Electrochemically generated bimetallic reductive mediator $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ for the degradation of CF_4 to ethanol by electro-scrubbing

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Abstract The remediation of the electronic gas, CF_4, using commercially available technologies produces another type of greenhouse gas (CO_2) and corrosive side products. The aim of this study was to degrade CF_4 gas at room temperature into useful products using an electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ mediator. The initial electrolysis of the bimetallic complex at the anodized Ti cathode produced $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$, which was confirmed by electron spin resonance spectroscopy. The degradation of CF_4 followed the mediated electrochemical reduction by electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$. The removal efficiency of CF_4 was 95% using this electroscrubbing process at room temperature. Fourier transform infrared spectroscopy in both the gas and solution phase showed that CH_3CH_2OH was the main the product formed during the removal of CF_4 by electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ at electroscrubbing with a small amount of CF_3CH_3 intermediate.

Keywords: Bimetallic mediator, $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$, MER, CF_4 degradation; Ethanol formation

1. Introduction

So called electronic gases (CF_4, NF_3 and SF_6) play a major role in human life either positively by new sophisticated electronic goods or negatively by environmental pollution. The increasing amount of electronic gas pollution has prompted innovations of new removal technologies. Two methods are currently and commercially available, combustion and plasma arc (Rittmeyer and Vehlow (1993); Lee *et al*. (1996); Lee *et al*. (2005); Gal *et al*. (2003)), which produce mostly another greenhouse gas, CO_2, and its derivatives (COF_2, CO, H_2O), with HF (Xu *et al*. (2007); Gandhi and Mok (2012); Narengerile *et al*. (2010); Zhang *et al*. (2005)) depending on the carrier gas. Recently, catalytic combustion has attracted considerable interest towards a more practical level (Xu *et al*. (2011); Takita *et al*. (1999)), particularly hydrolytic combustion because of its lower Gibbs free energy (-150 kJ/mol). Unfortunately, the final product obtained is highly corrosive HF, as shown in reaction 1, which leads to catalyst deactivation (Farris *et al*. (1992)). To minimize catalyst deactivation, a binary metal catalyst was attempted to degrade CF_4 by hydrolytic combustion process, with the idea of C-F bond breaking at the Lewis-acid catalysts to form metal fluorides, which can be hydrolyzed easily (El-Bahy *et al*. (2003); Takita *et al*. (1999)-2; Song *et al*. (2013)). El-Bahy *et al*. (2003)) assessed various bimetal combinations and found that Ga-Al and Ni-Al oxide catalysts were stable from HF deactivation. Xu *et al*. (2007) reported the conversion of CF_4 to CO_2 with minimal deactivation of the γ-Al_2O_3 catalysts by the addition of Zn, Ni, Mg, Sr, and Ba metals. Song *et al*. (2013) developed a Ce/Al_2O_3 binary catalyst that was not effective in the removal of CF_4 but the catalyst was stable. The catalytic combustion in the CF_4 decomposition process also produces another greenhouse gas, CO_2.

$$CF_4 + 2H_2O \longrightarrow CO_2 + 4HF \ (\Delta G = -150 \text{ kJ/mol})$$

--- (1)

At the same time, the electrochemical technique offers the degradation of chloro fluoro carbons (CFCs) at room temperature to non-fluoro compounds with the absence of CO_2 (Sonoyama and Sakata (1998); Cabot *et al*. (2004); Wagoner and Peters (2013)). Sonoyama and Saakta (1998)-2 performed metal (Cu) supported gas diffusion electrode on the degradation of $CClF_3$ (CFC-13), which resulted in methane formation, and on Ag-supported gas diffusion electrode to form CHF_3. In the solution phase electrochemical degradation process, the direct reduction of CFCs were performed in acetonitrile (Schizodimou *et al*. (1999)) and DMF (Wagoner *et al*. (2012)) on different metal electrodes due to the solubility of CFCs to produce, CF_2CF_2, CH_2F_2, CH_3F, CF_2CFCl, and $CHCF_3$, as the main products, which are used as raw materials in the production of polymers and refrigerants. Cabot *et al*. (2003) used a methanol/water mixture to degrade CFC-11 and CFC-113 using a Pb cathode with a Pd containing gas diffusion anode by constant potential electrolysis, where complete or partially dehalogenated products were achieved depending on the Pd contents. Taylor-Smith and Sayres (1999), who performed fundamental electrochemical studies on selective site-specific PFCs compounds that the reduction

