogen uptake. This value (550 units) was determined by injecting hydrogen pulses into an empty (unpacked) column and a column packed with fresh, untreated whetlerite. In both cases an area response of 550 units was obtained. The uppermost curve is for whetlerite treated at 458 K and pulsed at 303 K. The middle and bottom curves represent 490 K-treated whetlerite pulsed at 303 and 323 K, respectively. Each of these curves exhibits similar behavior; when the first hydrogen pulse is injected the uptake by whetlerite is quite large. However, when subsequent pulses are injected the amount of hydrogen taken up decreases until a constant value is reached. (This constant value of uptake per pulse was determined to be stable up to several hundred pulses. Total hydrogen uptake data indicate that approximately 5×10^5 pulses are required to completely "saturate" the surface.) The area response once the "steady state" has been attained is still substantially below the area obtained if no hydrogen was interacting with the whetlerite. The higher hydrogen uptake during the initial portion of the pulse experiments was thought to be a result of hydrogen reacting with highly active surface oxides on the charcoal support. This assumption was enhanced when it was determined that the magnitude of the initial uptake was reduced considerably when an oxygen trap was installed in the carrier gas line.

TABLE 3

Hydrogen Uptake by Whetlerite Samples as a Function of Pretreatment Temperature and Pulse Temperature

Pretreatment temperature (K)	Pulse temperature (K)	$\frac{Cu(+2)^a}{Cu(+1,0)}$	$\frac{Cr(+6)^a}{Cr(+3)}$	% Hydrogen uptake[b]
423	303	6.0	35.6	2.5
423	323	5.6	38.5	5.4
423	343	5.8	36.2	10.0
423	363	5.8	36.6	25.0
443	303	5.7	27.9	9.6
443	323	5.7	27.3	15.5
443	343	5.8	29.0	29.6
443	363	5.7	28.4	56.2
458	303	5.6	19.2	12.6
458	323	5.4	19.6	30.0
458	343	5.9	18.7	Not available
458	363	5.9	18.8	Not available
490	303	6.1	6.5	33.0
490	323	5.9	4.3	53.2
490	343	5.8	5.8	67.5
490	363	6.0	6.1	91.5

[a] Neither the Cu(+2) nor Cr(+6) species was reduced by the injection of hydrogen at these pulse temperatures.
[b] Percentage of the 0.1-ml pulse taken up at the "steady state."

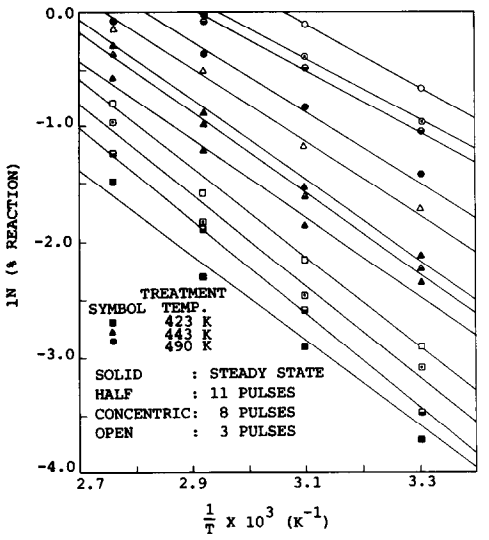


FIG. 5. Arrhenius plot for the pulse reactor experiments.

The data of Fig. 4 also show that the uptake of hydrogen increases as both the pulse temperature and the thermal treatment temperature increase. The fraction of the hydrogen pulse taken up in the whetlerite-packed columns as a function of pulsing temperature was used to construct the Arrhenius plot shown in Fig. 5. Fractional uptake or percentage reaction (fractional uptake × 100) was determined using the equation

$$\text{fractional uptake} = \frac{550 - A_c}{550}$$

where A_c is the area response once the "steady state" has been reached (550 units is the area response for no reaction of hydrogen). The relevant activation energy data (determined for both the initial and steady-state portions of the area response versus pulse number curve) are presented in Table 4. All activation energies are in the range between 5 to 8 kcal/mole.

