1 **Oxidation of Elemental Mercury Vapor over γ -Al₂O₃ Supported CuCl₂**
2 **Catalyst for Mercury Emissions Control**
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Abstract

In our previous studies, CuCl_2 demonstrated excellent $\text{Hg}(0)$ oxidation capability and holds potential for $\text{Hg}(0)$ oxidation in coal-fired power plants. In this study, the properties and performances of CuCl_2 supported onto $\gamma\text{-Al}_2\text{O}_3$ with high surface area were investigated. From various characterization techniques using XPS, XAFS, XRD, TPR, SEM and TGA, the existence of multiple copper species was identified. At low CuCl_2 loadings, CuCl_2 forms copper aluminate species with $\gamma\text{-Al}_2\text{O}_3$ and is inactive for $\text{Hg}(0)$ oxidation. At high loadings, amorphous CuCl_2 forms onto the $\gamma\text{-Al}_2\text{O}_3$ surface, working as a redox catalyst for $\text{Hg}(0)$ oxidation by consuming Cl to be converted into CuCl and then being regenerated back into CuCl_2 in the presence of O_2 and HCl gases. The 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst showed excellent $\text{Hg}(0)$ oxidation performance and SO_2 resistance at 140 °C under simulated flue gas conditions containing 6%(v) O_2 and 10 ppmv HCl . The oxidized $\text{Hg}(0)$ in the form of HgCl_2 has a high solubility in water and can be easily captured by other air pollution control systems such as wet scrubbers in coal-fired power plants. The $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst can be used as a low temperature $\text{Hg}(0)$ oxidation catalyst.

Keywords: Heterogeneous elemental mercury oxidation; Cupric chloride; $\gamma\text{-Al}_2\text{O}_3$; Redox catalyst; Coal combustion flue gas

1. Introduction

The new Mercury and Air Toxics Standards (MATS) rule that was effective on April 16, 2012 limits the emissions of mercury, acid gases, and other toxic heavy metals from coal-fired utility, industrial and commercial boilers.[1] Starting from 2016, most coal-fired power plants will need to reduce mercury emissions by >~90%. In addition, the new Transport Rule issued in 2010 regulates sulfur dioxide (SO₂) from power plants in 28 states from 2012. The U.S. EPA estimates a total 272.2 GW of flue gas desulfurization (FGD) units to be installed by 2020 in order to meet the Transport Rule requirements.[2, 3] In this context, the oxidation of elemental mercury (Hg(0)) vapor into a more soluble form (such as HgCl₂) followed by its capture in the subsequent wet FGD system is a viable solution for mercury emissions control in coal-fired power plants. In recent years, noble metals and metal oxides have been primarily studied for heterogeneous catalytic Hg(0) oxidation. Noble metal-based catalysts including gold, platinum and palladium were evaluated as Hg(0) specific catalysts.[4-7] Various metal oxide based Hg(0) oxidation catalysts including V₂O₅, MnO₂, Fe₂O₃, Cr₂O₃, MoO₃, CeO₂, CuO and RuO₂ have also been studied.[8-12] But, most of them showed limited Hg(0) oxidation performances at low HCl or Cl₂ concentrations of typical flue gases from PRB and lignite coals. Also, these catalysts are susceptible to SO₂ inhibition and showed degraded performances under high sulfur bituminous coal flue gas conditions (up to 2,000 ppm SO₂). In our previous studies of CuCl₂-impregnated sorbent and catalyst, CuCl₂ was proven to be effective in Hg(0) oxidation.[13-16] When CuCl₂ was impregnated onto non-carbonaceous substrates (such as alumina), the resultant oxidized mercury was not adsorbed onto the substrate surface. When CuCl₂ was dispersed over α -Al₂O₃, it consistently and reliably showed >90% Hg(0) oxidation performances in the presence of 10 ppmv HCl and 6%(v) O₂ with good resistance to SO₂ at 140 °C. While α -Al₂O₃ substrate did not

react with CuCl_2 and thus was effective in demonstrating the $\text{Hg}(0)$ reaction mechanisms for our previous study, a substrate with a high surface area is usually preferred for industrial applications. Therefore, in this study, the $\text{Hg}(0)$ oxidation over $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ with different loadings has been studied.

A $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst with KCl as a promoter was previously studied for the oxychlorination reaction of hydrocarbons.[17-22] However, no general agreement has been reported on the structure and nature of copper species formed onto $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts other than the existence of multiple phases of copper species. In addition, the active species and mechanisms responsible for the oxychlorination by CuCl_2 are still under study. It is difficult to find other applications of $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ as a catalyst from the literature. Therefore, the objective of this study is to investigate the copper speciation of $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst responsible for the $\text{Hg}(0)$ oxidation under different gas conditions at 140 °C, which is a typical flue gas temperature after the air preheater. Several characterization techniques, including BET, SEM, TGA-MS, TPR, XRD, and XPS, have been used to examine the copper speciation from fresh and spent $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts and to understand the $\text{Hg}(0)$ oxidation mechanism.

