Reactions of propane with CO₂ over Au catalysts

Anita Tóth, Gyula Halasi, Tamás Bánsági, Frigyes Solymosi

MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, H-6720 Szeged, Hungary

**Abstract**

The decomposition of C₃H₈ and its reaction with CO₂ have been investigated on Au deposited on ZnO, MgO and Al₂O₃. The reactions proceeded above 650–700 K. The conversion of C₃H₈ was only few percents on Au/MgO and Au/Al₂O₃, even at 873 K, but reached 17% on Au/ZnO. The selectivity of propylene formation was about 56%. CO₂ only slightly affected the reaction of C₃H₈ on Au/Al₂O₃ and Au/MgO, but significantly enhanced the conversion of C₃H₈ on Au/ZnO catalyst. The formation of large amount of CO indicates the involvement of CO₂ in the reaction of C₃H₈. From the product distribution it was inferred that beside the oxidative dehydrogenation and dry reforming reaction, the decomposition of C₃H₈ into CH₄ and surface carbon also occurred. The effect of ZnO is explained by an electronic interaction between n-type ZnO and Au particles leading to a formation of reactive CO₂.

**1. Introduction**

The production of synthesis gas, H₂ + CO, in the dry reforming of CH₄ is an important process for chemical technology and has been the subject of extensive studies [1–3]. From the first comparative work it was found that on the basis of turnover frequency determined on noble metals, Rh and Ru are the most active catalysts [4]. Attempts were also made to produce synthesis gas by the reactions of C₂H₆ and C₃H₈ with CO₂. Whereas in the absence of CO₂ the dehydrogenation of C₃H₈ was the major process, in the presence of CO₂ the formation of H₂ + CO₂ came into prominence [5–10]. As regards the dry reforming of C₂H₆, Rh and Ru also exhibited the highest specific activity [5]. Kinetic measurements revealed a zero-order dependence in C₃H₈ and a fractional dependence in CO₂ [6]. Many of the above cited studies revealed that the nature of the support plays an important role in the activity and selectivity of different catalysts. The best example is Mo₂C. Whereas Mo₂C/SiO₂ catalyzed the dehydrogenation of C₂H₆ [10], using ZSM-5 as a support the aromatization of C₃H₈ became the main reaction pathway [11]. Several studies have been also performed on the oxidative dehydrogenation of propane with molecular O₂ on oxide catalysts [12–15]. V₂O₅ containing catalysts proved to be the most effective and selective, particularly when C₃H₈ was in a great excess [14]. A great challenge was to avoid the over oxidation of olefins formed. The influence of several additives including Au/TiO₂ was tested [14]. Au/TiO₂ alone showed a low activity, but mixing with V₂O₅, yielded H₂ in larger concentration than obtained on either vanadium or gold [14]. Au/TiO₂ was also active in the selective oxidation of propane to propylene oxide [15].

In the present work the reaction of C₃H₈ with CO₂ is examined over supported Au nanoparticles. As was discovered by several decades ago, Au in nanosize exhibits a surprisingly high activity in many catalytic reactions [16–18]. Recently, we found that Au nanoparticles supported by n-type semiconducting oxides are very effective catalysts in the reaction of C₂H₆ with CO₂ [19].

**2. Experimental**

**2.1. Materials**

Supported Au catalysts with a gold loading of 1 wt% were prepared by a deposition–precipitation method. Chlorauric acid (HAuCl₄·aq p.a. 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the HAuCl₄ aqueous solution was adjusted to 7.5 pH by adding 25% ammonia solution, the fine powder of oxidic support was suspended and kept at 343 K for 1 h with continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K, calcined in air and reduced at 673 K for 4 h. Al₂O₃ (Degussa) and MgO (Reanal) were applied as a support. 1% Au/ZnO (AUROlite) sample was purchased from Strem Chem. The gases used were of commercial purity.