The enhanced hydrogen uptake exhibited by whetlerite thermally treated at high temperatures (but pulsed at 303 K) is of significance in this investigation. It was established (Fig. 2 and Table 2) that the Cr(+6)/Cr(+3) ratio in whetlerite decreased as the thermal treatment temperature increased. Thus, these data suggest (Fig. 4) that the hydrogen interacts with a Cr(+3)-containing species on the whetlerite in agreement with the work of Groeneveld *et al.* (*9*), Wittgen *et al.* (*10*), and Stone and Vickerman (*12, 13*).

(*b*) *Static Adsorption Studies*

The total amounts of hydrogen taken up by whetlerite, determined using the static adsorption apparatus, are reported in Table 5 and plotted in Fig. 7. The data show that the amount of hydrogen taken up per unit weight of whetlerite at 303 K is constant and independent of the heat treatment temperature. The data also suggest that the hydrogen uptake is repeatable. That is, the product(s) of hydrogen adsorption can be removed by heating to 378 K under vacuum, then the adsorption isotherm can be reproduced upon reexposure to hydrogen. The actual amount of hydrogen taken up is quite large (i.e., two to three orders of magnitude greater than the Cr(+3) content on an atom basis), suggesting that the charcoal support acts as a reservoir for hydrogen atoms.

DISCUSSION

The curves of Fig. 6 show that a quantitative relationship exists between the fractional hydrogen uptake and the Cr(+6)/

TABLE 4

Activation Energies for Hydrogen Uptake by ASC Whetlerite Samples

Determined at pulse number	Thermal pretreatment temperature		
	423 K	443 K	490 K
	E_a (kcal/mole)		
3	7.6	5.7	5.4
8	7.9	6.6	5.3
11	7.8	6.7	5.0
Steady state	7.5	6.5	5.2

TABLE 5

Hydrogen Uptake by ASC Whetlerite Samples[a]

Sample	Weight (mg)	Hydrogen uptake (mg)	mg hydrogen/mg whetlerite
		Total uptake	
490 K pretreatment	21.07	1.110	0.053
	19.83	1.036	0.052
	16.64	0.936	0.056
443 K pretreatment	17.34	1.000	0.058
	16.50	0.980	0.059
	13.50	0.792	0.058
Fresh whetlerite	17.07	0.900	0.053
	19.15	0.986	0.052
	18.37	1.012	0.055

Sample	Weight (mg)	First uptake (mg)	Second uptake (mg)	Third uptake (mg)	Average uptake (mg)	mg hydrogen / mg whetlerite
			Repeated uptake			
490 K pretreatment	21.07	1.110	1.230	1.115	1.152	0.055
443 K pretreatment	17.34	1.000	0.950	0.996	0.982	0.057
Fresh whetlerite	17.07	0.900	0.925	0.913	0.913	0.054

[a] Determined in the static adsorption system at 303 K.

Cr(+3) ratio for thermally treated whetlerite. As the Cr(+6)/Cr(+3) ratio decreases the fractional uptake of hydrogen increases, suggesting that hydrogen "interacts" with a Cr(+3)-containing species on the whetlerite. A Cr_2O_3-type species is proposed to be the active component for hydrogen uptake. Chromic oxide is the most stable of the chromic species; also, Cr_2O_3 has been identified by Schwartz *et al.* (*16*) as a thermal decomposition product of CrO_3 (chromium is impregnated on the charcoal as CrO_3). In addition, Cr(+3)-containing catalysts have been reported (*4–8*) to adsorb hydrogen readily over a wide range of temperatures. Also, Cr_2O_3 and supported Cr_2O_3 catalysts prepared by the reduction of CrO_3 impregnated on a support have been used extensively in reactions involving the adsorption and dissociation of hydrogen such as hydrogenation of olefins (*9, 10*), hydrogen–deuterium exchange (*11, 13*), and dehydrogenation of hydrocarbons (*17, 18*). Finally, chromium in the +3 oxidation state has been identified on whetlerite exposed to various types of deactivating conditions: exposure to cyanogen chloride (*1, 19, 20*), treatment at high temperatures (*21*), and exposure to both high temperatures and high humidities (*22, 23*).

