Limitation of $\text{K}_2\text{CO}_3$ as a Chemical Agent for Upgrading Activated Carbon

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Abstract: The chemical activation of a carbon precursor with KOH generally results in an activated carbon (AC) with a high specific surface area. However, this process generates a large volume of wastewater that includes dissolved alkali metals, existing mainly as $\text{K}_2\text{CO}_3$. Thus, wastewaters with a high concentration of dissolved $\text{K}_2\text{CO}_3$ can potentially be used in place of KOH as a chemical agent. In the present study, to reduce the thermal stability of $\text{K}_2\text{CO}_3$, which decomposes at temperatures greater than 891 °C, $\text{K}_2\text{CO}_3$ was chemically impregnated into carbon precursors prior to activation of the precursors. The thermochemical properties and activation efficiency of the carbon precursors treated with $\text{K}_2\text{CO}_3$ were compared with those of carbon precursors treated with KOH. Analysis by XPS indicated that C–O–K complexes formed on the surface of the carbon precursors; in addition, their peak intensities were approximately the same irrespective of the chemical agent used. However, the specific surface area of the $\text{K}_2\text{CO}_3$-impregnated AC was 2162 m$^2$/g, which was ~70% of that of the KOH-impregnated AC (3047 m$^2$/g) prepared using the same K/C molar ratio of 0.5. XRD results confirmed that both $\text{K}_2\text{CO}_3$ and KOH transformed into KHCO$_3$ and $\text{K}_2\text{H}_2\text{(CO}_3\text{)}_3\cdot 1.5\text{H}_2\text{O}$ during the impregnation. The peak intensities of these compounds in the XRD pattern of the $\text{K}_2\text{CO}_3$-impregnated carbon precursors were two times greater than those in the pattern of the KOH-impregnated carbon precursors. These compounds eventually transformed into $\text{K}_2\text{CO}_3$, which hardly participated as a chemical agent at the temperature used in the present study (880 °C). Therefore, recrystallisation of $\text{K}_2\text{CO}_3$, even during the impregnation, appeared to adversely affect the degree of activation. Nevertheless, the specific surface area of the $\text{K}_2\text{CO}_3$-activated AC was still ~1.6 times greater than that of the untreated carbon precursor (1378 m$^2$/g), suggesting that the use of wastewater as a chemical agent is feasible for resource recycling.

Keywords: activated carbon; chemical activation; KOH; $\text{K}_2\text{CO}_3$; impregnation; recycling

1. Introduction

Activated carbon (AC) has many reactive sites on its surface; it is therefore widely used as an adsorbent in the medical, automotive, water purification, and air-quality-control industries $^{[1,2]}$. The AC market in Korea is divided into price-leading and technology-leading markets $^{[3]}$. In particular, the demand for AC with a specific surface area greater than 2000 m$^2$/g has been increasing rapidly because of strengthened air-quality regulations. According to the Korea International Trade Statistics $^{[4]}$, the amount of high-specific-surface-area AC imported in 2018 was ~5000 tonnes (~9.1% of the total imported AC) and originated from two specific countries (i.e., the United States and Japan).

Both physical and chemical activation processes are used to prepare AC. However, harsher conditions (e.g., a longer residence time and a higher loading of reagents) are necessary to prepare AC with a high specific surface area. This phenomenon is more pronounced with physical activation, where pores are developed by oxidative gases (i.e., steam and $\text{CO}_2$). Chemical activation has advantages over physical activation with respect
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2. Materials and Methods

2.1. Preparation of Carbon Precursors and Chemical Activation

The carbon precursor in this study was commercial AC (JIG-SC-2040 BT, JAYEON SCI., Korea), which was produced from wood and exhibited a specific surface area of approximately 1378 m²/g. It has relatively high moisture (13.0%) and volatile (18.2%) contents while fixed carbon is about 63.4%, which is different from that of coconut-based AC [16]. For chemical activation, two types of K compounds (KOH, K₂CO₃) were used. Prior to the chemical activation, ~30 g of AC was mixed with 200 mL of K compound solution and then impregnated in a rotary evaporator (N-1300, Eyela, Japan); the K/C molar ratio...
ratio was varied. After evaporation of the solution, the samples were dried at 105 °C for 24 h in preparation for activation. Five grams of impregnated carbon precursor was placed in a tubular furnace under flowing N\textsubscript{2}, and the temperature of the furnace was increased at 5 °C/min until the activation temperature (850 °C) was reached; the activation temperature was then maintained for 2 h. After the activation was terminated, the sample was washed with distilled water several times until the leachates were neutral to remove impurities.

