Isotope Exchange and the Sodium-catalysed CO₂ Gasification of Carbon

John M. Saber,^a John L. Falconer,^{*a} and Lee F. Brown^b

^a Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309–0424, U.S.A.

^b Earth and Space Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

Distinct oxidation (reversible) and reduction steps, and the stoicheiometries of the catalytic species have been identified for sodium-catalysed CO_2 gasification of ¹³C.

By the use of temperature-programmed desorption and reaction (TPD and TPR)¹ in combination with carbon-13 tracers, we have separated and identified reaction steps in alkali metal-catalysed CO_2 gasification of carbon. A mechanism for a sodium catalyst is presented, but similar mechanisms occur for potassium, barium, and calcium catalysts. Two catalytic species with different stoicheiometries are identified, and separate oxidation and reduction steps are present in the mechanism. The oxidation step is reversible and incorporates surface carbon into carbon dioxide. The second step, reduction, is rate determining.

Dry mixtures of ${}^{13}C$ (100 mg) and unlabelled Na₂CO₃ (10 mg) were heated at a rate of 1 K/s to 1350 K in a quartz downflow reactor in flowing He (TPD), 10% CO₂-He (TPR), or 10% CO-He (TPR). Gaseous products were continuously analysed immediately downstream of the reactor with a computer-aided mass spectrometer that concurrently recorded signals for CO, ${}^{13}CO$, CO₂, and ${}^{13}CO_2$ (for clarity, ${}^{12}C$ is designated without a superscript).

To determine if the sodium catalyst cycled between oxidized and reduced forms, as proposed by others,²⁻⁷ carbonatecarbon mixtures were first heated in He. During heating, the amount of oxygen that desorbed as carbon monoxide and carbon dioxide was measured. The sample was then cooled to 800 K and oxidized by exposure to CO_2 flow. Oxygen uptake during the CO_2 exposure was determined by reheating the mixture to 1350 K and measuring how much additional oxygen desorbed. Subsequently, the solid mixtures were analysed by atomic absorption spectroscopy to determine their sodium content, since some sodium was lost by vaporization.

The Na₂CO₃- 13 C mixtures used to study CO₂ gasification by TPR were heated in flowing 10% CO₂-He to 1350 K to decompose the carbonate and form the active catalyst. The samples were then cooled to 300 K and reheated to 1350 K in the CO₂-He mixture while reaction products were observed with the mass spectrometer. This procedure avoided carbonate-decomposition contributions to the TPR spectra during the second heating, and yielded reproducible TPR spectra.

The Na₂CO₃-1³C mixtures were also heated in 10% CO-He flow to study the reverse reactions that may occur during gasification. During TPD of sodium carbonate-carbon mixtures in He, all the oxygen, both that in the carbonate and that originally present on the carbon, desorbed. Thus, the sodium complex that remained on the carbon apparently contained no oxygen. When the complex was exposed to CO_2 flow at 800 K, it took up one oxygen atom for each sodium atom. The number of sodium atoms present after heating to 1350 K was determined by atomic absorption analysis. The carbon alone did not take up significant amounts of oxygen.8 When the mixture was heated in CO_2 , the final stoicheometry of the sodium complex was one oxygen for every two sodium atoms. Thus, in CO₂, the sodium complexes can have a Na : O ratio of either one or two, and we assume that these are the catalytic species present during CO₂ gasification.

During TPR, as the flowing CO_2 gasified the ¹³C substrate to ¹³CO and CO, ¹³CO₂ product was also observed, as shown in Figure 1. Because of the experimental arrangement,¹ the amplitudes of the product signals in Figure 1 are proportional to the rates of reaction, and the areas under the curves are proportional to the amounts of products formed.

Several aspects of the spectra in Figure 1 are significant for the gasification mechanism. (i) The production rates of CO and ¹³CO *are not the same*; between 850 and 1050 K, CO forms at a significantly faster rate than ¹³CO. (ii) ¹³CO₂ forms in significant quantities in a broad peak between 900 and 1200 K, and the rate of ¹³CO₂ production is initially greater than the rate of ¹³CO production. (iii) At all temperatures, consumption of one mole of CO₂ produces one mole of CO, *but significantly less* ¹³CO (except at complete conversion of CO₂). TPR with barium,⁹ calcium,¹⁰ and potassium carbonate



Figure 1. Temperature-programmed reaction products for sodiumcatalysed ${}^{12}CO_2$ gasification of ${}^{13}C$. The carbon dioxide products are displaced vertically for clarity.

catalysts also yielded ${}^{13}CO_2$ and the apparent delay in ${}^{13}CO_2$ formation. The reason for the appearance of ${}^{13}CO_2$ was not identified previously.

These results mean that the overall catalytic gasification reaction is not as in equation (1), since the CO: 13 CO ratio is not unity. Also, carbon in the substrate is removed as 13 CO₂.

$$CO_2 + {}^{13}C \rightarrow CO + {}^{13}CO \tag{1}$$

When mixtures of ¹³C and the more oxidized form of the catalyst were heated in 10% CO–He, carbon dioxide (CO₂) was produced between 600 and 1200 K, but no ¹³CO₂ formed.

Equations (2)—(4) present a mechanism consistent with the TPD and TPR data. The parameters (x,y) that multiply each reaction step indicate the number of times that step must occur to yield the overall reaction (5), which when written per mole of $CO_2(g)$ and balanced, equation (6), has one parameter, a, which depends on conversion and thus on temperature. The above reaction sequence uses the stoicheiometries of the two complexes of sodium determined from the TPD experiments.