**2.2. Methods**

For FTIR studies a mobile IR cell housed in a metal chamber was used, which can be evacuated to 10⁻⁵ Torr using a turbo molecular
pumping system. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wave number accuracy of ±4 cm⁻¹. All the spectra presented in this study are difference spectra. The sizes of Au particles were determined in a transmission electron microscope. BET measurements were carried out by Ar adsorption at 77 K. Catalytic measurements were carried out in a fixed bed continuous flow reactor made of a quartz tube. The flow rate of reactant gases was 12 ml/min. The exit gas was analyzed by gas chromatograph (Hewlett-Packard 5890) on a Porapak QS column. The carrier gas was Ar which contained 12.5% of C₃H₈. In the study of CO₂ + C₃H₈ reaction we applied a gas mixture of 1:1 mole ratio. The selectivity for C₃H₆ was calculated as follows: C₃H₆ selectivity = 3 × nC₂H₄/nC₃H₆ × 100. In the temperature programmed desorption (TPD) and temperature programmed reduction (TPR), the heating rate was 5 K/min and the flow of Ar (TPD) and H₂ (TPR) was 20 ml/min. The products desorbed or formed were determined by gas chromatograph.

3. Results

3.1. Characterization of the catalysts

The main size of the Au particles in the Au/ZnO is small, 2–3 nm, and uniform. This value for Au/MgO and Au/Al₂O₃ falls in the range of 2–10 nm. BET surface area of the catalysts used is as follows: 50 m²/g for Au/ZnO, 170 m²/g for Au/MgO and 100 m²/g for Au/Al₂O₃. All catalysts have been also characterized by X-ray photoelectron spectroscopic measurements (XPS). In the analysis of the XPS spectra we accepted the BEs of three Au states: 84.0 eV for Au⁰, 84.6 eV for Au¹+ and 85.9 eV for Au³+. Binding energies obtained fell in the range of 84.1–84.3 eV suggesting that Au is in the form of Au⁰. Some characteristic data for supported Au are shown in Table 1.

3.2. IR spectroscopic studies

The adsorption of propane on Au/ZnO catalyst was performed around 215 K. FTIR spectra obtained are presented in Fig. 1A. Note that the gas-phase spectrum has been subtracted from each spectrum. At ~215 K absorption bands can be identified at 2981, 2967, 2960, 2901, 2875 cm⁻¹ in the high frequency region, and 1472, 1457, 1387, 1375 cm⁻¹ in the low frequency range. Heating the sample to 373 K, or adsorption of propane at 373 K led to a dramatic attenuation of all bands occurred with slight shifts in their position. In the low frequency region the absorption bands emerged only at higher temperature. Absorption bands observed at different temperatures and their possible assignments are shown in Table 2.

3.3. TPD measurements

The interaction of propane with Au/ZnO catalysts and ZnO support was also examined by means of TPD measurements. The sample was kept in the propane flow for 15 min at 300 K, and then it was washed with pure Ar until it contained propane (~15–20 min). TPD spectra are displayed in Fig. 1C and D. No weakly adsorbed C₃H₆ was detected, it desorbed very likely when washing the catalysts with Ar before TPD measurements. From pure ZnO the desorption of larger amount of CH₄ with Tₚ = 773 K, and the release of smaller amounts of C₂H₆ and C₃H₆ also above 700 K were registered. In the case of Au/ZnO catalyst almost twice as much CH₄ desorbed also with Tₚ = 773 K.

3.4. Dehydrogenation of C₃H₈

Conversion of propane on various Au samples as a function of reaction temperature is given in Fig. 2A. Au/Al₂O₃ and Au/MgO exhibited a very slight catalytic effect even at 873 K. A much higher activity was found on Au/ZnO. The reaction started above 725–750 K and the conversion of propane reached 17% at 873 K. The catalyst exhibited a remarkable stability. To establish the contribution of the Au similar experiments were performed with ZnO support alone. ZnO also catalyzed the dehydrogenation reaction, but the conversion of propane was much less, 6%, than that measured on Au/ZnO catalyst. The major products on ZnO and Au/ZnO are H₂ followed by C₂H₄, CH₄ and C₃H₆. Product distributions obtained on different catalysts are presented in Fig. 3. The selectivity for C₃H₆ formation on Au/ZnO is in the range of 83–90%. On the catalysts showing a low activity the product distribution is somewhat different.

