

# Effect of Support and Promoter on Activity and Selectivity of Gold Nanoparticles in Propanol Synthesis from CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>

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**Supporting Information** 



**ABSTRACT:** Direct propanol synthesis from  $CO_2$ ,  $H_2$ , and  $C_2H_4$  was investigated over  $TiO_2$ - and  $SiO_2$ -based catalysts doped with K and possessing Au nanoparticles (NPs). The catalysts were characterized by scanning transmission electron microscopy and temperature-programmed reduction of adsorbed  $CO_2$ . Mechanistic aspects of  $CO_2$  and  $C_2H_4$  interaction with the catalysts were elucidated by means of temporal analysis of products with microsecond time resolution.  $CO_2$ , which is activated on the support, is reduced to CO by hydrogen surface species formed from gas-phase  $H_2$  on Au NPs.  $C_2H_4$  adsorption also occurs on these sites. In comparison with  $TiO_2$ -based catalysts, the promoter in the K-Au/SiO\_2 catalysts was found to increase  $CO_2$  conversion and propanol production, whereas Au-related turnover frequency of  $C_2H_4$  hydrogenation to  $C_2H_6$  decreased with rising K loading. The latter reason was linked to the effect of the support on the ability of Au NPs for activation of  $C_2H_4$  and  $H_2$ . The positive effect of K on  $CO_2$  conversion was explained by partial dissolution of potassium in silica with formation of surface potassium silicate layer thus inhibiting formation of potassium carbonate, which binds  $CO_2$  stronger and therefore hinders its reduction to CO.

**KEYWORDS:** nanoparticles, Au, propanol, CO<sub>2</sub>, hydroformylation, TAP reactor

# 1. INTRODUCTION

Fossil carbon-containing materials are the primary source of energy and the main feedstock for the chemical industry for the production of a wide range of commodity chemicals. However, the amount of such raw materials is limited, and their above transformations are typically accompanied by formation of CO<sub>2</sub>. The scientific community now agrees that an increased concentration of CO<sub>2</sub> in the atmosphere comes from burning fossil fuels. This gas is deemed to be the major contributor to global warming due to the greenhouse effect.<sup>1,2</sup> Therefore, utilization of CO2 for green synthesis of fuels and useful chemicals is of enormous environmental and economic interest. There are already successful examples of commercially available technologies for one-step CO<sub>2</sub> conversion to methanol or methane.<sup>3,4</sup> Other approaches under investigation are CO<sub>2</sub> conversion into formic acid<sup>5,6</sup> or into synthetic fuels via Fischer-Tropsch synthesis.

Recently, our group demonstrated that  $CO_2$  in the presence of  $H_2$  and  $C_2H_4$  can be converted into *n*-propanol (propanol) with 100% selectivity with respect to  $CO_2$  over TiO<sub>2</sub>-supported catalysts with Au nanoparticles (NPs) and doped by  $K_2O$  or  $Cs_2O.^{8-11}$  Those studies also elucidated mechanistic aspects of product formation. Propanol was only formed when  $CO_2$ ,  $C_2H_4$ , and  $H_2$  were present in the feed, whereas CO and  $H_2O$  were the only products in the absence of  $C_2H_4$ . Irrespective of the promoter, propanol is formed according to the following mechanistic scheme.  $CO_2$  initially reacts with  $H_2$  to CO and  $H_2O$  via the reverse water–gas shift (RWGS) reaction followed by  $C_2H_4$  hydroformylation with CO to propanal. The latter is further hydrogenated to propanol.  $CO_2$  reaction with  $C_2H_4$  to propanol in the absence of  $H_2$  is thermodynamically not possible.

