Supporting information for

**Shedding light on solid sorbents: evaluation of supported potassium carbonate particle size and its effect on CO₂ capture from air**

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**Figure S.1.** Nitrogen adsorption-desorption isotherms for KetjenBlack support, KB10, KB25, and KB50 were measured to establish textural properties of the samples and support.
**Figure S.2.** SEM images and EDX mapping of KB50 (top) and KB25 (two bottom ones). EDX mapping indicate the presence of potassium, but extraction of an average particle size was not possible.
Note that background potassium is zero: SEM images and EDX mapping of the sample and an area on the sample holder. It shows that on the sample holder there is no background potassium.
Figure S.3. TEM images of one K$_2$CO$_3$ particle captured over time. Sample (KB50) was exposed to beam (a). Images on the same particle were captured in sequence of 10 seconds (b, c, and d). Images show fast changes of the K$_2$CO$_3$ under the beam. The K$_2$CO$_3$ particles disappeared under the beam if the image is not captured fast enough.
Quantitative XPS analysis

We used a model developed by Kerkhof and Moulijn\textsuperscript{1} to estimate $K_2CO_3$ particle sizes for KB10, KB25, and KB50. The model suggests that a relative XPS intensity ratio sourced from an element from a metal or metal oxide to an element from a high surface area support relates to the dispersion of the metal/metal oxide on the support. The model assumes that the sample consists of sheets of support with cubic particles of the promoter (here we consider cubes of $K_2CO_3$ particles) with size of $c$ in between support sheets (Scheme 1.a).

The thickness of the support sheets, $t$, is calculated as

$$t = \frac{2}{\rho_s S_0}$$

where $\rho_s$ is support density (carbon: 2.0 g/cm$^3$), and $S_0$ is the support surface area (for KetjenBlack: 1370 m$^2$/g) hence $t = 0.73$ nm.

It is assumed that electrons leave the sample only in a direction perpendicular to the surface. Using Lambert-Beer law, the model proposes formulas to calculate the amount of escaping electrons from one layer of the support ($I_{s,0}$) and one layer of the promoter ($I_{p,0}$):

$$I_{s,0} = A n_s \sigma_s \lambda_{ss} (1 - \exp (-t / \lambda_{ss}))$$

$$I_{p,0} = f A n_p \sigma_p \lambda_{pp} (1 - \exp (-c / \lambda_{pp}))$$

Where $A$ is the effective area of the sample from which electrons reach the detector; the atomic densities in promoter and support ($n_p$, $n_s$); the photoelectron cross sections ($\sigma_s$, $\sigma_p$); the escape depths of the electrons ($\lambda$); and $f$ is the fraction of support covered with promoter that follows:

$$f = \frac{x}{1-x} S_0 \rho_s c$$

Here, $x$ is the promoter weight fraction in the sample.

Further, the total amount of escaping electrons from an infinite number of sheets is summed up considering that the most contribution to the signal is from the top layers. Samples with high surface area support like the KB series sorbents are assumed to have an infinite number of sheets. Hence, we use the model suggesting following equation for the experimentally obtained relative XPS intensities of promoter and support, $(I_p/I_s)_{exp}$. In our case, $(I_p/I_s)_{exp}$ is the relative XPS

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme.png}
\caption{a) Schematic presentation of the sample described in the model and b) Supported $K_2CO_3$ particles on carbon: invisible and visible by XPS. In principal, the thickness of the blue layer should change because only perpendicular emission is assumed. Nevertheless, due to large size of particles compared to the penetration depth, this correction was waived.}
\end{figure}
intensities of potassium (K 2p) to carbon from support (C 1s, sp²), and they are experimentally obtained from the high resolution K 2p and C 1s XP spectra of the samples (Figure S.3, Table S.1).

\[
\frac{I_p}{I_s}_{exp} = \frac{D(\epsilon_p)I_{p,0}(1 + P_{ps}P_{pp})(1 - P_{ss}P_{sp}^2)}{D(\epsilon_s)I_{s,0}(1 - P_{ps}P_{pp}^2)P_{sp}}
\]