2. Experiment

2.1 Catalyst preparation

$\gamma\text{-Al}_2\text{O}_3$ substrate was obtained from Alfa Aesar (aluminum oxide-43855, $\phi 1/8''$ pellets). $\gamma\text{-Al}_2\text{O}_3$ pellets were activated at 400 °C for 2 hours and then ground and passed through a 40- μm sieve. $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was impregnated by wetness incipient method with an aqueous solution of CuCl_2 (Sigma-Aldrich, >98% purity). Different catalyst loadings ranging from 1 to 15%(wt) in terms of CuCl_2 were achieved by controlling the concentration of CuCl_2 in

the aqueous solution. After impregnation, the catalyst with different CuCl_2 loadings was dried in a vacuum oven at 105 °C for 2 hours.

2.2 Performance Evaluation of $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ Catalyst

The $\text{Hg}(0)$ oxidation performance of the $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was evaluated using a lab-scale fixed-bed quartz reactor with simulated flue gases. 25 mg of the catalyst was mixed with 4 g silica sand and the volume of the fixed bed was ~2.25 mL. Three different simulated flue gas conditions were used in this study: (1) N_2 (99.999% UHP, Wright Brothers, Inc.); (2) 10 ppmv HCl and 6%(v) O_2 (balanced with N_2); and (3) 2,000 ppmv SO_2 , 10 ppmv HCl , and 6%(v) O_2 (balanced with N_2). Mercury vapor was generated from a mercury permeation tube (Dynacal, VICI Metronics) and the inlet $\text{Hg}(0)$ vapor concentration was $250 \mu\text{g}/\text{Nm}^3$ (= 30 ppbv) in 1 L/min of a carrier gas flow. The reactor was placed in an oven maintained at 140 °C, targeting an installation of the $\text{Hg}(0)$ catalytic reactor after the air preheater. When a spent catalyst was prepared for characterization, silica sand was not used and the inlet $\text{Hg}(0)$ vapor concentration was increased to $\sim 2 \text{ mg}/\text{Nm}^3$ (= 240 ppbv) to saturate the catalyst in a short period of time. Elemental and oxidized mercury concentrations were measured at the outlet of the reactor using the Ontario Hydro method with a cold vapor atomic absorption mercury analyzer (Model 400A, Buck Scientific) or an online mercury analyzer (VM3000, Mercury Instruments). The detailed information about the system set-up can be found in our previous study.[16]

2.3 Catalyst characterization

Surface areas were calculated by using the BET equation for N_2 adsorption isotherms measured at 77 K with a Micrometrics ASAP 2020 system (Micromeritics Instrument Company, Norcross, GA). Thermal Gravimetric Analysis-Mass Spectrometry (TGA, TA Instruments Q5000IR, and MS, Pfeiffer-Vacuum ThermoStar) was used to evaluate the thermal stability of

95 pure CuCl_2 and $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts. Samples were heated up to 800 °C at a ramp rate of 5
96 °C/min under nitrogen flow (99.999% UHP). The H_2 -Temperature Programmed Reduction
97 (TPR) experiments were performed using a Micromeritics Autochem 2910 automated catalyst
98 characterization system. The samples were pretreated at 300 °C for 1 hr in ultra pure argon gas
99 at a flow rate of 30 mL/min. After the furnace temperature decreased to ~50 °C, the feed gas
100 (10%(v) H_2 balanced with Ar) was fed into the system at a flow rate of 30 mL/min. H_2 -TPR runs
101 were performed by heating the sample up to 600 °C at a linear heating rate of 6.5 °C/min. The
102 amount of hydrogen gas consumed during the TPR experiment was measured by a built-in
103 thermal conductive detector (TCD). The X-ray diffraction (XRD) measurement was carried out
104 with an X'Pert Pro MPD X-ray diffractometer under Cu $\text{K}\alpha$ radiation (wavelength=1.5406 Å).
105 The samples were loaded in an aluminum holder with a depth of 1 mm. The scanning range was
106 from 10 to 60° (2 θ) with a step size of 0.02° and a step time of 0.5 s. XPS (Kratos Axis Ultra,
107 with a monochromated Al $\text{K}\alpha$ source (1486.6 eV)) measurements were used to examine copper
108 speciation with a concentric hemispherical analyzer. The power applied to the X-ray gun was
109 130 W (I=10 mA, V=13 kV), and the base vacuum pressure was 1×10^{-7} Torr, and the pass
110 energy of the analyzer was set to 20 eV. The resolution of the spectra was ~0.2 eV with a step
111 size of 0.1 eV. The carbon 1s peak at 284.5 eV was used for calibration. Cu K edge X-ray
112 Absorption Fine Structure (XAFS) spectroscopy measurement was performed using the 9-BM-C
113 beamline of the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL,
114 Argonne, IL). All samples and standards (CuCl_2 and CuO) were pressed into pellets and
115 measured in both transmission and fluorescence modes. XAFS data collected were analyzed
116 using the Athena software.[23]