Usage of  $CO_2$  instead of CO enables to operate under less toxic conditions as compared to the industrial way of propanol formation through hydroformylation of  $C_2H_4$  with CO and  $H_2$ . Propanol could be used as an alternative to alcohol-based fuel stocks; it has a higher specific energy density than methanol and ethanol.<sup>12</sup> Furthermore, it can be easily converted into

Received: February 26, 2016 Revised: April 1, 2016 propylene, which is one of the core commodity chemicals. The major drawback of the above CO2-based approach is low propanol selectivity (<4.5%) with respect to C<sub>2</sub>H<sub>4</sub> due to high catalyst activity for nondesired C<sub>2</sub>H<sub>4</sub> hydrogenation to C<sub>2</sub>H<sub>6</sub>. It is, however, well-documented that the rate of olefin hydrogenation over supported catalysts with Au NPs can be tuned by metal loading and average NPs size.<sup>13–15</sup> For example, Sermon et al.<sup>14</sup> showed for Au/SiO<sub>2</sub> catalysts that the 1-pentene hydrogenation rate related to overall Au amount decreased with rising metal loading (0.05 to 5 wt %); the worst hydrogenationactive catalyst was Au(5 wt %)/SiO2, possessing Au NPs of about 23 nm. Chou et al.<sup>15</sup> systematically investigated micelleencapsulated Au NPs supported on TiO2, ZnO, ZrO2, and SiO2 in C<sub>3</sub>H<sub>6</sub> hydrogenation and found that Au/TiO<sub>2</sub> with the smallest Au NPs of 8 nm showed the highest hydrogenation activity. For liquid-phase cyclohexene hydrogenation over Au/  $SiO_2^{16}$  with Au NPs ranging from 10 to 20 nm, the catalyst with the smallest NPs was the most active one. In addition, our recent studies on CO<sub>2</sub> conversion into propanol in the presence of  $C_2H_4$  and  $H_2$  established that the nondesired  $C_2H_4$ hydrogenation to C2H6 over Au/TiO2 catalysts could be partially suppressed by the usage of promoters like K2O8 or  $Cs_2O.^9$  Unfortunately, the conversion of  $CO_2$  decreased with promoter loading, too.

The objective of this study was to elucidate the effects of support and promoter on the activity and selectivity of supported Au NPs in the conversion of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> into propanol. Our specific aims were (i) to increase propanol selectivity with respect to ethylene, that is, to reduce nondesired ethylene hydrogenation to ethane and (ii) to improve CO<sub>2</sub> conversion without significant loss of high propanol selectivity with respect to this feed component. To this end, we explored the potential of SiO<sub>2</sub>-supported catalysts containing similarly sized (around 5 nm) Au NPs but different amounts of K for their activity and selectivity in the target reaction. For comparative purposes,  $K-Au/TiO_2$  catalysts promoted by either potassium nitrate<sup>8</sup> or potassium silicate were also investigated. Fundamentals of CO<sub>2</sub> activation were studied by means of CO<sub>2</sub> temperature-programmed desorption tests and CO<sub>2</sub> pulse experiments in the temporal analysis of products reactor. The latter technique was also applied for analyzing C<sub>2</sub>H<sub>4</sub> adsorption. To determine the size of Au NPs, the used catalysts were characterized by high-angle annular dark field (HAADF) and annular bright field (ABF) scanning transmission electron microscopy (STEM).

# 2. EXPERIMENTAL SECTION

2.1. Preparation and Characterization of Au-Containing Catalysts. K-Au/SiO2 materials with the nominal Au loading of 2 wt % and different (1-4 wt %) amounts of K were prepared by sequential deposition-precipitation and incipient impregnation methods, similar to the procedure for K-Au/ TiO<sub>2</sub> catalysts.<sup>8</sup> SiO<sub>2</sub> (Grade 646, Davisil,  $S_{BET}$  of 301 m<sup>2</sup> g<sup>-1</sup>) was initially calcined in air at 773 K for 8 h. Two grams of calcined SiO<sub>2</sub> were suspended in 200 mL deionized water, and then the appropriate amount of  $HAuCl_4 \cdot xH_2O$  (41.1 wt % Au, Chempur) was added. The suspension was stirred at 343 K for 1 h and afterward cooled to room temperature. Ammonia (25% aqueous solution, Roth) used as a reducing agent was added to the aqueous suspension until a pH value of around 10-10.5 was reached. This pH range was chosen according to the results of Somodi et al.<sup>17</sup> After an additional 10 min of stirring, Au/ SiO<sub>2</sub> precursor was filtrated, thoroughly washed, dried at 353 K

overnight, and calcined in air at 573 K for 4 h. Doping of calcined samples with K was performed via incipient-wetness impregnation method with an aqueous solution of KNO<sub>3</sub> (>99%, Merck). Hereafter, drying and calcination steps were repeated yielding XK-Au/SiO<sub>2</sub> with "X" representing the particular K weight concentration.