Activation energies for adsorption on chromia catalysts have been reported to fall

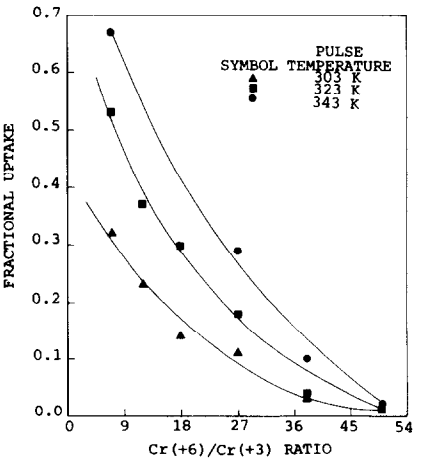


FIG. 6. Fractional hydrogen uptake versus Cr(+6)/Cr(+3)/ratio.

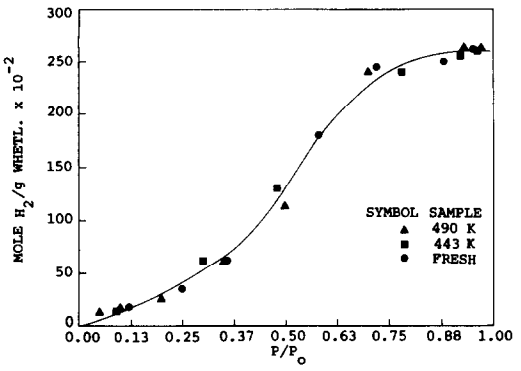


FIG. 7. Moles of hydrogen taken up per gram of whetlerite (at 303 K) versus partial pressure.

in the range of 0–21 kcal/mole depending on adsorption temperature (*4, 5*). A value of 10 kcal/mole was reported by Burwell and Taylor (*5*) for hydrogen adsorption and dissociation on amorphous chromia at 348 K. The activation energies obtained in this investigation at temperatures between 303 and 363 K were 5–8 kcal/mole. The activation energy did not vary with pretreatment temperature nor with pulse number (Table 4). This result suggested that the rate-determining step for hydrogen on whetlerite in the pulse experiments is most likely the adsorption and dissociation of hydrogen molecules by Cr_2O_3-type species. Stone and Vickerman (*13*) found a similar result for the low-temperature H_2–D_2 exchange reaction. They studied a series of chromia/α-alumina catalysts containing varying amounts of chromia for H–D exchange over the temperature range from 100 to 700 K. They determined that the rate-limiting step in their work was also the dissociation of hydrogen molecules by Cr(+3).

The total hydrogen uptake data obtained from the static adsorption experiments show that the amount of hydrogen taken up by the whetlerite, unlike the amount taken up by the pulse reactors, is independent of the Cr(+3) content of the whetlerite. The average amount of hydrogen taken up per gram of whetlerite (Table 5 and Fig. 7) is 0.028 mole/g or 3.37×10^{22} atoms/g. Similar values have been obtained for active carbon-supported platinum and palladium catalysts (*24–27*). Considering a 490 K-treated whetlerite sample having a Cr(+6)/Cr(+3) ratio equal to about 6, the amount of Cr(+3) present is 4.2×10^{-3} g Cr(+3)/g whetlerite, which is equivalent to 4.86×10^{19} atoms Cr(+3). A series of studies on chromia catalysts (*6, 8, 10–12*) have reported that one hydrogen atom can be taken up by one Cr(+3) atom. In the present study, if every Cr(+3) atom is assumed to be able to adsorb one hydrogen atom this turns out to be about 700 H atoms/Cr(+3) atom for whetlerite pretreated at 490 K (490 K-treated whetlerite contains the largest amount of Cr(+3) species). All other pretreatment temperatures have even larger H atom/Cr(+3) atom ratios. A number of investigators (*24–27*) have reported H atom/metal atom ratios much greater than 1 and have explained the phenomenon by hydrogen "spilling over" onto the carbon support. The results of this investigation support their view and suggest whetlerite charcoal acts as a "reservoir" for hydrogen atoms that have been adsorbed and dissociated by Cr_2O_3-like species.