\(D\) is detector efficiency as a function of the kinetic energy of the electrons. \(P\) is fraction of the electrons from one layer of promoter or support passing through another layer of promoter or support. The fraction of electrons from one support layer passing through a layer of support is \(P_{ss}\), and the fraction from one layer of promoter passing through a layer of support \(P_{ps}\) and etc. They are functions of particle size, support thickness and support coverage (\(f\)):

\[P_{ss} = \exp(-\beta 1)\]
\[P_{ps} = \exp(-\beta 2)\]
\[P_{sp} = 1 - f + f \exp(-\alpha 2)\]
\[P_{pp} = 1 - f + f \exp(-\alpha 1)\]

Where dimensionless particle sizes are defined as:

\[\alpha 1 = c/\lambda_{pp}\]
\[\alpha 2 = c/\lambda_{sp}\]

And dimensionless support thickness are defined as:

\[\beta 1 = t/\lambda_{ss}\]
\[\beta 2 = t/\lambda_{ps}\]

Here,

\(\lambda_{pp}\) is the escape depth of electrons from the promoter traveling through the promoter,

\(\lambda_{ss}\) is the escape depth of electrons from the support traveling through the support,

\(\lambda_{sp}\) is the escape depth of electrons from the support traveling through the promoter, and

\(\lambda_{ps}\) is the escape depth of electrons from the promoter traveling through the support.

**Figure S.4.** High resolution K 2p and C1s XPS spectra of the KetjenBlack support, KB10, KB25, and KB50 samples
We try to simplify the formula to have a direct relation of the particle size to the experimentally obtained relative XPS intensities.

First, we assumed for our samples $P_{sp} \approx P_{pp} \approx 1$. It seems a valid assumption when $f$, coverage of support by the promoter, is negligible. We examined the validity of this assumption for two extreme cases of $\mathrm{K}_2\mathrm{CO}_3$ loadings and particle sizes on carbon considering support surface area is not lost during $\mathrm{K}_2\mathrm{CO}_3$ deposition:

1. For 10 wt.% $\mathrm{K}_2\mathrm{CO}_3$ on Ketjen Black with hypothetical cubic particles of $\mathrm{K}_2\mathrm{CO}_3$ with size of $c=10$ nm, $f$ is 0.033
2. For 50 wt.% $\mathrm{K}_2\mathrm{CO}_3$ on Ketjen Black with hypothetical cubic particles of $\mathrm{K}_2\mathrm{CO}_3$ with size of $c=50$ nm, $f$ is 0.006

To experimentally confirm this assumption, we looked at the intensity of C 1s, $sp^2$, i.e. the carbon signal sourced from the Ketjen Black support, in Ketjen Black and KB50 spectra (Figure S.3). XPS spectra show that the intensity of C 1s, $sp^2$ in KB50 is not diminished compared to the intensity of C 1s, $sp^2$ in Ketjen Black. Hence, we at least experimentally observed that $P_{sp} \approx 1$.

Hence the formula simplifies to:

$$
\frac{I_p}{I_s} \exp = D_{(sp)} I_{p,0} \frac{(1 + P_{ps})(1 - P_{ss})}{D_{(sx)}} I_{s,0} \frac{1 - \exp(-\alpha_1)}{\alpha_1}
$$

By substituting $I_{p,0}$, $I_{s,0}$, and the bulk atomic ratio of the support and the promoter $(p/s)_b$:

$$(p/s)_b = x n_p \sigma_p / (1-x) n_s \sigma_s,
$$

the equation is elaborated to:

$$
\frac{I_p}{I_s} \exp = \left(\frac{p}{s}\right)_b D_{(sp)} \frac{1 - \exp(-\alpha_1)}{\alpha_1} \beta_1 \frac{1 + \exp(-\beta_2)}{2}
$$

When electrons with small differences in kinetic energy are studied like electrons of K2p and C1s, both at binding energies of ca. 290 eV (at constant $h\nu = 1486.6$ eV), $D_{(sp)} = D_{(sx)}$, $\lambda_{ps} = \lambda_{ss}$, and consequently $\beta_1 = \beta_2 = \beta$

$\beta$ is extracted by calculation of the $\lambda_{ss}$, the escape depth of electrons from the support traveling through the support. The escape depths of the electrons for C 1s was calculated as 3.67 nm in carbon media at 1486.6 eV photon energy. The escape depths of the electrons were extracted from NIST Electron Inelastic-Mean-Free-Path Database, software package version 1.2, according to predictive formulae of TPP-2M equation of Tanama, Powell and Penn. Since $t$ is 0.73, $\beta$ is 0.2.