Additionally, two batches of supported catalysts based on  $TiO_2$  anatase (BASF,  $S_{BET}$  of 58 m<sup>2</sup> g<sup>-1</sup>) were prepared. They differed in the source (KNO<sub>3</sub> vs K<sub>2</sub>SiO<sub>3</sub>) of K and the method of its deposition on  $TiO_2$ . For a first batch, Au was initially loaded onto  $TiO_2$  as described in ref 10. Thereafter, Au/TiO<sub>2</sub> was incipient-wetness impregnated with a mixture of KNO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub> (SiO<sub>2</sub>/K<sub>2</sub>O = 2.5:1 wt %, Alfa Aesar) with the portion of K<sub>2</sub>SiO<sub>3</sub> being 10%, 50%, or 100% gaining an overall K content of 3 wt %. These titania-supported catalysts were dried at 353 K overnight, and calcined in static air at 573 K for 4 h. Such catalysts are abbreviated as *XK*-YK(*Si*)-Au/TiO<sub>2</sub>, where "*X*" and "*Y*" stand for the particular K weight concentration from KNO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub>, respectively.

To prepare the second batch of catalysts, we first impregnated TiO<sub>2</sub> anatase with K<sub>2</sub>SiO<sub>3</sub> dissolved in concentrated ammonia (pH of solution 11-11.5) according to an incipient-wetness method. The nominal K loading was 1 wt %. In a next step, the obtained TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub> precursor was dried at 353 K and further impregnated with an aqueous solution of HAuCl<sub>4</sub>·xH<sub>2</sub>O to achieve a loading of Au of 2 wt %. After an additional drying step, a concentrated ammonia solution was added to the Au-loaded TiO2-K2SiO3 precursor for an incipient wetness deposition of Au(OH)<sub>3</sub>, held impregnated for 10 min, and washed with water under filtration for chlorine removal. Hereafter, Au/TiO2-K2SiO3 was dried overnight at 353 K and then doped with K through an incipient-wetness method using an aqueous solution of KNO<sub>3</sub> to obtain 1, 3, and 5 wt % K. After the last doping step, all the titania-supported catalysts were dried at 353 K overnight and calcined in static air at 573 K for 4 h. These catalysts were called XK-Au/TiO<sub>2</sub>- $K_2SiO_3$  where "X" stand for the particular K weight concentration from KNO<sub>3</sub>. Finally, all as-prepared precursors were pressed and sieved to yield particles of 250-450  $\mu$ m.

The weight content of Au and K in the fresh but calcined catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 715 emission spectrometer.

The Brunauer–Emmet–Teller specific surface areas  $(S_{BET})$  were determined from nitrogen adsorption–desorption isotherms collected at 77 K on BELSORP-mini II (BEL Japan, Inc.).

The size of Au NPs on the surface of the catalysts was determined by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) employing an aberration-corrected JEM-ARM200F microscope operated at 200 kV and equipped with a JED-2300 energy-dispersive X-ray spectrometer (EDXS, JEOL) for elemental analysis. Scanning transmission electron microscopy (STEM) operations were done using a Cs-corrector CESCOR (CEOS). Samples were deposited on a holey-carbon-supported copper grid of mesh size 300. Particle size distributions of supported Au NPs were calculated from at least 150 particles with ImageJ software.<sup>18</sup>

Powder X-ray diffraction (XRD) analysis was carried out using an X'Pert Pro (Panalytical, Almelo) at the  $2\theta$  range of 5–  $80^{\circ}$  and using a silicon standard. Phase composition of the samples was identified with the program WINXPow by STOE&CIE with inclusion of the Powder Diffraction File PDF2 of the ICDD (International Centre of Diffraction Data).