The proposed mechanism then involves a slow step of adsorption and dissociation of hydrogen molecules followed by surface migration of H atoms away from these active Cr(+3) centers to the charcoal support. Once on the support, the H atoms can readily react with surface oxides and/or hydroxides resulting in the formation of water. A mechanism of this type has been presented by Groeneveld *et al.* (*9*) and Wittgen *et al.* (*10*) for silica-supported chromia catalysts. Also, this form of hydrogen adsorption has been proposed by Burwell and Stec (*8*), and as previously noted, reported by Stone and Vickerman (*13*) on Cr(+3)/α-Al_2O_3 at room temperature and below. Our results support this type of mechanism. The total hydrogen uptake data show that the adsorption is reversible. That is, following adsorption the water formed and held by the charcoal support is desorbed by heating the sample to 378 K for 2 h under vacuum.

TABLE 6

Hydrogen Uptake in the Pulse System as a Function of Cr(+3) Content in Whetlerite Samples

Thermal pretreatment temperature (K)	Cr(+3) atoms/g whetlerite × 10^{-19}	H atoms taken up per pulse × 10^{-17}	H atoms/Cr(+3) atoms[a] (per pulse)
490	4.86	6.67	0.013
458	1.75	3.52	0.020
443	1.20	2.20	0.018
423	0.88	0.66	0.008

[a] Assuming each Cr(+3) atom adsorbs one H atom.

Wittgen *et al.* (*10*) have observed similar behavior with silica-supported chromia catalysts.

One very interesting feature of the pulse system experiments is the behavior of the hydrogen uptake per Cr(+3) atom as a function of the thermal pretreatment temperatures. Relevant data are listed in Table 6 and illustrated in Fig. 8. The behavior illustrated in Fig. 8 indicates that at the middle thermal treatment temperatures (i.e., intermediate level of Cr(+6) reduction to Cr(+3)) there is an intermediate fractional uptake of hydrogen; however, the number of H atoms taken up per Cr(+3) atom is at a maximum. On either side of this maximum the H atom/Cr(+3) atom value is roughly half of the maximum despite the fact that the fractional uptake is very low (~3%) at the lowest treatment temperature and very high (~30%) at the highest treatment temperature.

This rather unique behavior provides further insight into the role of the active metals on whetlerite. If it is assumed that one hydrogen atom is adsorbed per Cr(+3) atom, at the maximum H atom/Cr(+3) atom value (0.02) the fraction of Cr(+3) atoms exposed or available for reaction with hydrogen is about $\frac{1}{50}$. This value is in reasonably good agreement with the $\frac{1}{20}$ Cr(+3) ion exposure reported by Selwood (*11*) for Cr_2O_3 catalysts. However, at the lowest and highest thermal treatment temperatures where the H atom/Cr(+3) atom values are about half of the maximum, either the chromium atom exposure is different or some other factor is taking effect. The microscopy work (Fig. 9) shows the impregnant crystallite size to be extremely small. Particles in the range between 5 and 50 Å are found to be spread throughout the charcoal support. There does not appear to be any major change in crystallite morphology or dispersion with thermal treatment temperature. Szostak *et al.* (*28*) by EDX analysis, have shown that most of the larger crystallites (~30 Å) contain only copper, while many of the smaller particles contain a mixture of copper and chromium. They have also shown as have Berg *et al.* (*22*) and Hjermstad and Berg (*23*) that there is a distinct tendency for the impregnants to agglomerate and crystallize upon exposure to high humidity. Interest-