reaction follows a radical reaction with the formation of a carbanion with subsequent oligomeric products, such as C_3H_8, C_3F_8, and CH_4 from CF_4 and etc. Most of the electrochemical studies to degrade CFCs were performed in aprotic media or a combination of aprotic and protic solvents using CV or constant potential electrolysis; none were performed in only aqueous medium and a constant current in the degradation process. Recently, CF_4 removal was reported using a mediated electrochemical reduction (MER) in aqueous KOH medium at room temperature by the electrochemically generated mediator Co^{1+} in an electro-scrubbing process (Muthuraman and Moon (2017)). Ethanol and HF were the products found in the Co^{1+} MER of CF_4 (Muthuraman and Moon (2017)). The HF formation in this report may reduce the pH for long term electrolysis, which will affect the mediator generation process, finally reducing the removal efficiency. To avoid HF formation in the removal process, a binary metal complex or bimetallic complex was attempted, as reported in the catalytic combustion process for catalysts activation, for the MER of CF_4.

In the present investigation, a bimetallic complex $Cu^{2+}[Ni^{2+}(CN)_4]$ was used as a mediator precursor in the degradation of CF_4 gas. A cathodic half-cell in a divided electrolytic cell was used to generate a low valent active mediator generation in 10 M KOH medium using a constant current method. The electrolytic reduction of $Cu^{2+}[Ni^{2+}(CN)_4]$ was performed on an anodized Ti or TiO_2 cathode conducted in 10 M KOH. The oxidation/reduction potential (ORP) of Cu^{2+} and Ni^{2+} in a dissolved electrolyzed solution during electrolysis were taken as an indication and quantification by a potentiometric titration separately for the formation of a low oxidation state active mediator. In addition, electron spin resonance (ESR) spectroscopy was used to support the differentiation of Cu^{2+} or Ni^{2+} reduction in an electrolyzed solution. CF_4 degradation was carried out at electro-scrubbing, where CF_4 was fed continuously at a controlled rate and concentration through the bottom of the scrubber and the spent bimetallic complex was then sent to a cathodic half-cell to generate a low oxidation state active mediator. The CF_4 removal efficiencies were monitored using an online Fourier transform infrared (FTIR) gas analyzer. Solution phase and gas phase analyses were conducted to determine the final product.

2. Experimental methods

2.1 Preparation of mediator precursor

$Cu^{2+}[Ni^{2+}(CN)_4]$ was prepared using the literature procedure (Chippindale *et al.* (2015)). Briefly, $Cu^{2+}(NO_3)_2.3H_2O$ and $Ni^{2+}(CN)_4^{2-}$ were added to 200 ml of water at a Cu^{2+} to Ni^{2+} mole ratio of 1:4. A light blue precipitate formed slowly with constant stirring, which was separated by filtration, washed several times with water and dried in a desiccator prior to use. $Ni^{2+}(CN)_4^{2-}$ was prepared using the existing literature procedure (Fernclius *et al.* (2007)). Briefly, $Ni^{2+}(NO_3)_2.6H_2O$ was taken at a 1:4 mole ratio (Ni^{2+} to cyanide) to KCN, which was already dissolved in 200 ml cooled water (extreme care was taken when handling the KCN during complex preparation because it is highly dangerous to humans). To this reaction solution, an equal volume of chilled alcohol was then added. The resulting thin orange platelets were filtered rapidly, washed with cold alcohol, recrystallized in ethanol, dried in a vacuum desiccator, and stored in an air-tight brown bottle.