2.2. Analytical Methods

To identify thermal properties of activators and carbon precursors impregnated, thermogravimetric analysis (TGA) was performed. All of the samples were heated to 1000 °C at a rate of 1 °C/min under a N\textsubscript{2} atmosphere. To quantify the amount of K impregnated onto the carbon surface, we used X-ray fluorescence (XRF) spectroscopy (Shimadzu, Japan). The surface properties of the carbon were characterised by XPS (K-Alpha+, Thermo Fisher, Waltham, MA, USA) and X-ray diffraction (XRD, SmartLab, Rigaku). The specific surface area was measured by N\textsubscript{2} adsorption (ASAP-2010, Micromeritics, Norcross, GA, USA) at −196 °C.

We confirmed the pore distribution by varying the relative pressure (P/P\textsubscript{0}) of the specimen after pretreatment and calculated the sub-segment distribution using the Dubin–Astakhov formula and the Barrett-Joyner–Halenda method for intermediate and large-scale machining. The porous size distribution (PSD) was calculated using the density functional theory.

3. Results and Discussion

3.1. Changes in Thermal Stability of Chemical Agents

Figure 1 shows the TGA results for the commercial AC used as a carbon precursor, the chemical activation agents (KOH and K\textsubscript{2}CO\textsubscript{3}), and the AC impregnated with chemical agents. The weight losses of the specimens activated using KOH and K\textsubscript{2}CO\textsubscript{3} reflect the different thermal properties of the activating agents. K\textsubscript{2}CO\textsubscript{3} did not function as an activating agent at 850 °C because of its high thermal stability relative to that of KOH. However, the initial point of weight loss, which indicates the decomposition temperature, for AC impregnated with K\textsubscript{2}CO\textsubscript{3} shifted ~200 °C lower than that of K\textsubscript{2}CO\textsubscript{3}. In fact, the TGA curves for the AC samples impregnated with agents varied depending on the carbon-to-agent ratio in the mixture. Thus, the TGA curves for this type of mixture are generally plotted along with the thermal properties of the two materials. However, at temperatures greater than 750 °C, the AC impregnated with K\textsubscript{2}CO\textsubscript{3} exhibited a greater weight loss than the sample containing untreated AC. Given that K\textsubscript{2}CO\textsubscript{3} exhibits negligible weight loss until 891 °C because of its thermal stability, the greater weight loss of the K\textsubscript{2}CO\textsubscript{3}-impregnated compared with that of the untreated AC indicates that the thermal properties of K\textsubscript{2}CO\textsubscript{3} changed as a result of the impregnation. These results indicate that K\textsubscript{2}CO\textsubscript{3} dissolved in wastewater from the chemical activation with KOH can be reused through the impregnation process.

![Figure 1. Thermogravimetric analysis results of chemical agents and carbon precursors impregnated with each chemical.](image-url)
3.2. Changes in Surface Properties of Carbon Precursors Impregnated with KOH and K$_2$CO$_3$

3.2.1. XPS Analysis

Table 1 shows the XPS results used to verify the surface characteristics of the impregnated AC precursors. The XPS results confirm that the O and K contents of the samples increased with increasing amount of impregnated alkali metal. Because the surface properties of the carbon precursors are associated with an oxidation–reduction reaction during the activation process [17,18], an increase in O, which is an electron donor, on the carbon surface will strongly affect the pore development of the carbon matrix. Kopyscinski et al. [19] and Quyn et al. [20] have both proposed that C–O–K bound during the alkali-metal (i.e., K$_2$CO$_3$) impregnation is reduced to C–K at the surface of the carbon body, accompanied by the generation of CO. Lee et al. [21] and Punsuwan et al. [22], who qualitatively and quantitatively measured the gases emitted during the KOH activation of AC, also confirmed that CO is the main syngas (K$_2$O + C → 2K + CO at 800–850 °C [17,18]).