3.5. Reaction of CO₂ + C₃H₈

Adding CO₂ to propane caused only a slight increase in the extent of the reaction of C₃H₈ on Au/MgO and Au/Al₂O₃. CO₂ enhanced only moderately the extent of the reaction of propane on pure ZnO used for the preparation of Au/ZnO: the conversion of C₃H₆ reached only 13% at 873 K. A dramatic increase occurred, however, on Au/ZnO catalyst. The reaction started even at 650 K. The conversion of C₃H₆ approached 50% at 873 K (Fig. 2B). Similar conversion values were obtained for CO₂ (Fig. 2C). The product distribution also underwent a significant change. The reaction occurring between CO₂ and C₃H₈ is indicated by the formation of significant amount of CO, which exceeded even that of C₃H₆. This is shown in Fig. 4. Apart from the CO, CH₄ became the major product followed by H₂, C₂H₄ and C₃H₆. The experiments have been repeated by three times using always a fresh catalyst. The conversion value fell in the range of 45–50% and we obtained the same sequence of products with only a slight variation. The approximate error bars ±3%. Note that we did not experience a decrease in the activity of Au/ZnO at 873 K for several hours, but it drastically declined when the reaction temperature was raised above 923 K. The selectivity of C₃H₆ formation was the highest, 70–75%, at 773 K. This value became lower, 56.3%, at 873 K. However the yield of C₃H₆ production considerably increased from the value of 6–7 (773 K) to a value of 25–30 (873 K). A great effort was made to identify the formation of hexane and hexene, the products of dimerization of C₃H₇ and C₃H₆ species. Both compounds were detected only in trace quantities.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area, m²/g</th>
<th>Average size of Au particles, nm</th>
<th>BE values (eV) of the Au</th>
<th>Conversion of C₃H₆ (%) at 873 K</th>
<th>Formation of H₂, nmol/gs</th>
<th>Selectivity of C₃H₆, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/ZnO</td>
<td>50</td>
<td>2–3</td>
<td>84.1</td>
<td>16.5</td>
<td>50</td>
<td>56</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>100</td>
<td>2–10</td>
<td>84.3</td>
<td>4.2</td>
<td>4.9</td>
<td>35</td>
</tr>
<tr>
<td>Au/MgO</td>
<td>170</td>
<td>2–10</td>
<td>84.2</td>
<td>1.3</td>
<td>1.9</td>
<td>44</td>
</tr>
<tr>
<td>ZnO</td>
<td>60</td>
<td>–</td>
<td>8.0</td>
<td>13</td>
<td>21</td>
<td>62</td>
</tr>
</tbody>
</table>
When the amount of CO₂ is varied keeping the concentration of C₃H₈ constant, the extent of reaction of C₃H₈ at lower CO₂ content decreased. An increase in the CO₂:C₃H₆ ratio only slightly enhanced the conversion of C₃H₈ and altered only little the product distribution. Results obtained are plotted in Fig. 5A and B. The apparent activation energies for the formation of different products have been determined on Au/ZnO in the temperature range of 763–823 K. Some Arrhenius plots are displayed in Fig. 5C. We obtained the following values: 105.5 kJ/mol for C₃H₆; 129.6 kJ/mol for CO; 161.3 kJ/mol for H₂ and 186.7 kJ/mol for CH₄.

The amounts of carbon-containing deposit formed in the CO₂ + C₃H₈ reaction on Au/ZnO catalyst and its reactivity have been determined by TPR measurements. The formation of methane, ethylene and ethane was established. Methane peak was found at T_p = 874 K, but its continuous evolution was experienced even above this temperature. The formation of C₂H₆ occurred in two peaks with T_p values of 841 and 1039 K, while that of C₂H₄ with T_p ≈ 872 K and 1118 K. TPR spectra are displayed in Fig. 6.