Reduction and/or desorption behavior of preadsorbed  $CO_2$ on the catalysts were probed by temperature-programmed reduction measurements with H<sub>2</sub> (H<sub>2</sub>-TPR). Each fresh catalyst (80 mg) was loaded into a fixed-bed tubular quartz reactor and heated up to 523 K with 10 K min<sup>-1</sup> in a flow of 5 vol % H<sub>2</sub> in Ar. Afterward, the flow was replaced by a flow of 10 vol %  $CO_2$ in Ar for 2 h. The reactor was cooled in the same flow to ca. 300 K. After purging in Ar, it was heated in a flow of 5 vol % H<sub>2</sub> in Ar up to 1173 K with 10 K min<sup>-1</sup> and held at this temperature for 20 min. The feed components and the reaction products were analyzed by an online quadrupole mass spectrometer (Pfeiffer Vacuum OmniStar 200).

2.2. Continuous-Flow Catalytic Tests. Catalytic tests were performed at 473 and 523 K and 2 MPa using an in-house developed setup equipped with 50 continuous-flow fixed-bed reactors operating in parallel. CO<sub>2</sub> (4.5, Air Liquide), H<sub>2</sub> (5.0, Air Liquide),  $C_2H_4$  (3.0, Linde), and  $N_2$  (5.0, Air Liquide) were the reactants and used without further purification. Subsequently, 300 mg of each catalyst (fraction of 250–450  $\mu$ m) was placed in stainless-steel tube reactors (ID = 4 mm) with 3fold weight of SiC for dilution and heated up to 523 K in a N<sub>2</sub> flow (6.67 mL min  $^{-1}$  per reactor). Hereafter, the  $N_2$  flow was replaced by a flow (6.67 mL min<sup>-1</sup> per reactor) of a reaction feed  $CO_2/H_2/C_2H_4/N_2 = 4:2:1:1$  for 24 h. Then, a  $CO_2/H_2/$  $C_2H_4/N_2 = 1:1:1:1$  mixture was fed to the reactors at 473 and 523 K. The contact time was kept constant at 45 g min  $l^{-1}$ . Steady-state data were collected after at least 10 h stabilization. The feed components and the reaction products were analyzed by an online GC (Varian CP-3800) equipped with FID (HP-Plot Q) and TCD (HP Plot Q and Molsieve 5A) detectors. Yield of propanol/propanal (eq 1) was calculated on the  $CO_2$ or  $C_2H_4$  basis taking into account that one oxygenate molecule is formed from one CO<sub>2</sub> and one C<sub>2</sub>H<sub>4</sub> molecule. Conversion of both  $C_2H_4$  and  $CO_2$  (eq 2) was calculated as the sum of yields of products from the corresponding feed components. Equation 3 was used for calculating product selectivity.

$$Y(i, f) = \frac{\dot{n}_i - \dot{n}_{i,0}}{\dot{n}_{f,0}} \times 100\%$$
(1)

$$X(f) = \sum_{i} Y(i, f)$$
(2)

$$S(i, f) = \frac{Y(i, f)}{X(f)} \times 100\%$$
 (3)

In these equations,  $\dot{n}_{\rm f}$  and  $\dot{n}_{\rm i}$  are the molar flows of feed components and reaction products, respectively. Subscript "0" refers to an inlet molar flow. Turnover frequency (TOF) was calculated according to eq 4:

$$TOF = \frac{F \times X(f) \times c(f, F) \times N_{A}}{m(cat) \times V_{m} \times N_{Au \text{ atoms}}}$$
(4)

where *F* is the total feed flow, c(f,F) the concentration of feed component,  $V_{\rm m}$  the molar volume, m(cat) the mass of catalyst, and  $N_{\rm Au\ atoms}$  the amount of surface Au atoms calculated according to ref.<sup>19</sup>