Table 1. XPS survey analysis of the KOH/K$_2$CO$_3$-impregnated carbon precursors.

| Preparation of Carbon Precursors | K/C Ratio | C 1s (285.15 eV) | K 2p (294.25 eV) | N 1s (401.11 eV) | O 1s (532.73 eV) |
|----------------------------------|-----------|------------------|------------------|------------------|------------------|
| KOH impregnation                 | 0.5       | 27.1             | 9.17             | N.D              | 63.7             |
| K$_2$CO$_3$ impregnation         | 0.2       | 77.5             | 0.99             | 0.89             | 20.6             |
|                                  | 0.4       | 34.0             | 17.2             | 1.09             | 47.7             |
|                                  | 0.5       | 23.9             | 8.19             | N.D              | 67.9             |

To more closely investigate these binding properties of the carbon precursors, we deconvoluted the K and O peaks in the XPS spectra (Table 2). The K peak was deconvoluted into two peaks with binding energies of 293.0 eV (K 2p$_{3/2}$) and 295.6 eV (K 2p$_{1/2}$). The peaks for each of these main peaks were further deconvoluted into two peaks, which were identified as the K component of K–O bound to the surface (K$_o$) and K surrounded by carbonate (K$_{CB}$) [19]. These deconvolution characteristics are similar for the K 2p$_{3/2}$ and K 2p$_{1/2}$ peaks of carbon precursors impregnated with KOH and K$_2$CO$_3$. Deconvolution of the C 1s spectra for both KOH-impregnated AC and K$_2$CO$_3$-impregnated AC reveals peaks attributable to C=C (284.4 eV), C–C (285.9 eV), C–O (287.1 eV), C=O (288.5 eV) and COOH (289.7 eV). The intensity of the deconvoluted C 1s peaks varies depending on the K/C ratio but is independent of the agent at the same K/C ratio of 0.5. Thus, the increase in the specific surface area after activation of carbon precursors impregnated with KOH and K$_2$CO$_3$ at the same K/C ratio would be similar irrespective of the agent.

Table 2. Deconvolution of K 2p and C 1s XPS spectra of the KOH/K$_2$CO$_3$-impregnated carbon precursors.

| Agent | K/C Ratio | K 2p$_{3/2}$ | K 2p$_{1/2}$ | C=C | C–C | C=O | C=O | COOH |
|-------|-----------|--------------|--------------|-----|-----|-----|-----|------|
|       |           | K$_o$ (293.0)| K$_{CB}$ (295.7) | K$_o$ (294.5) | K$_{CB}$ (296.6) | C=C (284.4) | C–C (285.9) | C=O (287.1) | C=O (288.5) | COOH (289.7) |
| KOH   | 0.5       | 49.6         | 15.9         | 25.7 | 8.88 | 51.7 | 22.5 | 7.59 | 10.2 | 7.95 |
|       | 0.2       | 53.9         | 11.5         | 25.9 | 8.68 | 71.7 | 16.8 | 5.65 | 3.62 | 2.15 |
|       | 0.4       | 54.2         | 10.3         | 30.9 | 4.54 | 56.3 | 14.5 | 6.79 | 8.36 | 14.1 |
|       | 0.5       | 50.0         | 15.2         | 26.3 | 8.59 | 50.8 | 23.7 | 7.62 | 10.4 | 7.40 |

K$_o$: K–O groups, K$_{CB}$: potassium surrounded by carbonate, Numbers in parentheses represent binding energy in eV.