We are assuming that the forms of the complexes obtained by TPR in CO_2 and by reoxidation after TPD in He are similar to those present during CO_2 gasification.

The oxidation reaction (2) forms one mole of CO for each mole of CO₂ that reacts, as observed. Because CO is observed before ¹³CO, equation (2) must be a distinct reaction from equation (3); *i.e.*, previously proposed 2-step reaction sequences are directly verified by this work. Also, the Na₂O-¹³C species can be oxidized by CO₂ at 800 K without producing ¹³CO. The reduction by carbon, reaction (3), thus appears to be the rate-determining step, since ¹³CO is only formed at temperatures well above those at which CO₂ will oxidize the reduced form of the catalyst.

Reaction (2) is written as a reversible reaction because heating the oxidized catalyst in CO forms CO₂. Reaction (4) is the reverse of reaction (2) but written for ¹³CO and ¹³CO₂. The same steps that occur for ¹²CO must also occur for ¹³CO. This step is also necessary to explain the formation of ¹³CO₂. Significant quantities of ¹³CO₂ are continuously formed during isothermal reaction. The rate constants for reaction (2) and the reverse of reaction (4) must be the same since a significant kinetic isotope effect is not expected for ¹³CO substitution.

Oxidation: x,

$$Na_2O^{-13}C + CO_2(g) \rightleftharpoons (NaO)_2^{-13}C + CO(g)$$
 (2)

Reduction by carbon: y,

$$(NaO)_{2}^{-13}C + {}^{13}C \rightarrow Na_{2}O^{-13}C + {}^{13}CO(g)$$
 (3)

Reduction by CO:
$$(x-y)$$
,
 $(NaO)_2^{-13}C + {}^{13}CO(g) \rightarrow Na_2O^{-13}C + {}^{13}CO_2(g)$ (4)

The ${}^{13}\text{CO}_2$ product is produced when ${}^{13}\text{CO}$ is consumed in reaction (4). The delay in ${}^{13}\text{CO}$ production is due to consumption of ${}^{13}\text{CO}$ by reaction (4), and as shown below, ${}^{13}\text{CO}$ is consumed until equilibrium is attained for this reaction. The ratio of carbon monoxide to carbon dioxide is the same for each isotope over the range of temperatures used. That is, equation (7) is satisfied, where the brackets indicate concentrations in the exit stream from that reactor. This indicates that reactions (2) and (4) are in equilibrium. At equilibrium the forward and reverse rates are the same for each of these reactions, as indicated in equations (8) and (9). Division of equation (8) and (9) and rearrangement yields equation (7). Thus, as expected if reaction (3) is rate-limiting, reactions (2) and (4) are in equilibrium.

$$x \operatorname{CO}_2 + y \,{}^{13}\mathrm{C} \rightleftharpoons x \operatorname{CO} + (x - y) \,{}^{13}\mathrm{CO}_2 + (2y - x)^{13}\mathrm{CO}$$
 (5)

$$CO_2(g) + a {}^{13}C \rightleftarrows CO(g) + (1 - a) {}^{13}CO_2(g) + (2a - 1) {}^{13}CO(g)$$
 (6)

$$\frac{[\text{CO}]}{[\text{CO}_2]} = \frac{[^{13}\text{CO}]}{[^{13}\text{CO}_2]} \tag{7}$$

$$k_1[Na_2O^{-13}C][^{12}CO_2] = k_{-1}[(NaO)_2^{-13}C][^{12}CO]$$
 (8)

$$k_1[Na_2O_{-13}C][^{13}CO_2] = k_{-1}[(NaO)_2^{-13}C][^{13}CO]$$
 (9)

The above mechanism is similar to the one-step reduction, one-step oxidation mechanisms previously proposed for uncatalysed and catalysed gasification. Gadsby *et al.*¹¹ suggested the mechanism in equations (10) and (11) for the uncatalysed reaction. Evropin *et al.*¹² proposed a similar mechanism, but with reaction (10) being reversible. Kapteijn and Moulijn² proposed a similar two-step mechanism, shown in equations (12) and (13), for the alkali metal-catalysed reaction. The oxidized and reduced forms of the catalyst may be different for different alkali metals.^{2,7,8}

$$CO_2(g) + C \rightarrow CO(a) + CO(g)$$
 (10)

$$CO(a) \rightleftharpoons CO(g)$$
 (11)

$$(M_xO_y)-C + CO_2(g) \rightleftharpoons (M_xO_{y+1})-C + CO(g)$$
 (12)

$$(M_x O_{y+1}) - C + C \rightleftharpoons (M_x O_y) - C + CO(g)$$
 (13)

We have directly verified the presence of the oxidation and reduction steps and determined the catalyst stoicheiometries. We have also shown that the oxidation step is reversible and at equilibrium at reaction conditions. The reverse of the oxidation step is shown to be responsible for the formation of carbon dioxide that contains substrate carbon. Alkali and alkaline earth catalysts may have different stoicheiometries, but they must contain oxygen since Na, K, Ca, and Ba catalysts all form carbon dioxide from substrate carbon.

For CO_2 gasification of ¹³C, a one-step oxidation (reversible), one-step reduction mechanism accurately predicts the experimentally-observed product distributions.

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