3. Results and Discussion

3.1 Hg(0) Oxidation Performance

The Hg(0) oxidation performances of CuCl₂/γ-Al₂O₃ catalyst with different CuCl₂ loadings under N₂ gas are shown in Figure 1. With 1%(wt) and 3.5%(wt) loadings, CuCl₂/γ-Al₂O₃ showed almost no Hg(0) oxidation capability. When the CuCl₂ loading increased to 10%(wt), CuCl₂/γ-Al₂O₃ could oxidize >95% Hg(0) during the first 20 hours in N₂ flow and lost its oxidation capability after ~80 hours. A baseline test with 0% CuCl₂ loading was also conducted, and the adsorption of Hg(0) by γ-Al₂O₃ and silica was negligible (Figure S1). As shown in our previous study, CuCl₂ is the active species responsible for Hg(0) oxidation when doped onto α-Al₂O₃. [16] The Hg(0) oxidation performances under different CuCl₂ loadings indicate that at low loadings (i.e. 1 and 3.5%), Cu species on γ-Al₂O₃ may not be CuCl₂ and thus is inactive for Hg(0) oxidation. This inactive Cu species may result from other copper species formed from CuCl₂ and γ-Al₂O₃. At 10%(wt) CuCl₂ loading, extra CuCl₂ covers the surface of inactive Cu species and has Hg(0) oxidation capability. The presence of multiple Cu species on high loading CuCl₂/γ-Al₂O₃ catalyst is studied and discussed in the following sections.

The Hg(0) oxidation performances of 10%(wt) CuCl₂/γ-Al₂O₃ catalyst under different simulated flue gas conditions are also shown in Figure 1. Regardless of a gas condition, the catalyst could oxidize >95% Hg(0) for the first 20 hours. Under N₂, the catalyst gradually lost its Hg(0) oxidation activity after 20 hours and becomes completely inactive after 80 hours. However, in the presence of both 6%(v) O₂ and 10 ppmv HCl, CuCl₂/γ-Al₂O₃ catalyst continues to oxidize Hg(0) vapor during the entire evaluation period (~140 hours). Selected Hg mass balance during this test is shown in Figure S2. When γ-Al₂O₃ and silica without CuCl₂ were used in the reactor, >90% of total Hg was collected at the outlet of the reactor. The amount of

Hg(0) adsorbed by γ -Al₂O₃ and silica was negligible, indicating that Hg(0) removal is due to oxidation. Also, an addition of 2,000 ppmv SO₂ gas did not show any negative effect on Hg(0) oxidation. These performance results of 10%(wt) CuCl₂ loading onto γ -Al₂O₃ support were similar to those of CuCl₂/ α -Al₂O₃ obtained from our previous study.[16] The different Hg(0) oxidation performance of CuCl₂/ γ -Al₂O₃ catalysts with respect to different CuCl₂ loadings and gas conditions led us to conducting the following characterization studies of the fresh and spent catalysts to gain a better understanding of the CuCl₂ speciation and Hg(0) oxidation mechanisms.

3.2 BET and SEM

γ -Al₂O₃ used as a catalyst support in this study has a high surface area (220 m²/g) with mesopores (medium pore diameter ~7 nm, average pore volume 0.62 cm³/g). In comparison, α -Al₂O₃ has a very small surface area (0.25 m²/g). The SEM images of 10%(wt) CuCl₂/ γ -Al₂O₃ and raw γ -Al₂O₃ are shown in Figure 2. No visible CuCl₂ crystal can be observed from the γ -Al₂O₃ surface, indicating that CuCl₂ is in a highly dispersed amorphous phase.

3.3 TGA-MS

The thermal stability of unsupported CuCl₂·2H₂O, CuCl, raw γ -Al₂O₃, and CuCl₂/ γ -Al₂O₃ with different loadings was examined by TGA-MS as shown in Figure 3. Unsupported CuCl₂·2H₂O lost ~21% of its weight at 100 °C, corresponding to the vaporization of the dihydrate, and then all CuCl₂ evaporated between 350 °C and 550 °C where chlorine evolution was detected by MS. Unsupported CuCl lost most of the weight between ~410 and 560 °C, but chlorine release was not detected by MS. Pure CuCl melts and vaporizes at ~420 °C, and the CuCl vapor is too heavy to reach the MS capillary tube inlet. These results indicate that dehydrated CuCl₂ loses additional 21% by releasing chlorine and turns into CuCl at 438 °C and