One of the referees noted that the carbon mass balance is very important, particularly when the conversion exceeds 70%. Although the conversion in our case was always below 50%, we calculated the carbon balance for all measurements performed on Au/ZnO. About 6–11% of C was missing in average, which was

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**Fig. 1.** (A) Infrared spectra of adsorbed C₃H₈ on Au/ZnO at different temperatures: (a) 215 K; (b) 273 K; (c) 373 K; (d) 573 K; (e) 873 K. TPD spectra of C₃H₆ following its adsorption on ZnO (B) and Au/ZnO (C).
attributed to the low reactivity of the carbon deposit formed in the reaction at 873 K.

3.6. Reactions of propylene

In order to find out the fate of propylene formed in the decomposition propane, its reaction with CO$_2$ was also examined on Au/ZnO. Propylene underwent relatively little decomposition over this catalyst. The conversion reached only 4.5% at 873 K. The main product was H$_2$. Less amount of CH$_4$ was also detected. Adding CO$_2$ to C$_3$H$_6$ increased the conversion with few percents and led to the formation of CO. An enhanced formation of CH$_4$ also occurred, which exceeded that of H$_2$. Raising the temperature above 823 K caused a decline of the conversion of C$_3$H$_6$.

4. Discussion

4.1. IR spectroscopic studies

The interaction of propane with supported Rh [8], Re [9] and Mo$_2$C [10] catalysts has been investigated before by means of FTIR spectroscopy. Adsorption of propane on Au/ZnO at 200–215 K caused the appearance of intense absorption bands at 2981, 2967, 2960, 2901, 2877 cm$^{-1}$ in the CH stretching region and 1472, 1457, 1387, 1375 cm$^{-1}$ in the low frequency range. The spectrum shows a good agreement with those obtained on other catalysts at low temperature [20–25]. These absorption bands are characteristic for molecularly adsorbed propane, and their assignments are presented in Table 2. Although the catalytic reactions of propane proceed at high temperatures (Figs. 2 and 3) changes in the IR spectra indicate the occurrence of a surface interaction at or above room temperature. As in the previously studied catalysts, the formation of $\pi$-bonded propylene, di-$\sigma$-bonded propylene and propylidene is postulated (Table 2). These adsorbed species appear to be strongly bonded to the catalysts surface, as no change was experienced in the IR spectra even at high temperatures.

TPD measurements showed that a fraction of strongly adsorbed C$_3$H$_8$ remained on both the ZnO and Au/ZnO. It decomposed only above 700 K resulting in the formation of CH$_4$, C$_2$H$_6$ and C$_2$H$_4$.

4.2. Catalytic studies

The dehydrogenation of propane
is strongly endothermic and also equilibrium limited. Higher conversion will require either higher temperature or lower pressures. In the case where the feed gas is only propane, the equilibrium propane conversion is given by the formula

\[ K_p = \frac{P_x^2}{(1 - x)^2} \]

with \( K_p \) the equilibrium constant, \( x \) the equilibrium conversion and \( P \) the total pressure.

From the supported Au catalysts examined only the Au/ZnO exhibited a moderate catalytic effect for the dehydrogenation of propane Au/MgO and Au/Al₂O₃ were found almost inactive below 873 K. The conversion on Au/ZnO reached a value of 17–18% even at 823 K. We notice that the conversion of the propane never matched with the chemical equilibrium at any temperatures. The amount of \( \text{H}_2 \) is more than 2 times larger than that of \( \text{C}_3\text{H}_6 \). Note that we did not experience such a behavior in the case of pure ZnO up to 823 K, when the \( \text{H}_2/\text{C}_3\text{H}_6 \) ratio was 1.0–1.3. This indicates that Au nanoparticles are responsible for the large deviation in the amount of \( \text{H}_2 \) and \( \text{C}_3\text{H}_6 \). In the explanation of this feature we assume that a significant fraction of \( \text{C}_3\text{H}_8 \) underwent a complete decomposition to carbon

\[ \text{C}_3\text{H}_8 = \text{CH}_4 + \text{H}_2 + 2\text{C}(s) \] (2)

and the \( \text{C}_2\text{H}_4 \) formed in the primarily process (Eq. (1)) also decomposed further

\[ 2\text{C}_3\text{H}_8 = 2\text{CH}_4 + \text{C}_2\text{H}_4 + 2\text{C}(s) \] (3)

The fact that we found \( \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \) in the products supports the occurrence of these reactions.