3.2.2. XRD Results

Figure 2 shows the results of the XRD analysis of the carbon precursors impregnated with KOH and K$_2$CO$_3$ at a K/C molar ratio of 0.5. Similar XRD peak patterns are observed for the carbon precursors impregnated with the different activating agents. The main peak is attributed to KHCO$_3$; however, weak peaks of K$_4$H$_2$(CO$_3$)$_3$ were also observed. Although K$_4$H$_2$(CO$_3$)$_3$ is known as an intermediate composition of KHCO$_3$ crystals exposed to a CO$_2$
atmosphere [23,24], it eventually transforms to KHCO₃: K₄H₂(CO₃)₃⋅1.5H₂O(s) + CO₂(g) ⇌ 4KHCO₃ + 0.5H₂O(l). Nevertheless, the large differences in the specific surface areas of the upgraded ACs impregnated with KOH and K₂CO₃, as shown in Figure 3, are difficult to explain. Because KHCO₃ also transforms into K₂CO₃ at temperatures greater than 140 °C (2KHCO₃(s) ⇌ K₂CO₃(s) + H₂O(g) + CO₂(g)) [25], the amounts of K₂CO₃ formed on the carbon precursors would adversely affect the degree of activation. Given that the peaks of K₄H₂(CO₃)₃ and KHCO₃ are more intense for the carbon precursor impregnated with K₂CO₃ that for that impregnated with KOH, the K₂CO₃-impregnated sample would favor the formation of K₂CO₃ during activation. Because K₂CO₃ is thermally stable to 891 °C, it hardly participated as a chemical agent at the highest temperature used in the present study (850 °C), which is why the specific surface area of the carbon precursor impregnated with K₂CO₃ was lower than that of the precursors impregnated with KOH.

![Figure 2. XRD patterns for KOH/K₂CO₃-impregnated carbon precursors.](image)

![Figure 3. (a) N₂ isotherms and (b) pore size distributions of activated carbons prepared by impregnation with KOH and K₂CO₃ at different K/C molar ratios.](image)

3.3. Chemical Activation with KOH and K₂CO₃

For chemical activation, carbon precursors were prepared by being physically and chemically mixed with KOH and K₂CO₃. The specific surface area of the AC after chemical activation with KOH was superior to that of the AC after chemical activation with K₂CO₃, irrespective of the mixing method (Figure 3). The specific surface area of the AC activated with KOH at a K/C ratio of 0.5 increased from 1400 m²/g to 3047 m²/g, which is ~30% greater than that of the AC activated with K₂CO₃ (2162 m²/g) under otherwise identical conditions. These results clearly show differences in the thermal properties of the ACs treated using KOH and K₂CO₃. However, the specific surface area of the AC impregnated with K₂CO₃ at the same K/C ratio was ~24% greater than that of the AC mixed with K₂CO₃ physically. Thus, the physical properties of K₂CO₃ were changed during the impregnation (Figure 1), enabling the K doped into the carbon precursors to more easily intercalate into the carbon matrixes.

Figure 3 shows the N₂ isotherms and PSD for the ACs treated using KOH and K₂CO₃ at various K/C ratios. The shape of the N₂ isotherms and PSDs varies with the K/C ratio;
however, no substantial differences are observed between the ACs treated using these two agents. Nevertheless, AC impregnated with K$_2$CO$_3$ at a twofold K loading during the activation process was similar to that of AC treated with KOH at a K/C ratio of 0.25. These results reflect the relatively low reactivity of K as a chemical agent when impregnated as K$_2$CO$_3$ compared with that of K impregnated as KOH at the same K/C ratio.

4. Conclusions

In the present study, the reactivity of K$_2$CO$_3$ as a chemical agent was compared with that of KOH to evaluate the feasibility of recycling alkaline wastewaters generated as a byproduct during chemical activation. Wet impregnation with K$_2$CO$_3$ on carbon precursors effectively lowered the thermal stability of K$_2$CO$_3$, as indicated by a decrease in its melting point. However, the specific surface area (2162 m$^2$/g at K/C = 0.5) of the K$_2$CO$_3$-impregnated AC was still only ~70% of that of the KOH-impregnated AC (3047 m$^2$/g at K/C = 0.5). The XPS and XRD results showed similar surface binding properties (C–O–K) and potassium compounds (KHCO$_3$, K$_4$H$_2$(CO$_3$)$_3$) in the precursors impregnated with these two agents (K$_2$CO$_3$ and KOH). However, the intensity of KHCO$_3$ peaks in the XRD patterns differed dramatically dependent on the agent used. This result indicated that the degree of formation of C–O–K complexes, which participate in the activation reaction, strongly affected the carbon surface even if the binding energies and peak intensities were similar. Consequently, the specific surface area of the K$_2$CO$_3$-impregnated AC was lower than that of the KOH-impregnated AC even though the high thermal stability of K$_2$CO$_3$ had been overcome. Nevertheless, the specific surface area of the K$_2$CO$_3$-activated AC was still ~1.6 times greater than that of the carbon precursor (1378 m$^2$/g), suggesting the possibility of resource recycling by reusing wastewaters as a chemical agent.

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