The equation is reduced to

$$
\frac{I_p}{I_s} \exp = \left(\frac{p}{s}\right)_b \frac{\sigma_p (1 - \exp(-\alpha_1))}{\alpha_1}
$$

Here, $\alpha_2$ contains particle size information and is obtained as follows.

For a hypothetical monolayer of promoter on the support, $\alpha$ is small and $(1 - \exp(-\alpha_2))/\alpha_2$ goes to 1. Hence hypothetical $(I_p/I_s)_\text{monolayer}$ is equal to $(p/s)_b (\sigma_p/\alpha_2)$ and needs to be calculated for KB50, KB25, and KB10 samples. The bulk atomic ratio of the support and the promoter $(p/s)_b$ is known for these three samples (Table S.1). The photoelectron cross sections for C1s and K 2p were extracted from calculations of Scofield at a
The photon energy of 1486.6 eV. The photoelectron cross section for C1s is 1, for K 2p\(\frac{1}{2}\) is 1.35 and for K 2p\(\frac{3}{2}\) is 2.62. In total \(\sigma_p/\sigma_s = (1.325+2.62)/1 = 3.97\).

Further, the percentage of the monolayer is calculated as \((I_p/I_s)_{\text{exp}} / (I_p/I_s)_{\text{monolayer}}\). This percentage is equal to \((1 - \exp(-\alpha_j))/\alpha_j\). From a graph (Figure S.4) that relates \((1 - \exp(-\alpha_j))/\alpha_j\) to \(\alpha_j\), corresponding \(\alpha_j\) is obtained for KB50, KB25, and KB10 samples (Table S.1).

![Figure S.5. General relation of \((1 - \exp(-\alpha_j))/\alpha_j\) to \(\alpha_j\) showing the percentage of a monolayer promoter on the support](image)

The escape depths of the electrons for K 2p is calculated as 3.3 nm in K\(_2\)CO\(_3\) media at 1486.6 eV photon energy. The escape depths of the electrons were calculated with NIST Electron Inelastic-Mean-Free-Path Database, software package version 1.2, according to predictive formulae of TPP-2M equation of Tanuama, Powell and Penn.\(^2\) The TPP-2M equation is a function of electron energy (1486.6 eV), density (2.43 g/cm\(^3\)), number of valence electrons per atom (24), and the bandgap energy (3.697 eV)\(^4\) of K\(_2\)CO\(_3\). Accordingly, particle sizes for KB50, KB25, and KB10 are calculated as shown in the table.

| Sample | K (mol) | C from support (mol) | K/C (mol/mol) | Calculated \((I_p/I_s)_{\text{monolayer}}\) | Monolayer percentage (%) | \(\alpha_j\) | Estimated particle size by the model (nm) |
|--------|--------|----------------------|---------------|---------------------------------|-----------------|-------------|---------------------------------|
| KB10   | 0.14   | 7.50                 | 0.02          | 0.05                            | 66              | 0.88        | 3 ± 2                           |
| KB25   | 0.36   | 6.25                 | 0.06          | 0.15                            | 42              | 2.11        | 7 ± 3                           |
| KB50   | 0.72   | 4.17                 | 0.17          | 0.46                            | 8               | 9.00        | 30 ± 8                          |
Figure S.6. TGA on KetjenBlack support, bulk K₂CO₃, KB10, KB25, and KB50 samples. Samples heated up to 920 °C under flow of N₂ (50 mL/min). Under flow of nitrogen, oxidation of carbon occurred at temperatures around the melting point of the K₂CO₃. No meaningful heat flow could be attributed to the K₂CO₃ melting. Hence, air was used instead of inert N₂. According to thermodynamic calculations by HSC software, the reduction of K₂CO₃ to gaseous potassium takes place at the presence of carbon as a reducing agent at temperatures above 900 °C (Figure S.7). This reaction and the heat flow associated with that eclipsed the melting of the K₂CO₃.
Figure S.7. Thermodynamically stable components under nitrogen at high temperatures obtained by thermodynamic database of the HSC 8 software.

