



Development of Novel Approaches to Rejuvenate Degraded PEI Adsorbents with Catalytic Hydrogenation

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Abstract. PEI immobilized solid adsorbents are highlighted to be used in carbon capture technology due to its high CO₂ selectivity, suitable adsorption temperature and tolerance of moisture. However, the oxidation and degradation of PEI are still a hard nut to crack, which is the main limitation of PEI adsorbents application. Oxygen-containing functionalities formation, urea formation and amine group loss in result in the PEI carbon capture ability and CO₂ selectivity reduction. Effective measures that can be potentially used to rejuvenate the spent PEI adsorbents is of great importance to further improve both the economic and environmental performance of carbon capture technologies. However, little work has been conducted on how or if the degraded PEI can be effectively rejuvenated or converted to other value-added products. A new approach for PEI rejuvenation were proposed by catalytic hydrogenation, which improve the degraded PEI carbon capture ability to equal to that of the original PEI. After the catalytic hydro-treatment, the majority of degradation-derived carboxyl and amide groups were reduce to hydroxy and amine group, which increase adsorption active site of degraded PEI. But, the amine group loss lead to the heavily degraded PEI carbon capture ability just was improve to the 60% of the original PEI.

Keywords: Carbon Capture, Degraded PEI, Rejuvenation.

1 Introduction

Carbon capture storage technology (CCS) is widely regarded as being the critically important technology that can dramatically cut CO₂ emissions without compromising energy security. More than 3000 CCS projects will be required around the world in order to achieve the target of 50% reduction in CO₂ emissions by 2050 [1]. Solid adsorbents looping technology are currently under intensive development as an alternative technology to aqueous amine scrubbing, it has been widely recognised as having the potential to be a viable post-combustion capture technology with significantly reduced energy penalty and improved process efficiency. Of all the adsorbents being developed, polyethyleneimine (PEI)-based solid adsorbent systems, including both supported and grafted PEIs, have received the most attention, due to their high carbon capture capacity, high CO₂ selectivity, favourable adsorption temperatures, and higher

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regeneration and recycling stability [2-5]. Meanwhile, the siliceous mesocellular foam is one of the appropriate supports due to its high surface area, large pore volume, narrow pore size distribution, and excellent regeneration stability [6]. Therefore, PEI-silica adsorbent is a typical amine-based adsorbent for the CCS technology.

The main limitation of PEI based adsorbents/adsorbents is the degradation in the adsorption or absorption and desorption process. There are two kinds of PEI degradation: thermal degradation and oxidative degradation. The degradation of PEI adsorbent can reduce the carbon capture capacity, CO₂ selectivity and regeneration and recycling stability and increase the cost. Owing to high percentage of primary amine group in branch PEI, the thermal degradation and oxidative degradation mechanisms are similar to the mechanisms of MEA. Therefore, the main PEI thermal degradation products contain hydroxyl, carbonyl, methoxy group and the main PEI oxidative degradation products contain oxygen functional groups, such as hydroxyl, carbonyl, aldehyde, carbonate ester, carboxyl, ester, imide, nitroso, nitro et al [7-9].

All amine-based adsorbents for CO₂ capture will ultimately reach their working life, despite the improved thermo-stability that can be potentially achieved with various types of measures that have examined above and in other investigations [10-13]. Therefore, effective measures that can be potentially used to rejuvenate the spent amine adsorbents is of great importance to further improve both the economic and environmental performance of carbon capture technologies. However, no such investigations have been carried out to the best of our knowledge to date. In this paper, an exploratory investigation has been performed to examine the potentials of using catalytic hydrogenation to rejuvenate the degraded PEI adsorbents carbon capture ability to equal to that of the original PEI under 50bar hydrogen and blow 200 °C.

2 Methodology

2.1 Chemicals

Polyethyleneimines (PEI, Mw=600), platinum nitrate (Pt(NO₃)₂, 15%w/w) were obtained from Sigma-Aldrich. PQ silica (269m²/g, 1.7cm³/g) and 40%PEI-PQsilica was supplied by PQ Corporation.