The situation is different when \( \text{CO}_2 \) was added to \( \text{C}_3\text{H}_8 \). While \( \text{CO}_2 \) only slightly increased the conversion of \( \text{C}_3\text{H}_8 \) on pure ZnO (see Fig. 2), it exerted a drastic enhancement in the conversion of \( \text{C}_3\text{H}_8 \) on Au/ZnO. The amounts of all products found in the dehydrogenation of \( \text{C}_3\text{H}_8 \) considerably increased. The fact that a large amount of \( \text{CO} \) formed clearly indicates the involvement of the \( \text{CO}_2 \) in the reaction of propane. In light of the formation of products we can account with the dry reforming of propane

\[ \text{C}_3\text{H}_8 + 3\text{CO}_2 = 4\text{H}_2 + 6\text{CO} \] (4)

and with the oxidative dehydrogenation of propane

\[ \text{C}_3\text{H}_8 + \text{CO}_2 = \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2\text{O} \] (5)

An interesting feature of the \( \text{CO}_2 + \text{C}_3\text{H}_8 \) reaction is the production of a large amount of \( \text{CH}_4 \), which was one order of magnitude higher than in the absence of \( \text{CO}_2 \). We may assume the occurrence of the extended hydrogenolysis of propane in the presence of a large amount of \( \text{H}_2 \)

\[ \text{H}_2 + \text{C}_3\text{H}_8 = \text{CH}_4 + \text{C}_2\text{H}_6 \] (6)

However, \( \text{C}_2\text{H}_6 \) was not detected even in traces, which excludes this route of methane formation. In addition this route of \( \text{CH}_4 \) production does not need the presence of \( \text{CO}_2 \). A possible explanation of the extended formation of \( \text{CH}_4 \) is the hydrogenation of \( \text{CO}_2 \)

\[ 4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \] (7)

Supported Au samples, however, were found to be completely inactive for the above reaction below 500 K [26]. Control measurement performed on the same Au/ZnO catalyst used in the present study revealed that \( \text{H}_2 \) does react with \( \text{CO}_2 \) at 723–773 K resulting in

\[ \text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O} \]
Fig. 4. Product distribution in the reaction of CO$_2$ + C$_3$H$_8$ on various catalysts at different temperatures: (A) Au/ZnO; (B) ZnO; (C) Au/Al$_2$O$_3$; (D) Au/MgO.

Fig. 5. Effects of CO$_2$/C$_3$H$_8$ ratio on the conversion of C$_3$H$_8$ (A), and on the formation of various products on Au/ZnO at 823 K (B). Arrhenius diagram for the formation of different products on Au/ZnO (C).
only in CO and H\textsubscript{2}O. Methane was detected only in a very small quantity. Similarly, we found no methane formation in the hydrogenation of CO on the same catalyst. Accordingly, we may assume that CH\textsubscript{4} is formed in the decomposition of C\textsubscript{3}H\textsubscript{5} radical (see below, Eq. (11)).

In the explanation of much greater activity of Au/ZnO compared to Au/Al\textsubscript{2}O\textsubscript{3} and Au/MgO we should take into account that ZnO is an n-type semiconductor, while Al\textsubscript{2}O\textsubscript{3} and MgO are insulating oxides. Based on the work function of ZnO (3.95–4.25 eV) and Au (5.5 eV), we expect an electronic interaction between ZnO and Au particles at the Au/ZnO interface [27]. This may result in the activation of rather inert CO\textsubscript{2} on Au particles in the form of negatively charged CO\textsubscript{2}\textsuperscript{−}. It has been demonstrated in several studies that negatively charged CO\textsubscript{2} is much more reactive than the neutral one [28,29]. Recently, it was reported that n-type oxidic supports for Au are much more efficient in the reaction between CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} compared to Au samples deposited on insulating oxides [19].