Thermodynamic calculation for $K_2CO_3$ TGA/DSC under $N_2$
**Figure S.8.** The relation of the melting point to the $\text{K}_2\text{CO}_3$ particle size according to the Gibbs-Thomson equation. At temperatures higher than 880 °C, slight variation in melting point leads to a considerable change in particle diameter.
Figure S.9. TGA mass increase upon exposure to wet air. Bulk K$_2$CO$_3$ physically mixed with the Ketjen Black (around 2 mg of sample), Pre-treated at 200 °C under 150 mL/min flow of dry synthetic air (that did not contain CO$_2$) for 1 hour, Adsorption at 60 °C under 150 mL/min flow of air that contained different amount of water for 3 hours. Post treatment at 200 °C under 150 mL/min flow of dry synthetic air for 1 hour.

The figure shows the mass increase upon exposure of the bulk K$_2$CO$_3$ (K$_2$CO$_3$ which physically mixed in a mortar with the Ketjen Black support) to a wet air flow with different water content during TGA. More water content of the flow led to a more calculated CO$_2$ uptake. We suspect that the CO$_2$ uptake measured by TGA is subject to error due to interfering water uptake that overestimates the CO$_2$ uptake. On the other hand, water concentration may affect the sorption of CO$_2$ and/or water. These two effects are not easily distinguishable. Hence kinetics reported under TGA condition is not representative of the kinetics of the reaction in a flow reactor.

Table. CO$_2$ sorption capacity of the bulk K$_2$CO$_3$ under different amount of water

|                    | Mass increase upon exposure to air (%) | Calculated CO$_2$ uptake (mmol CO$_2$/g sorbent) | CO$_2$ uptake (mol CO$_2$/mol K$_2$CO$_3$) |
|--------------------|---------------------------------------|-----------------------------------------------|-----------------------------------------|
| 60 ppm water       | 2.45                                  | 0.35                                          | 0.10                                    |
| ~1 % water         | 4.76                                  | 0.67                                          | 0.19                                    |
| 2.6 % water        | 9.01                                  | 1.27                                          | 0.36                                    |

CO$_2$ uptake is measured by weight increase upon exposure to air assuming 1:1 stoichiometric ratio of water and CO$_2$ uptake.
Figure S.10. TGA on KB10, KB25, and KB50 samples and corresponding heat flows during decarbonation. Samples that were stored in atmospheric conditions were heated up to high temperatures under flow of synthetic air (50 mL/min, zero CO₂). The temperature of decarbonation during TGA matches the decarbonation temperature in the flow unit.

The enthalpy of decarbonation was calculated as 120 kJ/mol. It is more than reported value of 107 kJ/mol. CO₂ uptake was also more than 1 mol/mol K₂CO₃. It means part of the mass loss is due to dehydration instead of decarbonation.
Details of the calculation of the apparent activation energy for decarbonation steps

Redhead analysis provides a simple way for the estimation of apparent activation energies for a first order desorption step in a typical temperature programmed desorption measurement. The analysis is based on Arrhenius equation and assumes the apparent activation energy of desorption \( E_d \) and pre-exponential factor (A) are coverage independent.

The analysis suggests the following equation to relate the heating rate \( \beta \) to the temperature that a maximum desorption peak \( T_p \) appears,

\[
\frac{E_d}{R T_p^2} = \frac{A}{\beta} \exp \left( \frac{-E_d}{R T_p} \right)
\]

Where R is the gas constant. By rearranging the formula the following is obtained,

\[
\ln \beta \frac{T_p^2}{T_p} = -\frac{E_d}{R T_p} + \frac{A R}{E_d}
\]

Hence, by plotting the \( \ln \beta \frac{T_p^2}{T_p} \) vs \( \frac{1}{T_p} \), (below figure), where \( T_p \) is the temperature of the first and second decarbonation steps, we obtained the apparent activation energies for both decarbonation steps as 69 kJ/mol and 93 kJ/mol.

**Table S.2.** Variables of the Redhead analysis from the decarbonation upon heat treatment data

| Heating rate, \( \beta \) (°C/min) | Temperature of first decarbonation step, \( T_{p1} \) (K) | Temperature of second decarbonation step, \( T_{p2} \) (K) |
|-------------------------------------|--------------------------------------------------------|-------------------------------------------------------|
| 5                                   | 377                                                    | 413                                                   |
| 10                                  | 389                                                    | 420                                                   |
| 20                                  | 400                                                    | 433                                                   |

**Figure S.11.** Arrhenius plot of the decarbonation steps
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