2.2 Preparation of Adsorbents and Catalyst

2.2.1 Synthesis of PEI-PQ silica

0.5g PEI was dissolved in 10ml water with vigorous stirring. After 15mins, 0.5g PQ silica was gradually poured into the solution. The mixture was stirred overnight at room temperature. Then the mixture was dried at 40°C in a vacuum oven. After 24 hours, the impregnated adsorbents were collected for further testing.

2.2.2 Synthesis of degraded PEI

The degradation product of PEI-silica solid adsorbents is prepared in the simulated gas-fired flue gas stream (5% CO₂/12% O₂ in N₂) at a temperature of 75 °C by 20

days. Then, the degraded PEI was washed off from oxidative PEI-silica adsorbents by methanol. The degraded PEI methanol solution was stirred overnight at room temperature. After that, the mixture was dried at 40°C in a vacuum oven. After preparation, the chemical structure of obtained products will be further tested.

2.2.3 Synthesis of Pt-PQ Silica Catalyst

757 mg of 15% platinum nitrate and 1 g PQ silica was added into 5ml deionized water and the mixture was stirred overnight at room temperature. Then the mixture was dried at 40°C in a vacuum oven. The Pt-PQ silica catalyst was then subjected to calcination at 500 °C in air for 5 hours, followed by a reductive treatment at 300 °C in H₂ (100 ml/min) for 2 hours to yield the final Pt-silica catalyst.

2.2.4 Synthesis of Oxidative PEI-Catalyst adsorbent

0.5g degraded PEI was dissolved in 10ml water with stirring. After 15mins, the 0.5g catalyst was gradually poured into the solution. The mixture was stirred overnight at room temperature. After that, the mixture was dried at 40°C in a vacuum for 24hours. Then, the sample was collected for further testing.

2.3 Degraded Sorbents rejuvenation

The oxidative degraded PEI-silica solid adsorbents reacted by hydrogen with/without catalyst in 175°C or 200 °C and 50bar by Hydrolysis(HyPy). As to evaluate the effect of rejuvenation, the characterisations of products are carried out in terms of the carbon capture capacity and their chemical structure.

2.4 Characterizations of adsorbents and degraded PEI

2.4.1 CO₂ adsorption experiment

The CO₂ adsorption capacity of the adsorbents was examined by Thermogravimetric Analyser (TGA) Q500. Prior to adsorption experiment, the sample (15-20mg) was preheated to remove any moisture by keeping isothermal at 115°C under a nitrogen flow of 105ml/L and then the temperature was set to adsorption temperature which is 75°C at 25°C/min. With the aim of testing the availability of PEI impregnated silicas for both coal-fired power plants, the CO₂ adsorption experiments were implemented with 15% CO₂/N₂.

2.4.2 Characterizations of degraded PEI and rejuvenated PEI

The surface functional group of degraded PEI and rejuvenated PEI were measured by FTIR (Nicolet iS10, Thermo Scientific) and 13C NMR (Ascend 400).

3 Result and discussion

3.1 Degraded PEI

The sorbent materials were sampled periodically for CO₂ adsorption measurements. Fig. 1 shows that the CO₂ capacity decreased continuously during the 20 days of the accelerated degradation tests, while the sorbent changed in colour from white to dark brown in just 10 days. The CO₂ uptake capacity decreased by nearly 30% in just 6 days, from its initial capacity of 9.47 % to 6.80 %. There appears to be a sharp decrease in CO₂ uptake when degradation reached a critical stage. The CO₂ uptake of the PEI adsorbents decreased drastically from 6.80 wt% to 2.81 % when the duration time of the accelerated test increased from 6 days to 15 days, and to just 1.3 wt% when the duration time increased to 20 days. This gave rise to a cumulative loss in CO₂ capacity of 86% in 20 days, an average loss of 4.3 % per day, highlighting the severe oxidative degradation of the PEI adsorbents in the simulated gas-fired flue gas stream. Therefore, anti-oxidative degradation measures must be taken to mitigate the impact of the oxidative flue gas conditions, particularly for the natural gas fired power plants where the excess O₂ levels are usually significantly higher than those of coal-fired power plants.