then the remaining CuCl starts to evaporate without any chlorine release. It should be noted that the 3.5%(wt) CuCl₂/γ-Al₂O₃ and raw γ-Al₂O₃ samples showed very similar weight loss curves, indicating that there are strong interactions between CuCl₂ and γ-Al₂O₃ surface at the loading, and the copper species formed appears to be thermally stable. As demonstrated in the Hg(0) oxidation performance section, the copper species formed onto γ-Al₂O₃ at 1 and 3.5%(wt) loadings did not exhibit any significant catalytic activities. In contrast, 10%(wt) CuCl₂/γ-Al₂O₃ lost 5.7% more weight and this additional weight loss is derived from H₂O and the thermal decomposition of CuCl₂. The results from TG analysis indicate that CuCl₂ forms thermally stable species with γ-Al₂O₃ first, then extra CuCl₂ is deposited on the surface. For 10%(wt) CuCl₂/γ-Al₂O₃, 4.3%(wt) of CuCl₂ is converted into nonreactive forms, and the rest 5.7% appears to be in the form of CuCl₂. Previous studies reported that the threshold concentration of copper in copper aluminate formation between CuCl₂ and γ-Al₂O₃ is 0.95% (wt) Cu per 100 m² surface area.[18, 19] According to the estimate, the copper aluminate content formed with the γ-Al₂O₃ used in this study (with a surface area of 220 m²/g) is estimated to be 4.42%(wt) in terms of CuCl₂ loading, and this is consistent with our TGA result. For 10%(wt) CuCl₂/γ-Al₂O₃, the release of water was similar to that of unsupported CuCl₂·2H₂O. However, the release of chlorine had a different pattern. Chlorine started to be released at a lower temperature ~200 °C (compared to ~350 °C for unsupported CuCl₂) and continued to be released slowly up to higher temperatures. This is also in agreement with the formation of copper aluminate. Since copper aluminate does not contain chlorine, the chlorine left from the reaction between CuCl₂ and γ-Al₂O₃ was weakly bonded to the surface and was released at lower temperatures.

3.4 TPR

H₂-TPR was used for 3.5%(wt) CuCl₂/γ-Al₂O₃, 10%(wt) CuCl₂/γ-Al₂O₃ and 10%(wt) CuCl₂/α-Al₂O₃ to measure the redox activity of the supported CuCl₂ in terms of temperature as shown in Figure 4. The H₂-TPR profile of 3.5%(wt) CuCl₂/γ-Al₂O₃ did not show any peak below 600 °C, indicating that the Cu species formed at the loading on γ-Al₂O₃ was inactive or Cu was in a reduced state. This is in consistent with the TGA result. This Cu species (presumably copper aluminate) formed at this CuCl₂ loading appears to have strong interactions with the γ-Al₂O₃ surface, resulting in high thermal stability and no redox activity.

For the cases of 10%(wt) CuCl₂ loading, the 10%(wt) CuCl₂/γ-Al₂O₃ catalyst had two H₂-TPR peaks at 200 °C and 375 °C. As previously reported, these peaks were assigned to the two-step reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0), respectively.[24] The 10%(wt) CuCl₂/α-Al₂O₃ catalyst also showed two peaks at 340 °C and 400 °C. The higher reduction temperature was possibly due to the larger CuCl₂ particle size on α-Al₂O₃ and poor dispersion. [25] The H₂-TPR profile showed that 10%(wt) CuCl₂/γ-Al₂O₃ had higher redox activity at lower temperature than 10%(wt) CuCl₂/α-Al₂O₃. It should be beneficial to CuCl₂ working as a redox catalyst.

3.5 XRD

The XRD patterns of raw γ-Al₂O₃ and CuCl₂/γ-Al₂O₃ with different loadings (1%, 3.5% and 10%) are shown in Figure 5. No CuCl₂·2H₂O or CuCl₂ peaks were detected from all the samples, indicating the highly dispersed amorphous phase of CuCl₂ on the γ-Al₂O₃ surface. At 1 and 3.5% loadings, no additional peak was detected. At 10%(wt) loading, two peaks at 32.5° and 39.9° appeared and these peaks can be assigned to Cu₂(OH)₃Cl (paratacamite). Paratacamite can be formed from the hydrolysis of CuCl₂·2H₂O, and it is not stable at elevated temperatures,

changing into CuCl_2 by losing hydroxyl groups.[18, 19, 26] In order to confirm this, a 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample was heated at 140 °C under a vacuum for 2 hours before XRD measurement. The paratacamite peaks disappeared after the heat treatment, indicating that at the reaction temperature (140 °C), Cu does not exist in the form of paratacamite. In our previous studies, paratacamite peaks were never detected on $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$, due to a lack of active hydroxyl groups on $\alpha\text{-Al}_2\text{O}_3$ surface.[16] The XRD patterns of a spent 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample under different gas conditions including (1) 30 ppbv $\text{Hg}(0) + \text{N}_2$; (2) 30 ppbv $\text{Hg}(0) + 6\%(\text{v}) \text{O}_2 + 10 \text{ ppmv HCl} + \text{N}_2$; and (3) 30 ppbv $\text{Hg}(0) + 6\%(\text{v}) \text{O}_2 + 10 \text{ ppmv HCl} + 2,000 \text{ ppmv SO}_2 + \text{N}_2$ were also examined. All the spent samples showed similar patterns to that of raw $\gamma\text{-Al}_2\text{O}_3$ and no new noticeable peaks were observed (10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ spent in N_2 is shown in Figure 5). It should be noted that no CuCl peaks were detected by XRD characterization, which were expected to appear from the spent samples as an intermediate compound of CuCl_2 derivatives from the reaction of $\text{Hg}(0)$ and CuCl_2 .[16] In this regard, the amorphous nature of copper species on $\gamma\text{-Al}_2\text{O}_3$ requires the use of other surface characterization techniques.