2.2 Setup and procedure for mediator generation and degradation

A divided flow-through electrolytic cell was used, as in a previous publication (Muthuraman and Moon (2017)), under suitable additional conditions. Briefly, a 4 cm^2 working electrode area capacity thin layer plate and frame divided cell (divided with Nafion324) was connected to the catholyte (200 ml of mediator precursor in 10 M KOH) and anolyte (200 ml of 5 M H_2SO_4) glass tanks through polycarbon tubing to allow the anolyte and catholyte to circulate (using peristaltic pumps) through the respective anode and cathode compartments. The electrolysis experiments were conducted in constant current mode using a DC power supply. All solutions were prepared using reverse osmosis purified water (Human Power III plus, South Korea) with a resistivity of 18 MΩ-cm.

For the electro-scrubbing process, a 50 cm^2 electrode area capacity divided plate and frame electrochemical cell was connected to a 40 cm high and 5.5 cm (i.d) column packed with 1 cm^2 of Teflon tubes as the packing material on top of the catholyte tank (1 L capacity), as in the previous published literature (Muthuraman and Moon (2017)). The electrolyte solutions (500 ml) were circulated continuously to flow through the electrolytic cell at different flow rates (1 to 5 L min^{-1}) using magnetic pumps. The catholyte solution as a scrubbing solution (electrolyzed mediator in a KOH solution) was pumped separately into the scrubber column at a flow rate of 3 L min^{-1}. CF_4 gas (from RIGAS (1000 ppm), Korea) and N_2 mixtures, which were obtained by the controlled mixing of air and CF_4 gas using mass flow controllers (MFCs), were introduced to the bottom of the scrubber at a set gas flow rate. An online gas analyzer (FTIR) was attached to the scrubber exit to facilitate the instantaneous degradation measurements. Before each electrolysis experiment, the Ti electrode (cathode) was pretreated separately by an anodization process in 0.1 M KNO_3 at a constant current of 1 A for 5 min. All experiments were conducted at room temperature (20 ± 2 ℃).

2.3 Quantification of mediator ion

The electrolyzed solution containing the Cu^{1+} or Ni^{1+} concentrations were determined using a potentiometric titration method (Muthuraman and Moon (2017)). In the present case, the electrolyzed sample solution was titrated against a standard $Fe^{3+}(CN)_6^{3-}$ (From Sigma Aldrich, USA) solution (0.001 M) and the potential variation was monitored using an ORP (oxidation/reduction potential) electrode (EMC 133, 6 mm Pt sensor electrode and Ag/AgCl reference electrode containing a gel electrolyte) connected to an iSTEK multimeter. The initial catholyte ($Cu^{2+}[Ni^{2+}(CN)_4]$) solution potential was approximately -170 mV, which was then decreased as electrolysis progressed at a constant current density. By titration against 0.001 M $Fe^{3+}(CN)_6$, the initial ORP value showed that the Fe^{3+} concentration can be used to derive the concentration of Cu^{1+}, as shown in eqn. 2

Concentration of Cu^{1+} with respect to the initial Cu^{2+} in $Cu^{2+}[Ni^{2+}(CN)_4] = (C_{Cu2+} \times C_{Cu1+})/C_{Cu2+-Ni2+}$ --- (2)

2.4 Analysis

Gas phase online analysis was performed using an online FTIR gas analyzer (from MIDAC Corporation, USA). Solution phase sample analysis was carried out by attenuated total reflectance – Fourier transform infrared (ATR-FTIR, Thermo scientific, Nicolet iS5, USA) spectroscopy using a 2 µL drop of the reaction sample on the diamond sample holder to derive the products. To understand the change in oxidation state of the metal ion and its influence in CF_4 degradation process, ESR spectroscopy was performed with focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The ESR spectra were measured at the X-band (~9.7 GHz) and under liquid nitrogen conditions (77 K) with a Bruker EMX model spectrometer.