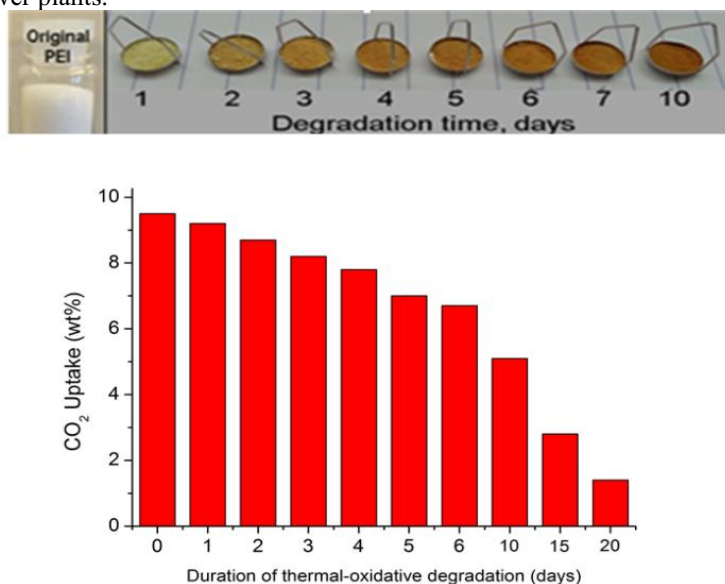


Fig. 1. Variation of CO₂ adsorption capacity with duration times of the accelerated degradation test with large quantities of PEI adsorbents in a horizontal furnace at 75 °C in 5% CO₂/12% O₂ in N₂.

Fig. 2 presents the Fourier transform Raman spectra for the 40% PEI-600-silica adsorbent after subjected to different period of the thermo-oxidative degradation in 5% CO₂/12% O₂/N₂ at the typical adsorption temperature of 75 °C. It indicates that a vari-

ety of functionalities arising from the thermo-oxidative degradation were observed and with their intensity increasing with increase in the duration times of the degradation treatment, including the cyclic urea (1663 cm^{-1}), open-chain urea (1628 cm^{-1}), oximes/imines (1600 cm^{-1} , $\text{R}_1\text{R}_2\text{C}=\text{NOH}$ and $\text{R}_1\text{R}_2\text{C}=\text{N}$), hydroxyl (900-1200 cm^{-1}) and carboxylic groups (1256 cm^{-1}) etc. It is noteworthy that the formation of carboxylic groups became significant after the PEI adsorbent was subjected for 6 days to the thermo-oxidative adsorption environment. This finding is consistent with the results shown in Fig. 1 where the loss in CO_2 capacity was found to accelerate dramatically also after 6 days treatment.

To further reveal the chemical constitution of the degradation products, aqueous NMR spectroscopy was used to characterise the degraded PEI isolated via Soxhlet extraction with methanol from the PEI sorbent after the thermo-oxidative treatment for 10 days. Fig. 3 shows the ^{13}C NMR spectra for the selected samples. Being consistent with the FTIR results, a range of carboxylic and amide compounds or functionalities were identified in the PEI extracts, as shown by the peaks between 160 and 180 ppm. Carboxylic groups acidify the sorbent surface and/or react with amine groups to form amides, thus de-activating the PEI sorbent. In addition, compared to the undegraded PEI, the amine functional groups present in the degraded PEI sorbent also appeared to be chemically altered as can be seen from the complex peaks obtained, which may also inevitably impact the CO_2 adsorption performance.