3.6 Solvent Extraction

The copper species in 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ identified by the above characterization techniques were further quantified by solvent extraction experiment. Among all potential copper species that can be formed on the $\gamma\text{-Al}_2\text{O}_3$ surface including copper chlorides, oxychlorides, hydroxychlorides, and oxides, CuCl_2 is the only copper compound that is soluble in ethanol.[27] Solvent extraction of 100 mg of 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was performed in 100 mL of ethanol for 4 hours and the extracted Cu was measured by UV-vis spectroscopy. It was determined that 60.8%(wt) of all the Cu was able to be extracted, indicating that it was in the

form of CuCl_2 (i.e. $\sim 6.1\%$ (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$). This result was in agreement with the result obtained from TGA analysis (i.e. $\sim 4.4\%$ (wt) copper aluminate in 10% (wt)). For 3.5% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, no Cu was extracted using ethanol, suggesting that the Cu species is not CuCl_2 .

3.7 XPS

The 3.5% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, 10% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, unsupported CuCl_2 and CuCl standards measured by XPS are shown in Figure 6. The standards show the Cu $2p_{3/2}$ binding energies of 934.5 eV for Cu(II) in CuCl_2 and 932.0 eV for Cu(I) in CuCl . The results obtained from the low CuCl_2 loading sample (i.e. 3.5% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$) showed only one major peak at a binding energy of 932.0 eV, which can be assigned to Cu(0) or Cu(I) species. At this stage, the Cu species formed over the 3.5% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample is not determined. According to previous studies, it could be either atomically dispersed Cu species interacting via oxygen bonds with the support,[28] or surface copper aluminates through isolated copper ions occupying the octahedral vacancies of the alumina surface.[19] The presence of the surface copper aluminate on the $\gamma\text{-Al}_2\text{O}_3$ surface requires the formation of a Cu-O-Al bond with the elimination of Cl, while the Cl released from CuCl_2 is bound to alumina, which was suggested by multiple characterization techniques.[18, 19]

For fresh 10% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, one additional peak at a binding energy 934.5 eV was observed. This peak position matched that of Cu(II) in CuCl_2 , supporting our hypothesis that at higher CuCl_2 loadings, extra CuCl_2 is deposited on the surface and exists in the form of amorphous CuCl_2 . Spent 10% (wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample under different gas conditions including (1) 30 ppbv $\text{Hg}(0) + \text{N}_2$ and (2) 30 ppbv $\text{Hg}(0) + 6\%$ (v) $\text{O}_2 + 10$ ppmv $\text{HCl} + \text{N}_2$ were also measured and the high resolution Cu $2p_{3/2}$ spectra were obtained as shown in Figure 7. As discussed in the $\text{Hg}(0)$ oxidation performance section, the reaction could proceed for a certain

period of time even without the presence of HCl. The XPS spectra of the sample spent in Hg(0)+N₂ showed an increased intensity of the Cu(I) peak, and the Cu(II) peak corresponding to CuCl₂ significantly decreased. In the presence of 10 ppmv HCl, the CuCl₂ peak was much stronger, indicating that HCl can help regenerate CuCl to CuCl₂ to attain the Hg(0) oxidation capability. It was also observed from survey XPS spectra (data not shown) that the peak intensities for Al and O did not significantly change from the CuCl₂/γ-Al₂O₃ samples before and after Hg(0) oxidation.

3.8 Extended X-ray Absorption Fine Structure (EXAFS)

The k²-weighted and Fourier transformed EXAFS spectra ($|\chi(R)|$) for 3.5%(wt) CuCl₂/γ-Al₂O₃, 15%(wt) CuCl₂/γ-Al₂O₃, and two standards (CuCl₂ and CuO) are shown in Figure 8. CuO showed a single peak at 1.55 Å corresponding to the Cu-O bond (position marked by the solid vertical line in Figure 8). CuCl₂ showed one major peak at 1.86 Å derived from the Cu-Cl bond (position marked by the dashed vertical line) and a minor shoulder peak at a lower R region representing the Cu-O bond due to the interaction between Cu and the dihydrate.[29] The 3%(wt) CuCl₂/γ-Al₂O₃ sample had only one peak indicating the Cu-O bond and no Cu-Cl bond was detected. This further suggests the formation of copper aluminate when low CuCl₂ loading such as 3.5%(wt) was doped onto γ-Al₂O₃. Since no Cu-Cl bond was found to exist from the 3.5%(wt) sample, the catalysts with such low CuCl₂ loadings did not show mercury oxidation capability. On the other hand, the 15%(wt) CuCl₂/γ-Al₂O₃ sample showed a broad peak that shifts to higher R region, indicating the co-existence of both of the Cu-O and Cu-Cl bonds. These results are in agreement with the other characterization results and corroborate the co-existence of multiple copper species on the CuCl₂/γ-Al₂O₃ catalysts at high CuCl₂ loadings.