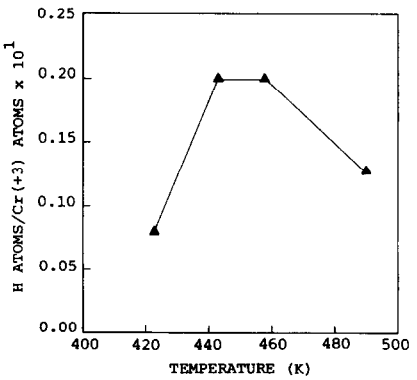
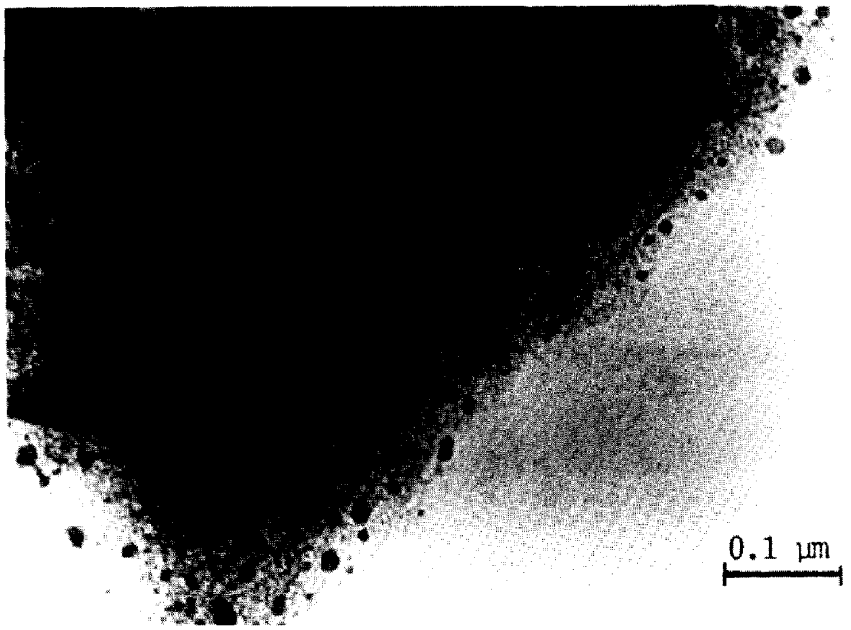
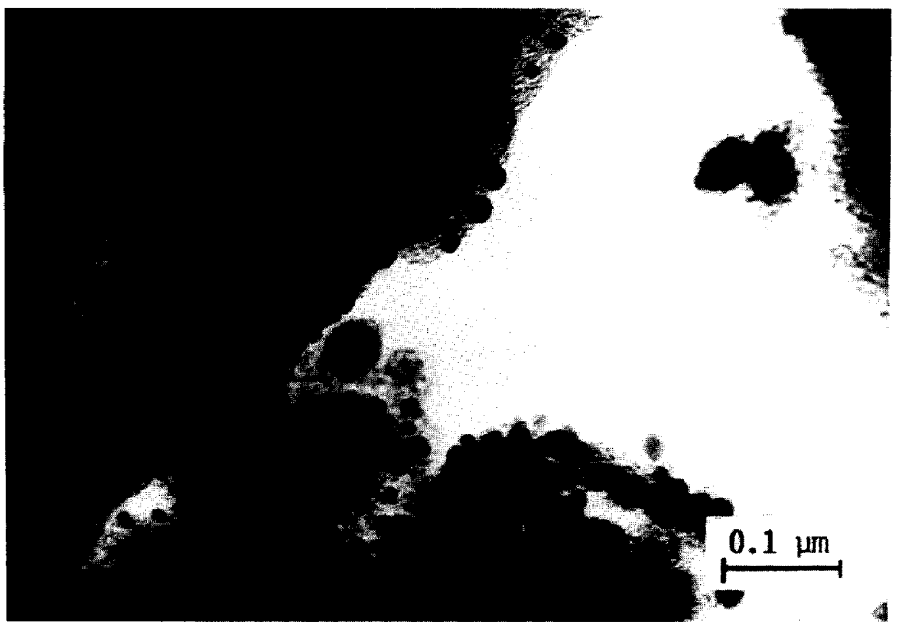


FIG. 8. Hydrogen atoms taken up per chromium atom versus thermal pretreatment temperature.



fresh whetlerite



490 K treated whetlerite

FIG. 9. Transmission electron micrographs.

ingly, regions of the support where no particles could be distinguished indicated the presence of chromium, signifying a high level of dispersion.