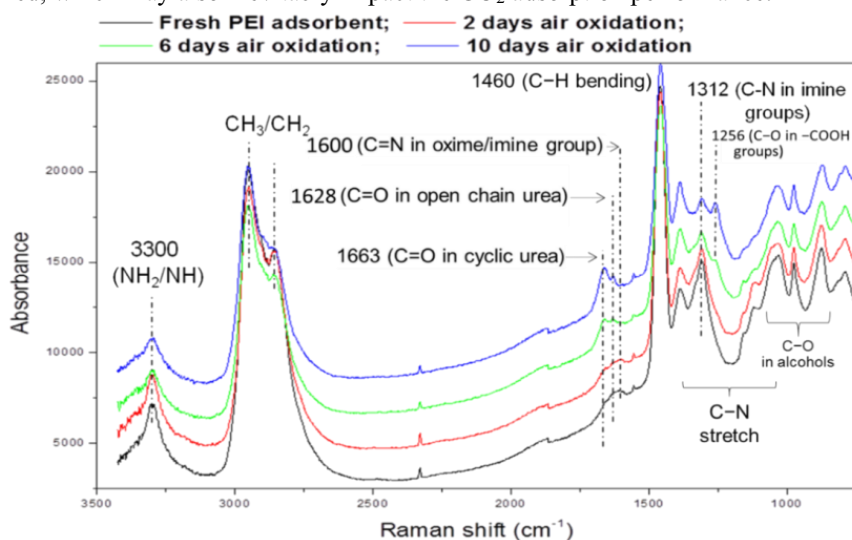


Fig. 2. Fourier transform FTIR Spectra of the PEI sorbents after subjected to different periods of thermo-oxidative degradation in 5% $\text{CO}_2/12\% \text{O}_2/\text{N}_2$ at 75 °C.

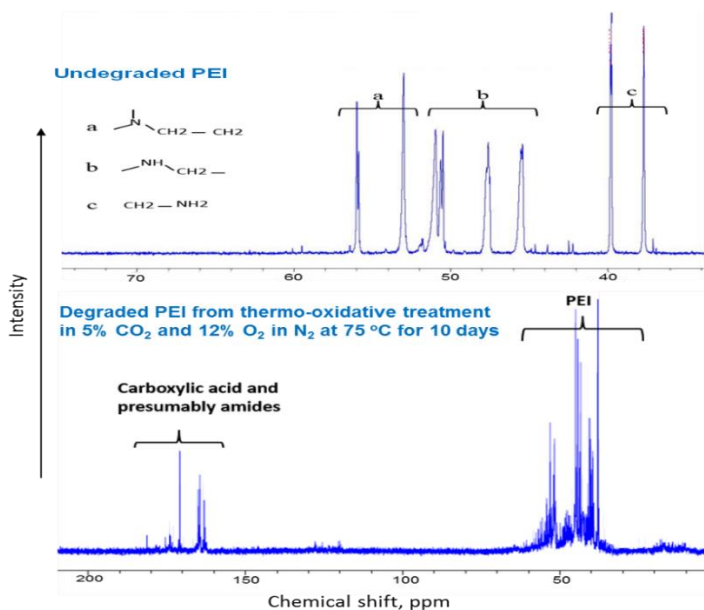


Fig. 3. Aqueous ^{13}C NMR spectra of PEI adsorbent before and after the thermo-oxidative treatment in 5% CO_2 /12% O_2 / N_2 at 75 °C

3.2 Rejuvenation of heavily degraded PEI adsorbents with catalytic hydrogenation

Two of the degraded PEI sorbent samples were selected for rejuvenation, including the one from the 4 days thermo-oxidative treatment (silica-PEI-600-4) and another from the 15 days treatment (silica-PEI-600-15) in 5% CO_2 /12% O_2 / N_2 at 75 °C. The degraded PEI amine were first recovered from the silica support by washing with methanol and the recovered PEI amine from each sample was then subjected to HyPy with the above mentioned silica-supported Pt as the catalyst. The rejuvenated PEI amine was then re-used for preparing the silica-PEI sorbent following the same procedures as used for preparing the original PEI sorbent.