3.9 Hg(0) Oxidation over CuCl₂/γ-Al₂O₃

From the above characterization results obtained from the CuCl₂/γ-Al₂O₃ catalyst and the results reported in the literature with different CuCl₂ loadings, the following findings are summarized: (1) at low CuCl₂ loadings, copper aluminate is the only species and it is inactive for Hg(0) oxidation; (2) as CuCl₂ loading increases, the extra Cu will exist in the form of paratacamite and amorphous CuCl₂; and (3) at the reaction temperature of 140 °C, paratacamite will be converted back into CuCl₂ by losing hydroxyl groups and CuCl₂ is believed to be the active species for Hg(0) oxidation. Leofanti et al. reported that in low CuCl₂ loading samples, Cu occupies the octahedral vacancies of the alumina surface with the formation of diluted surface aluminate and the chloride anions released upon the dissociation of CuCl₂ molecules do not contribute to the first coordination shell of Cu.[18, 19] The reaction between CuCl₂ and hydroxylated alumina surface can be represented by Eqs. (1)-(3).

In this study, the γ-Al₂O₃ support was used to provide a high surface area for the Hg(0) oxidation. Although highly dispersed CuCl₂ provides more active sites for Hg(0) adsorption and oxidation, some of CuCl₂ is used to form copper aluminate and paratacamite phases. In the absence of HCl and O₂ gases, CuCl₂/γ-Al₂O₃ can still oxidize Hg(0) by consuming lattice Cl atoms and CuCl₂ is reduced to CuCl. This suggests that Hg(0) oxidation over CuCl₂/γ-Al₂O₃ via a Mars-Maessen mechanism.[30, 31] In the presence of HCl and O₂ gases, CuCl can be converted back into CuCl₂ and the catalyst is regenerated. In this context, CuCl₂/γ-Al₂O₃ works

as a redox catalyst for Hg(0) oxidation. It has been proposed that the conversion from CuCl to CuCl₂ involves two steps: CuCl forms Cu₂OCl₂ by oxidation with O₂ gas and is subsequently converted into CuCl₂ with HCl gas.[32, 33] In our previous study on Hg(0) oxidation over CuCl₂/α-Al₂O₃ [16], all Cu species are in crystalline form and the intermediate Cu₂OCl₂ was detected by XRD. However, for CuCl₂/γ-Al₂O₃, Cu₂OCl₂ was not detected due to the amorphous nature of Cu species formed onto γ-Al₂O₃ and its formation is not clear. Despite that, the reactions involved in the Hg(0) oxidation over CuCl₂/γ-Al₂O₃ can be summarized as follows:

Compared with Hg(0) oxidation over CuCl₂/α-Al₂O₃, the CuCl₂/γ-Al₂O₃ catalyst also forms the Cu₂(OH)₃Cl phase. It involves a transfer of Cl atoms between CuCl₂ and the surface alumina. Cu₂(OH)₃Cl is not thermally stable as shown from the XRD result. At the reaction temperature of 140 °C, it will be completely converted into CuCl₂ and catalyze the oxidation of adsorbed Hg(0) via Eq. (5). As shown in Eq. (7), it should be noted that for the regeneration of CuCl to CuCl₂, both HCl and O₂ gases are required.[16] Compared with most noble metal- and metal oxides-based Hg(0) oxidation catalysts, the advantages of CuCl₂/γ-Al₂O₃ catalyst include its excellent SO₂ resistance, high performance and low cost. In addition, CuCl₂/γ-Al₂O₃ is a low

temperature catalyst ($< \sim 250$ °C), which can be installed even after a particulate matter control device.

4. Conclusion

When CuCl_2 is impregnated onto $\gamma\text{-Al}_2\text{O}_3$ support using wet incipient method, multiple Cu species were found to be formed. This is different from the impregnation onto $\alpha\text{-Al}_2\text{O}_3$, as only a single CuCl_2 phase was formed. At low CuCl_2 loadings (e.g. $< 4.3\%$ (wt)), strong interactions were found between CuCl_2 and $\gamma\text{-Al}_2\text{O}_3$ to form copper aluminate (CuAlO_2). It is thermally stable and chemically inert for $\text{Hg}(0)$ oxidation. As the loading increases, additional CuCl_2 dopant will cover the copper aluminate surface to form paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) and highly dispersed amorphous CuCl_2 . At the reaction temperature of 140 °C, paratacamite will lose hydroxyl groups to be converted into CuCl_2 , and the latter is the active species responsible for the $\text{Hg}(0)$ oxidation reaction. CuCl_2 works as a redox catalyst and oxidizes $\text{Hg}(0)$ by reducing itself to CuCl , following a re-chlorination back to CuCl_2 under O_2 and HCl gases. High loadings of CuCl_2 onto the $\gamma\text{-Al}_2\text{O}_3$ support showed excellent $\text{Hg}(0)$ oxidation performance and SO_2 resistance under 10 ppmv HCl . The $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst has the potential to be used as a low temperature $\text{Hg}(0)$ oxidation catalyst in coal-fired power plants for mercury emissions control.