**2.3. Transient Experiments.** Mechanistic aspects of  $CO_2$  and  $C_2H_4$  interactions with K-Au/TiO<sub>2</sub> and K-Au/SiO<sub>2</sub> catalysts as well H/D exchange were studied in the temporal analysis of products (TAP) reactor.<sup>20,21</sup> The fresh catalyst (70

mg) was packed between two layers of quartz particles (sieve fraction of 250–450  $\mu$ m) into a quartz reactor (ID = 6 mm, length = 40 mm) within the isothermal zone of the reactor. It was heated at ambient pressure to 523 K with a ramp of 10 K  $\mathrm{min}^{-1}$  in a flow of  $\mathrm{H}_2$  and Ar fed with rates of 5 and 15 mL  $\min^{-1}$ , respectively. After exposition to this mixture for 1 h, the reactor was evacuated to ca.  $10^{-5}$  Pa followed by cooling to 473 K. Hereafter, single pulse experiments with  $CO_2/Ar = 1:1$ ,  $C_2H_4/Ar = 1:1$  or  $H_2/D_2/Ar = 1/1/1$  mixtures were performed.  $CO_2$  (4.5), Ar (5.0),  $H_2$  (5.0), and  $C_2H_4$  (3.0) were supplied by Linde, whereas D<sub>2</sub> was purchased from CK Special Gases Ltd. An overall pulse size was approximately 10<sup>15</sup> molecules or Ar atoms, respectively. At this pulse size, gas-phase collisions are suppressed (Knudsen diffusion regime),<sup>20</sup> so purely heterogeneous reaction steps were analyzed. For each atomic mass unit (AMU), the pulses were repeated 10 times and averaged to improve the signal-to-noise ratio. The feed components and reaction products were quantitatively analyzed by an online quadrupole mass spectrometer (HAL RC 301, Hiden Analytics). The following AMUs were used for massspectrometric analysis: 44 (CO<sub>2</sub>), 28 (CO and CO<sub>2</sub>), 26  $(C_2H_4)$ , 4(D<sub>2</sub>), 3(HD), 2(H<sub>2</sub>) and 40 (Ar). The concentration of feed components and reaction products was calculated from the areas of signals recorded at the respective AMUs using standard fragmentation patterns and sensitivity factors. The fragmentation patterns and respective sensitivities of feed components and reaction products were determined from separate calibration experiments using a reactor filled with quartz particles (rinsed in HNO<sub>3</sub>; 250–355  $\mu$ m), which were inert for the reactions studied.

## 3. RESULTS AND DISCUSSION

**3.1.** Physico-Chemical Catalysts Characterization. Table 1 presents the weight concentrations of Au and K,

| Table 1.  | Catalysts | and | Their | Selected | Physicochemical |
|-----------|-----------|-----|-------|----------|-----------------|
| Propertie | es        |     |       |          |                 |

| catalysts  | Au/wt % | K/wt % | $\frac{S_{\rm BET}}{m^2 g^{-1}}^{a}$ | $\frac{S_{\text{BET}}}{m^2 g^{-1}}$ | d <sub>Au NPs</sub><br>/nm |  |  |  |  |
|--|---------|--------|--------------------------------------|-------------------------------------|----------------------------|--|--|--|--|
| Au/SiO <sub>2</sub>  | 1.5     | -      | 277                                  | 225                                 | 4.5                        |  |  |  |  |
| 1K-Au/SiO <sub>2</sub>   | 1.6     | 0.9    | 261                                  | 222                                 | 5                          |  |  |  |  |
| 2K-Au/SiO <sub>2</sub>   | 1.6     | 1.8    | 260                                  | 156                                 | 4.0                        |  |  |  |  |
| 3K-Au/SiO <sub>2</sub>   | 1.6     | 2.7    | 234                                  | 53                                  | 4.5                        |  |  |  |  |
| 4K-Au/SiO <sub>2</sub>   | 1.5     | 3.6    | 223                                  | 34                                  | 4.5                        |  |  |  |  |
| 2.7K- $0.3$ K $(Si)$ -Au/TiO <sub>2</sub>  | 1.7     | 2.7    | -                                    | 46                                  | 5                          |  |  |  |  |
| 1.5K- $1.5$ K $(Si)$ -Au/TiO <sub>2</sub>  | 1.6     | 2.6    | -                                    | 45                                  | 6                          |  |  |  |  |
| 3K(Si)-Au/TiO <sub>2</sub>   | 1.6     | 2.8    | -                                    | 47                                  | 3                          |  |  |  |  |
| $1$ K $-$ Au $/$ TiO $_2$ $-$ K $_2$ SiO $_3$  | 1.6     | 0.9    | 55                                   | 57                                  | 4 and<br>23                |  |  |  |  |
| 3K-Au/TiO <sub>2</sub> -K <sub>2</sub> SiO <sub>3</sub>  | 1.5     | 2.6    | 48                                   | 46                                  | 4                          |  |  |  |  |
| $5K-Au/TiO_2-K_2SiO_3$   | 1.5     | 4.6    | 41                                   | 42                                  | -                          |  |  |  |  |
| <sup>a</sup> As-prepared catalysts. <sup>b</sup> Spent catalysts. <sup>c</sup> Size determined by HAADF- |         |        |                                      |                                     |                            |  |  |  |  |