Fig. 4 shows the performance of rejuvenated samples. It can be seen that for the less degraded amine sample, silica-PEI-4, the CO_2 uptake performance can be largely restored with the capacity increased from 7.8 wt% to ca. 9.3 wt%, which is essentially equal to that of the original sorbent sample (ca. 9.5 wt%). For the more heavily degraded sample of silica-PEI-15, a much greater performance improvement was obtained, with its CO_2 capacity increased remarkably to 6.2 wt% after the rejuvenation with HyPy, more than doubled the 2.8 wt% of the original degraded sample before rejuvenation. However, it must be noted that despite the great improvement, the CO_2 uptake capacity of the rejuvenated silica-PEI-15 sample is still significantly lower than that of the original sorbent before degradation (9.47 wt%). This indicates that higher reaction temperatures may be needed to effectively remove the oxygen and

other functionalities present in the heavily degraded sample, but this may risk the amine groups being removed altogether or the amines being totally destroyed at higher hydrogenation temperatures. It is therefore believed that the functionalities formed at early stages of degradation may undergo transformation to form more stable structures as the degradation proceeds further. The above results demonstrate that once heavily degraded, such as the one silica-PEI-600-15, the PEI-based adsorbents could be more difficult to rejuvenate, compared to degraded lower molecular mass amines that could be easier to restore their CO₂ adsorption performance via potential measures, such as steam treatment[14]. Therefore, for heavily degraded silica-supported PEI adsorbents, it may be more economical to recover the porous silica substrate that can be re-used for sorbent preparation with fresh PEIs.

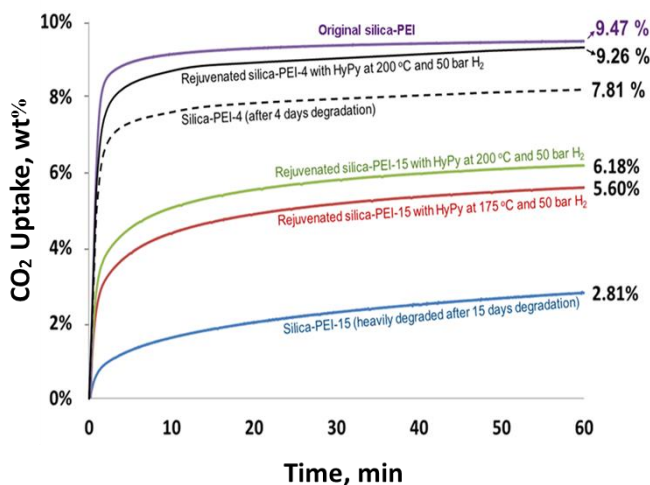


Fig. 4. CO₂ uptake performance of degraded PEI amines before and after rejuvenation with catalytic HyPy at different temperatures.

Aqueous ¹³C NMR spectroscopy was applied for the structural characterisation of selected PEI samples from the catalytic rejuvenation tests, and Fig. 5 shows the ¹³C NMR spectra for the selected samples, including the undegraded PEI-600 and the degraded samples before and after the catalytic hydro-treatments. As shown in Fig. 5(A), the undegraded PEI contained a range of aliphatic primary amine (40–43 ppm), secondary amine (50–53 ppm) and tertiary amine functional groups (54–60 ppm)[15]. It is evident from Fig. 6.30(B) that the 15 days thermo-oxidative treatment of PEI (PEI-600-15) in 5% CO₂/12% O₂/ N₂ led to the formation of a variety of new functionalities exhibiting peaks between 160 and 180 ppm, including carboxylic acids and carboxamides and ketones, while the chemical constitution of the amine functionalities in the degraded PEI became much more complicated. Fig. 5(C, D) indicate that the majority of degradation-derived carboxyl and amide groups were removed after the catalytic hydro-treatment and the presence of these functionalities became negligible when the hydrogenation temperature increased from 225 to 275 °C. However, it was also found that despite the mild hydrogenation conditions used, the loss of some

of the amine functionalities appeared to inevitable as highlighted by the formation of a range of alkyl groups, which increased with increasing hydrogenation temperatures. This explains, at least partly if not wholly, why the CO₂ capacity of the heavily degraded PEI sorbents could not be fully restored, despite the near complete removal of the degradation-derived functionalities under the mild conditions used.