3. Results and discussion

3.1 Generation of reductive mediator

Fig.1 ORP variation during electrolysis of different mediator precursors in a 10 M KOH solution: (a) 50 mM $Cu(OH)_4^{2-}$; (b) 50 mM $[Ni^{2+}(CN)_4]$; (c) 50 mM $Cu^{2+}[Ni^{2+}(CN)_4]$ (Cu to Ni ratio 1:4). Electrolysis conditions: Electrodes (4 cm^2) = Pt (anode) and anodized Ti (cathode); Current density = 30 mA cm^{-2}; Solution flow rate = 70 ml min^{-1}. The insert figure shows the formation of Cu^{1+} from $Cu^{2+}[Ni^{2+}(CN)_4]$ during electrolysis under the
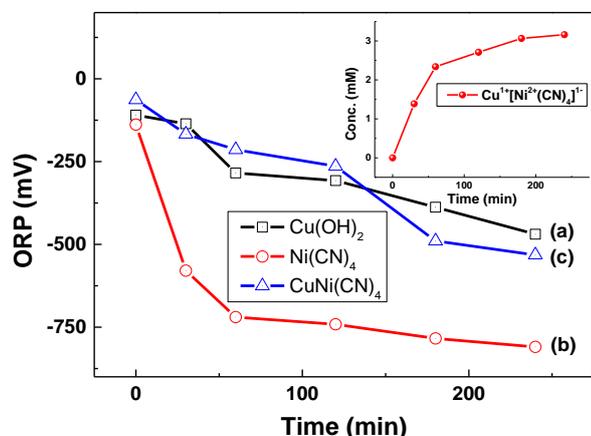
above conditions.

Fig. 1 shows the changes in ORP changes during the electrolysis of different mediator precursor containing the electrolyzed solution ($Cu^{2+}(OH)_4^{2-}$, $Ni^{2+}(CN)_4^{2-}$, and $Cu^{2+}[Ni^{2+}(CN)_4]$). The ORP values of the electrolyzed solution reached a maximum of -450 mV for $Cu^{2+}(OH)_4^{2-}$ in 1h electrolysis (Fig. 1 curve a). In the case of the $Ni^{2+}(CN)_4^{2-}$ electrolysis, the ORP value reached approximately -800 mV in 1h (Fig. 1 curve c). On the other hand, the ORP value of the $Cu^{2+}[Ni^{2+}(CN)_4]$ electrolyzed solution was ~ − 500 mV after 1h electrolysis indicating that Cu^{2+} is reduced instead of Ni^{2+} in the heterobimetallic complex. To confirm whether Cu^{2+} is reduced, the electrolyzed solution of $Cu^{2+}[Ni^{2+}(CN)_4]$ was analyzed by ESR and the results are shown in Fig.2. The ESR spectra showed a typical pattern for the polycrystalline Cu^{2+} ion