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References

- [1] "Federal Implementation Plans To Reduce Interstate Transport of Fine Particulate Matter and Ozone; Correction." 40 CFR Parts 51, 52, 72, 78, and 97. Federal Register 75:177 (September 14, 2010) p. 45210.
- [2] EPA, Integrated Planning Model (IPM) v.4.10 Model Runs, 2010.
- [3] R. Meij, L.H.J. Vredenburg, H.t. Winkel, The Fate and Behavior of Mercury in Coal-Fired Power Plants, Journal of the Air & Waste Management Association 52 (2002) 912-917.
- [4] Y. Zhao, M.D. Mann, J.H. Pavlish, B.A.F. Mibeck, G.E. Dunham, E.S. Olson, Application of Gold Catalyst for Mercury Oxidation by Chlorine, Environ. Sci. Technol. 40 (2006) 1603-1608.
- [5] M.L. Toebes, M.K. van der Lee, L.M. Tang, M.H. Huis in't Veld, J.H. Bitter, A.J. van Dillen, K.P. de Jong, Preparation of carbon nanofiber supported platinum and ruthenium catalysts: comparison of ion adsorption and homogeneous deposition precipitation, The Journal of Physical Chemistry B 108 (2004) 11611-11619.
- [6] A.A. Presto, E.J. Granite, Noble Metal Catalysts for Mercury Oxidation in Utility Flue Gas, Platinum Metals Review 52 (2008) 144-154.
- [7] J.A. Hrdlicka, W.S. Seames, M.D. Mann, D.S. Muggli, C.A. Horabik, Mercury Oxidation in Flue Gas Using Gold and Palladium Catalysts on Fabric Filters, Environ. Sci. Technol. 42 (2008) 6677-6682.
- [8] W.J. Lee, G.N. Bae, Removal of Elemental Mercury (Hg(O)) by Nanosized V₂O₅/TiO₂ Catalysts, Environ. Sci. Technol. 43 (2009) 1522-1527.

360 [9] N. Yan, W. Chen, J. Chen, Z. Qu, Y. Guo, S. Yang, J. Jia, Significance of RuO₂ Modified
 361 SCR Catalyst for Elemental Mercury Oxidation in Coal-fired Flue Gas, *Environ. Sci. Technol.*
 362 45 (2011) 5725-5730.

363 [10] P. Wang, S. Su, J. Xiang, F. Cao, L. Sun, S. Hu, S. Lei, Catalytic oxidation of Hg⁰ by
 364 CuO–MnO₂–Fe₂O₃/γ-Al₂O₃ catalyst, *Chemical Engineering Journal* 225 (2013) 68-75.

365 [11] W. Xu, H. Wang, X. Zhou, T. Zhu, CuO/TiO₂ catalysts for gas-phase Hg⁰ catalytic
 366 oxidation, *Chemical Engineering Journal* 243 (2014) 380-385.

367 [12] H. Kamata, S.-i. Ueno, N. Sato, T. Naito, Mercury oxidation by hydrochloric acid over
 368 TiO₂ supported metal oxide catalysts in coal combustion flue gas, *Fuel Processing Technology*
 369 90 (2009) 947-951.

370 [13] K.S. Park, Y.C. Seo, S.J. Lee, J.H. Lee, Emission and speciation of mercury from various
 371 combustion sources, *Powder Technology* 180 (2008) 151-156.

372 [14] S.-S. Lee, J.-Y. Lee, T. Keener, Elemental Mercury Control by Novel Oxidant and Sorbent
 373 in an Entrained-Flow System, *Water, Air, Soil Pollution: Focus* 8 (2008) 343-347.

374 [15] X. Li, J.-Y. Lee, S. Heald, XAFS characterization of mercury captured on cupric chloride-
 375 impregnated sorbents, *Fuel* 93 (2012) 618-624.

376 [16] X. Li, Z. Liu, J. Kim, J.-Y. Lee, Heterogeneous catalytic reaction of elemental mercury
 377 vapor over cupric chloride for mercury emissions control, *Applied Catalysis B: Environmental*
 378 132 (2013) 401-407.

379 [17] E.M. Fortini, C.L. García, D.E. Resasco, Stabilization of the active phase by interaction
 380 with the support in CuCl₂ oxychlorination catalysts, *Journal of Catalysis* 99 (1986) 12-18.