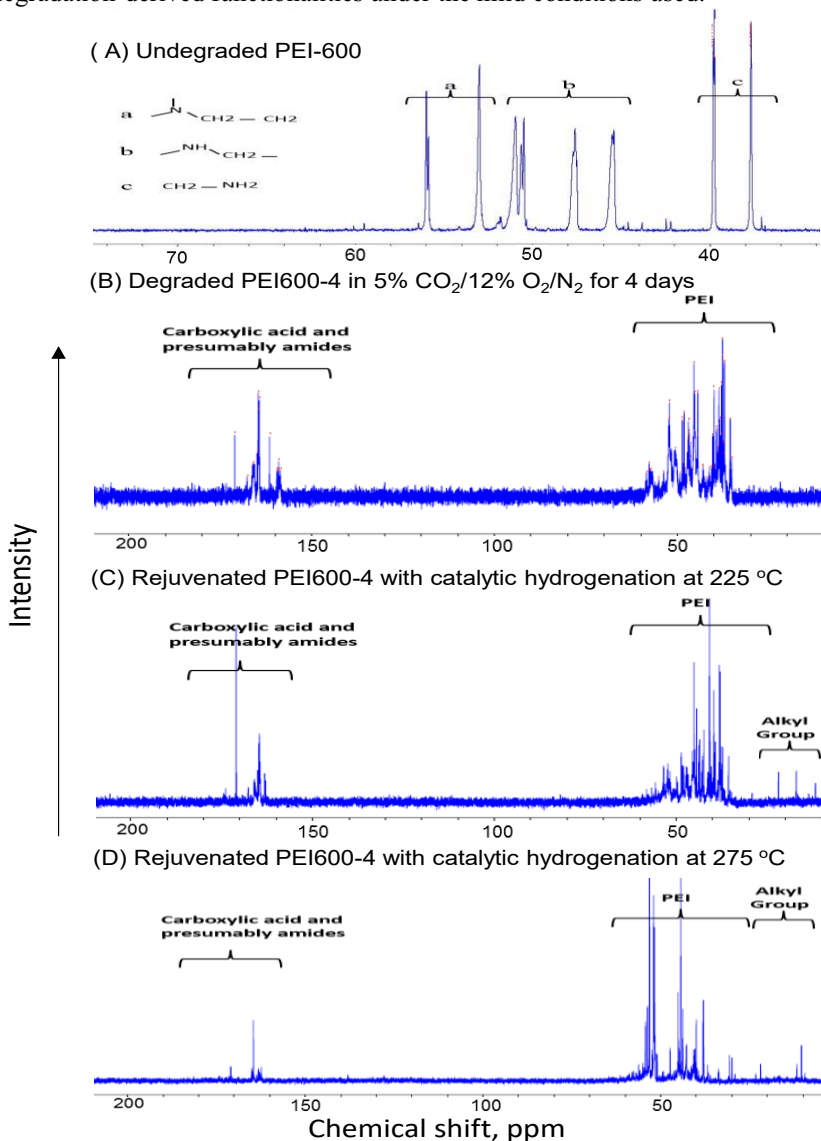


Fig. 5. Aqueous ¹³C NMR spectra for selected degraded PEI samples before and after catalytic hydro-treatments.

4 Conclusion

In accelerated oxidative degradation tests, the color of PEI adsorbent was change from white to dark brown in just 10 days. Although the carbon capture capacity of PEI decreased by nearly 30% in just 6 days, which result from the formation of urea and oxygen-containing functional group, the amine group in PEI also have been kept. However, after 6 day oxidative degradation tests, the carbon capture capacity of PEI drop sharply due to the amine group loss. Thus, the degraded PEI after 6day oxidative degradation tests can be considered as severely degraded PEI.

The exploratory investigation also found that catalytic hydrogenation could be effectively used to rejuvenate degraded PEI sorbent samples, the loss of carbon capture ability due to the formation and accumulation of urea and other thermo-oxidative degradation products which can be largely restored. However, for severely degraded PEI sorbents, the sorbent de-activation appears to be unlikely to be reversed with catalytic hydrogenation due to the inevitable loss of functional amine groups during hydrogenation even under mild conditions. Therefore, it may become uneconomical to rejuvenate the heavily degraded PEI sorbents. As a result, the recovery of the porous silica substrate for preparing new PEI sorbent materials, rather the rejuvenation of the supported PEIs, could be more economical.

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