having near axial symmetry with $g_{xx} \approx g_{yy}$ (~2.04) and g_{zz} (~2.26) and $A_{xx} \approx A_{yy}$ (~ 35 G) and A_{zz} (~190 G) values.
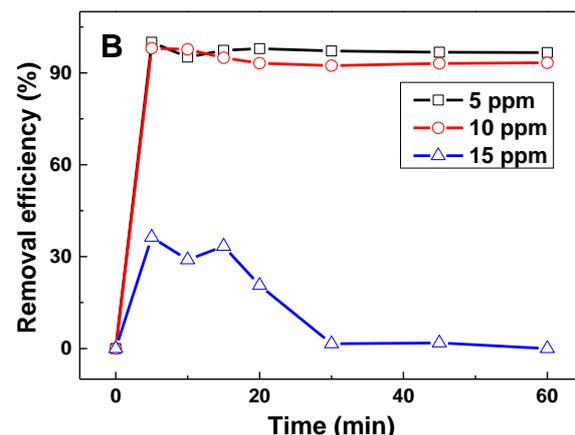
The g values and A_{xx}, A_{yy} and a large A_{zz} value, which is greater than 140 G confirmed the Cu^{2+} complex with a square-planar geometry (Savelieff *et al*. (2008)) (Fig.2 curve a). On the other hand, its reduced monovalent Cu^{1+} species was ESR silent. Therefore, at the same time, the electrolyzed $Cu^{2+}[Ni^{2+}(CN)_4]$ samples showed a reduced intensity without a change in the symmetrical values indicating Cu^{1+} formation with square planar geometry (Fig.2 curve b). The inset figure in Fig.1 shows the changes in Cu^{1+} concentration with electrolysis time. The Cu^{1+} concentration reached a maximum of 3.1 mM out of
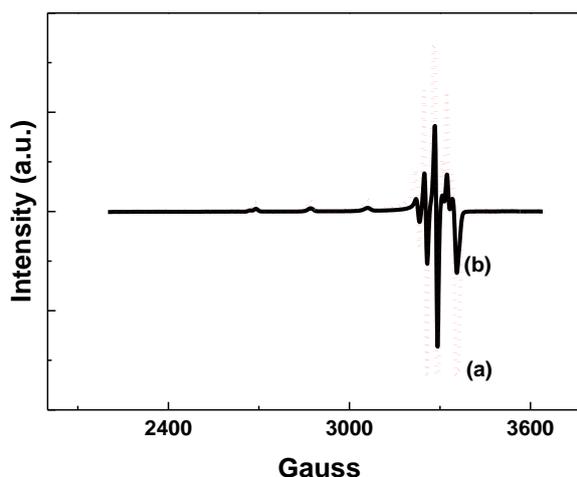
12 mM in the bimetallic complex under the given conditions.

Fig.2 ESR spectra of frozen $Cu^{2+}[Ni^{2+}(CN)_4]$ in a 10 M KOH solution (a) before and (b) after electrolysis. The electrolysis conditions were the same as in legend of Fig.1.

3.2 CF₄ degradation

Once the Cu^{1+} concentration reached approximately 3 mM by electrolysis, the electrolyzed solution of $Cu^{1+}/Cu^{2+}[Ni^{2+}(CN)_4]$ was pumped into the scrubbing column through the top of the scrubbing column. Subsequently, 10 ppm of CF_4 was injected at 0.2 L min^{-1} into the bottom of the scrubbing column, while electrolysis was continued to regenerate the Cu^{1+}. Fig. 3 shows the results obtained under these conditions; there was almost 0 ppm at the scrubber and 0.2 ppm of CF_4 started come out at the scrubber exit in 1h, which is equal to a removal efficiency of 96%. This explains CF_4 removal at room temperature by the electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]$ is

possible. Noteworthy here that CF_4 absorption into a 10 M KOH solution reached saturation in 5 min (Muthuraman and Moon (2017)). The Cu^{1+} concentration variation during the CF_4 removal process can determine if the electrogenerated Cu^{1+} is involved in the CF_4 removal reaction.
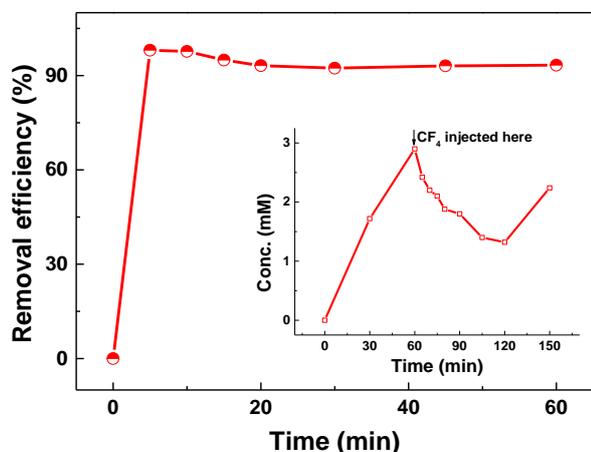
Fig.3 CF_4 removal efficiency variation during electro-scrubbing by scrubbing a solution of electrolyzed $Cu^{2+}/Cu^{1+}[Ni^{2+}(CN)_4]^{1-/0}$ solution. Conditions: Feed concentration of CF_4 = 10 ppm; Gas flow rate = 0.2 L min^{-1}; Scrubbing solution flow rate = 3 L min^{-1}. Solution flow rate to electrolytic cell = 2 L min^{-1}; Current density = 30 mA cm^{-2}; Electrodes area = 50 cm^2. Insert figure shows electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ concentration variation during removal of CF_4 pollutant.