381 [18] G. Leofanti, M. Padovan, M. Garilli, D. Carmello, G.L. Marra, A. Zecchina, G. Spoto, S.
 382 Bordiga, C. Lamberti, Alumina-Supported Copper Chloride: 2. Effect of Aging and Thermal
 383 Treatments, *Journal of Catalysis* 189 (2000) 105-116.
 384 [19] G. Leofanti, M. Padovan, M. Garilli, D. Carmello, A. Zecchina, G. Spoto, S. Bordiga, G.T.
 385 Palomino, C. Lamberti, Alumina-Supported Copper Chloride: 1. Characterization of Freshly
 386 Prepared Catalyst, *Journal of Catalysis* 189 (2000) 91-104.
 387 [20] P.S. Prasad, K.S. Prasad, P.K. RAO, V. Kaushik, Redistribution of copper in KCl-promoted
 388 $\text{CuCl}_2/\text{Y-Al}_2\text{O}_3$ catalyst during oxychlorination of ethylene, *Journal of materials science* 32
 389 (1997) 1479-1482.
 390 [21] C. Prestipino, S. Bordiga, C. Lamberti, S. Vidotto, M. Garilli, B. Cremaschi, A. Marsella, G.
 391 Leofanti, P. Fisicaro, G. Spoto, A. Zecchina, Structural Determination of Copper Species on the
 392 Alumina-Supported Copper Chloride Catalyst: A Detailed EXAFS Study, *The Journal of*
 393 *Physical Chemistry B* 107 (2003) 5022-5030.
 394 [22] R. Vetrivel, K. Seshan, K. Krishnamurthy, T.P. Rao, X-ray photoelectron spectroscopy
 395 studies on ethylene oxychlorination catalysts, *Bulletin of Materials Science* 9 (1987) 75-80.
 396 [23] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray
 397 absorption spectroscopy using IFEFFIT, *Journal of Synchrotron Radiation* 12 (2005) 537-541.
 398 [24] A.J. Rouco, TPR study of Al_2O_3 - and SiO_2 -supported CuCl_2 catalysts, *Applied Catalysis A:*
 399 *General* 117 (1994) 139-149.
 400 [25] K. Tonge, Particle size effects in temperature programmed topochemical reactions,
 401 *Thermochimica acta* 74 (1984) 151-166.
 402 [26] A. Pollard, R. Thomas, P. Williams, Synthesis and stabilities of the basic copper (II)
 403 chlorides atacamite, paratacamite and botallackite, *Mineralogical Magazine* 53 (1989) 557-563.

- [27] J.W. Laist, Comprehensive Inorganic Chemistry Vol 2. Copper, Silver and Gold, 1954.
- [28] G.C. Bond, S.N. Namijo, J.S. Wakeman, Thermal analysis of catalyst precursors: Part 2. Influence of support and metal precursor on the reducibility of copper catalysts, Journal of Molecular Catalysis 64 (1991) 305-319.
- [29] S. Brownstein, N.F. Han, E. Gabe, Y. LePage, A redetermination of the crystal structure of cupric chloride dihydrate, Zeitschrift für Kristallographie-Crystalline Materials 189 (1989) 13-16.
- [30] P. Mars, J. Maessen, The mechanism and the kinetics of sulfur dioxide oxidation on catalysts containing vanadium and alkali oxides, Journal of Catalysis 10 (1968) 1-12.
- [31] A.A. Presto, E.J. Granite, Survey of Catalysts for Oxidation of Mercury in Flue Gas, Environ. Sci. Technol. 40 (2006) 5601-5609.
- [32] A.P. Amrute, C. Mondelli, M.A.G. Hevia, J. Pérez-Ramírez, Temporal Analysis of Products Study of HCl Oxidation on Copper- and Ruthenium-Based Catalysts†, The Journal of Physical Chemistry C 115 (2011) 1056-1063.
- [33] H.Y. Pan, R.G. Minet, S.W. Benson, T.T. Tsotsis, Process for Converting Hydrogen Chloride to Chlorine, Industrial & Engineering Chemistry Research 33 (2002) 2996-3003.

Captions:

Figure 1. Catalytic performance of $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts with different CuCl_2 loadings under different gas conditions with 30 ppbv inlet $\text{Hg}(0)$ vapor in 1 L/min of a carrier gas flow at 140 °C.

Figure 2. SEM images of (a) raw $\gamma\text{-Al}_2\text{O}_3$ and (b) 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$.

Figure 3. TGA –MS results for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuCl and $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst with different loadings.

Figure 4. H_2 -TPR profiles of 3.5%, 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$, and 10%(wt) $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$.

Figure 5. XRD patterns of $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts with different CuCl_2 loadings.

Figure 6. Cu $2p_{3/2}$ high resolution XPS results for fresh $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ samples and standards.

Figure 7. Cu $2p_{3/2}$ high resolution XPS results of spent 10%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ samples under different gas conditions.

Figure 8. k^2 -weighted and Fourier transformed Cu EXAFS signals ($|\chi(R)|$) for CuO, CuCl_2 , 3.5%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ and 15%(wt) $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$. The vertical lines indicate the Cu-O and Cu-Cl bonding distances.

Figure 1

Figure 2_a

Figure 2_b

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8