These results, coupled with the ESCA data, can be used to help explain the behavior of Fig. 8. It is proposed that the active species for adsorption and dissociation of

hydrogen by whetlerite involves both the chromium and copper species acting synergistically. This agrees with the hypothesis that the active species for effective removal of noxious vapors consists of a copper–chromium combination. Charcoals impregnated with either copper or chromium alone were found to be inadequate for the hydrolysis of many light gases (*1*). Also, there appears to be an optimum copper-to-chromium ratio which produces whetlerites with maximum chemical/catalytic activity. Specifically, for hydrogen adsorption and dissociation the Cr(+3) species should be present as Cr(+3)–Cr(+3) ion pairs dispersed throughout the support material. Indovina *et al.* (*29*) and Stone and Vickerman (*13*) have suggested this idea of Cr–Cr ion pairs. Stone and Vickerman (*13*) in a rather interesting paper report that the activity of chromia–alumina catalysts for H_2–D_2 exchange is not a monotonic function of Cr(+3) content. They observed maxima in both the adsorption isotherms of hydrogen and the exchange activity for catalysts containing varying amounts of chromium. The regions of high hydrogen uptake and optimum exchange activity were attributed to coupled Cr(+3)–Cr(+3) ion pairs. It is hypothesized in this work that the high hydrogen uptakes at the intermediate pretreatment temperatures (illustrated in Fig. 8) may be a result of Cr(+3)–Cr(+3) ion pairs on the whetlerite "isolated" by the copper species. The copper may act to somehow isolate and perhaps activate the chromium pairs (similar to the role of the aluminum in the work of Stone and Vickerman (*13*)), although its exact function has not been elucidated at this time. At the lowest thermal pretreatment temperature, the level of Cr(+6) reduction to Cr(+3) is fairly low and only a small number of the Cr(+3)–Cr(+3) ion pairs are formed. In contrast, at the highest thermal treatment temperature even though a large amount of hexavalent chromium is reduced to the trivalent form, the copper species sinter and segregate away from the Cr(+3) pairs (as suggested by our ESCA results) destroying the delicate electronic balance needed to maintain Cr(+3)–Cr(+3) coupling. The ESCA data clearly showed a loss in intensity of the copper signal when the thermal treatment temperature was increased. This suggests that larger copper crystallites are forming. At the same time, the chromium signal is constant suggesting no change in chromium dispersion. The microscopy data show that the largest particles contain exclusively copper and although the heterogeneous nature of the whetlerite makes it difficult to confirm, it appears that more of the large Cu-only containing particles are present on whetlerites treated at the higher temperatures. These results further support the hypothesis that the role of the copper species is to help maintain the dispersed, isolated chromium ion pairs on the whetlerite.

CONCLUSIONS

A hydrogen pulse technique has been developed for determining the oxidation state of chromium on temperature-deactivated, copper/chromium/silver impregnated charcoal. The magnitude of the activation energy suggests that the rate-determining step is the adsorption-dissociation of hydrogen on the Cr(+3)-containing species on whetlerite. In addition, total hydrogen uptake, determined in a static adsorption system, was much larger than a 1 : 1 correspondence between hydrogen atoms and Cr(+3) atoms. This result suggested that hydrogen atoms migrate or "spill over" from the chromium ions to the charcoal support where they may react with surface oxides and/or hydroxides resulting in the formation of water. Finally, the steady-state hydrogen uptake per Cr(+3) atom obtained in the pulse reactors passes through a maximum at the intermediate thermal pretreatment temperatures. It is proposed that this maximum region of hydrogen uptake is due to isolated Cr(+3)–Cr(+3) ion pairs on whetlerite maintained in a highly dispersed state by the presence of the copper species. These data also imply that the deactivation

of the whetlerite may be associated with or in part due to copper separation from the active chromium species.

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