The insert figure of Fig.3 shows that there is a decrease in Cu^{1+} concentration from 3.1 mM to 2.1 mM while inject 10 ppm of CF_4 into the scrubber that then decreases further to 1.2 mM in 1h CF_4 removal time. This suggests that the CF_4 removal reaction follows the MER by electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$.

Fig. 4A presents the CF_4 removal at different gas flow rates. Initially, there was almost 100% removal of CF_4 up to 1 L min^{-1}, but this decreased to 55% with increasing gas flow rate at later removal times. The decrease in CF_4 removal efficiency at high gas flow rates could be because the feed CF_4 is higher than the generation rate of Cu^{1+}.
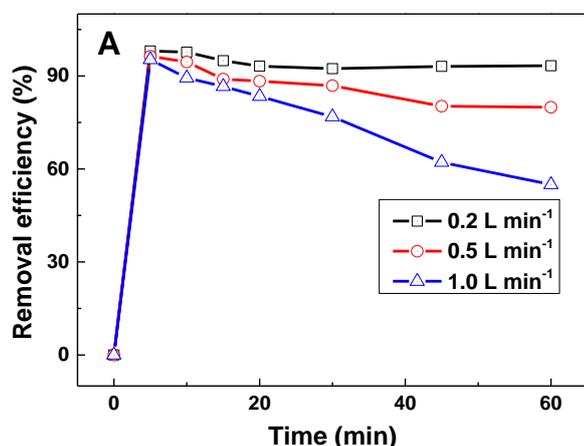
Fig.4 (A) Effect of the gas flow rate (mentioned in the figure) with time on the removal of CF_4 using

electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ in a 10 M KOH solution at electro-scrubbing. (B) Effect of the CF_4 feed concentration variation with time on its removal by electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ in 10 M KOH solution by electro-scrubbing. The remaining experimental conditions are the same as in the legend of Fig.3.

In the case of a feed concentration variation, up to 10 ppm of CF_4 feed showed almost 95% removal efficiency (Fig.4B curve a & b). Beyond 10 ppm of CF_4, the removal efficiency was approximately 40% at the initial stages but then decreased to 0% removal efficiency in 30 min (Fig.4B curve c), which explains the Cu^{1+} generation rate does not at all meet the feed CF_4 concentration or a 10 ppm CF_4 feed is optimum at the given conditions.

3.3 Product identification
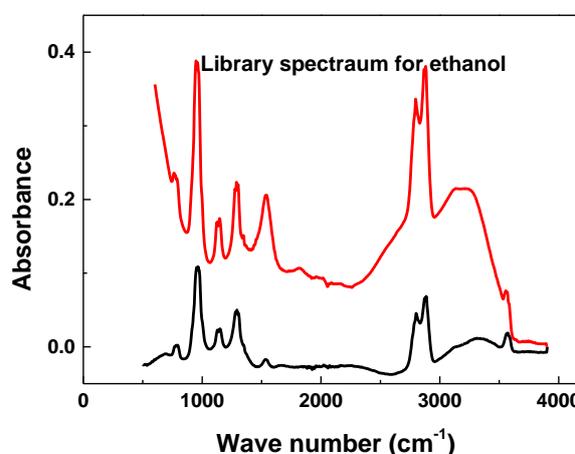
Fig.5 Online FTIR gas analyzer results of the exit gas products (mentioned in the figure) during CF_4 removal at electro-scrubbing by electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ in 10 M KOH solution by electro-scrubbing. The remaining experimental conditions are the same as in the legend of Fig.3.