In light of this consideration we describe the CO\textsubscript{2} + C\textsubscript{3}H\textsubscript{8} reactions with following elementary steps. We assume that the partially negatively charged CO\textsubscript{2} enters reaction with the stable hydrocarbons, C\textsubscript{3}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{6}, producing more reactive C\textsubscript{x}H\textsubscript{y} fragments:

\begin{align*}
\text{C}_3\text{H}_8 + \text{CO}_2 \to \text{C}_3\text{H}_7 + \text{CO} + \text{OH}^+ \\
\text{C}_3\text{H}_7 + \text{CO} \to \text{C}_3\text{H}_6 + \text{H}^+ \\
\text{C}_3\text{H}_6 + \text{CO}_2 \to \text{C}_3\text{H}_5 + \text{CO} + \text{OH}^+ \\
\text{C}_3\text{H}_5 + \text{C}_2\text{H}_4 + 2\text{C}(s) + \text{H}_2 \\
2\text{OH}^+ \to \text{H}_2\text{O} + \text{O}^2- \\
2\text{H}_2 \to \text{H}_2\text{g} 
\end{align*}

Accordingly CH\textsubscript{4} can be formed in the decomposition of C\textsubscript{3}H\textsubscript{7} radical (Eq. (11)).

In the study of the reactions of C\textsubscript{x}H\textsubscript{y} fragments over metal single crystals in UHV it was found that a fraction of C\textsubscript{3}H\textsubscript{6} species is dimerized beside their decomposition [30–33]. In the case of C\textsubscript{3}H\textsubscript{7} hexane (C\textsubscript{6}H\textsubscript{14}) and hexene (C\textsubscript{6}H\textsubscript{12}) were identified. This process was more expressed on less reactive Au(111) [30,31] compared to Rh(111) [32] and Mo\textsubscript{2}C/Mo(100) [33] surfaces. In the present study we found no sign of the formation of these compounds. The possible reason is that the reaction of propane occurred at very high temperature, above 650 K, when the favorite route of the C\textsubscript{3}H\textsubscript{7} and C\textsubscript{3}H\textsubscript{5} is their decomposition.

We may compare the catalytic performance of supported Au in the CO\textsubscript{2} + C\textsubscript{3}H\textsubscript{8} reaction with other catalysts examined under exactly the same experimental conditions. A general feature is that CO\textsubscript{2} markedly accelerated the reaction of C\textsubscript{3}H\textsubscript{8} on all catalysts. Over Al\textsubscript{2}O\textsubscript{3}–supported Pt metals the dehydrogenation of propane occurred at 823–923 K with selectivities of 40–55% [5]. The activity of the catalysts depended on the nature of the metal: on the most effective Rh/Al\textsubscript{2}O\textsubscript{3}, the conversion reached a value of 63.5%, and on the less effective Pd/Al\textsubscript{2}O\textsubscript{3} this value was only 4.3%. These catalysts were found to be effective for the dry-reforming of propane to produce synthesis gas at 823–923 K [5]. Over Re/Al\textsubscript{2}O\textsubscript{3} the decomposition of C\textsubscript{3}H\textsubscript{8} sets in at 873–923 K with selectivity to propylene of 43–74% [9]. Adding CO\textsubscript{2} to C\textsubscript{3}H\textsubscript{8} changed the reaction pathway of C\textsubscript{3}H\textsubscript{8}, and the dry reforming of C\textsubscript{3}H\textsubscript{8} came into prominence. Mo\textsubscript{2}C deposited on SiO\textsubscript{2} catalyzed the dehydrogenation of C\textsubscript{3}H\textsubscript{8} at 773–873 K [10]. The selectivity of propylene formation attained a value of 35–50% at a conversion of 25–35%.

5. Conclusions

(i) Propane interacts with Au/ZnO even below 300 K yielding adsorbed propylene and propylidene.

(ii) Dehydrogenation of C\textsubscript{3}H\textsubscript{8} and its reaction with CO\textsubscript{2} are limited on Au/MgO and Au/Al\textsubscript{2}O\textsubscript{3}.

(iii) In contrast, Au/ZnO exhibited a much higher activity in the dehydrogenation of propane. Adding CO\textsubscript{2} to propane further increased the conversion.

(iv) The catalytic performance of Au/ZnO was explained by the occurrence of an electronic interaction between Au and n-type ZnO leading to the activation of CO\textsubscript{2}.

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References