According to Fig.3, almost 95% CF_4 removal was achieved from the beginning of the removal process, but no products were observed at the scrubber in the first 30 min (Fig.5). After 30 min, a huge concentration of ethanol (CH_3CH_2OH) suddenly emerged at the scrubber exit at approximately 125 ppm (Fig.5 curve a). In a similar time interval, trifluoroethane (CH_3CF_3) began to exit around 10 ppm (Fig.5 curve b). Surprisingly, no HF was coming out of the scrubber. Interestingly, no greenhouse gases were observed in the exit gas (Fig.5 curve c). Note that ethanol and HF were produced from the beginning of the removal process while the electrogenerated Co^{1+} mediator was used to remove CF_4 gas (Muthuraman and Moon (2017)). The CF_4 removal process followed mediated degradation to soluble products that exited after a saturation point was attained, which could explain the late exit of CH_3CH_2OH and CH_3CF_3. The scrubbing solution underwent an ATR-FTIR analysis after the electro-scrubbing process was completed and reaction solution showed only CH_3CH_2OH present (-O-H and -C-O stretching frequencies well matched with the instrument library CH_3CH_2OH sample) in solution (Fig.6), confirming that the reaction product is CH_3CH_2OH. Many electrochemical reports have shown

that CFCs form CH_4 and fluorine-reduced derivatives, such as CF_3CH, CH_2F_2, CH_3F, and CF_2CFCl (Schizodimou *et al.* (1999); Wagoner *et al.* (2012); Cabot *et al.* (2003); Taylor-Smith and Sayres (1999)), but there are no reports on the formation of CH_3CH_2OH during the degradation of CF_4. Recently, direct ethanol formation was observed on a copper electrode during the reduction of CO_2 through carbon dioxide dimer formation (Song *et al.* (2016); Kuhl *et al.* (2012)). Similarly, a carbon tetrafluoride dimer could have formed via the electrogenerated Cu^{1+}, which might have easily hydroxylated to ethanol, because the scrubbing solution is 10 M KOH, as shown by the proposed scheme 1. The possibility of dimerization was confirmed by the additional product CF_3CH_3 (Fig.6 curve b) found at the scrubber exit, which may be due to incomplete reaction or intermediate formation.

$$CF_4 \xrightarrow[\text{in 10 M KOH}]{\substack{\text{Electrogenerated}\\ Cu^{1+}[Ni^{2+}(CN)]^{1-}}} \underset{\text{Intermediate}}{CF_3CH_3} \longrightarrow \underset{\text{Product}}{CH_3CH_2OH + 2F_2}$$

Scheme 1 Plausible reaction pathway for CF_4 degradation to ethanol

Fig.6 Subtracted (from before and after electro-scrubbing) solution phase offline ATR-FTIR spectrum for the product formed in the solution during the removal of CF_4. The experimental conditions are the same as in the legend of Fig.3.

4. Conclusions

Electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ successfully degraded CF_4 to ethanol without forming HF. The electrogeneration of Cu^{1+} from the bimetallic complex of $Cu^{2+}[Ni^{2+}(CN)_4]$ was identified and confirmed by the ORP variation in ESR spectroscopy. The Cu^{1+} concentration variation during the injection of CF_4 into the scrubber column or the CF_4 removal process confirmed the mediated reduction. The online and offline FTIR analyzer results demonstrated that CH_3CH_2OH is a final product along with an intermediate or incomplete product CF_3CH_3 during the degradation of CF_4 using the electrogenerated $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ in a highly KOH medium.

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