STEM images of spent catalysts.

 $S_{\text{BET}}$  of fresh and used catalysts, and the mean size of Au NPs on used catalysts. For SiO<sub>2</sub>-supported catalysts, the K loading was close to the nominal one, while the Au loading was around 1.6 wt % instead of the intended 2 wt %. The specific surface area of fresh K–Au/SiO<sub>2</sub> catalysts slightly decreased from 277 m<sup>2</sup> g<sup>-1</sup> to 223 m<sup>2</sup> g<sup>-1</sup> with an increase in the K loading from 0 to 4 wt %. However, the surface area significantly declined after catalytic tests. This effect became more pronounced with rising

K loading. For example, the area of the fresh 4K–Au/SiO<sub>2</sub> catalyst decreased from 223 m<sup>2</sup> g<sup>-1</sup> to only 34 m<sup>2</sup> g<sup>-1</sup>, whereas the corresponding values for 1K–Au/SiO<sub>2</sub> were 261 m<sup>2</sup> g<sup>-1</sup> and 222 m<sup>2</sup> g<sup>-1</sup>. Such changes may be caused by partial dissolution of the dopant in the support resulting in formation of thermodynamically more stable K<sub>2</sub>SiO<sub>3</sub> compared with K<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub>. TiO<sub>2</sub>-based catalysts possessed lower BET surface areas, which did not depend on K content.

The size of supported Au NPs and their distribution on the surface of spent catalysts were analyzed by HAADF-STEM. Compared with the previously investigated K-Au/TiO<sub>2</sub> catalysts,<sup>8,9</sup> no visible effect of K loading on the size of Au NPs could be established for the K-Au/SiO<sub>2</sub> catalysts. The nanoparticles on the surface of the latter materials were in the range between 4 and 5 nm. The representative images and the size distribution profiles are shown in Figure S1 in the Supporting Information (SI). To check if the size changed under reaction conditions, we also analyzed fresh 3K-Au/SiO<sub>2</sub>, which significantly lost its surface area after catalytic tests (Table 1). The surface of this material was populated by Au NPs of 4 nm (Figure S2). In other words, the nanoparticles did not change their size under reaction conditions. Due to the low contrast between K and Si, it is difficult to reveal where the promoter is located. However, our previous studies with Cs-Au/TiO<sub>2</sub> catalysts demonstrated that Cs is homogeneously distributed on the surface of both support and Au NPs.<sup>9</sup> No significant changes in Cs distribution were observed after reaction. Taking into account similar chemical nature of Cs and K, it can be expected that reaction-induced changes of K distribution are also minimal.

**3.2. Steady-State Catalytic Performance.** Propanol and CO were the main products formed from  $CO_2$ , whereas  $C_2H_4$  was converted into propanol and  $C_2H_6$ . Propanal was detected in traces owing to high catalyst activity for hydrogenation of this aldehyde to propanol. No significant changes in catalytic performance were observed within 170 h on stream under different reaction conditions (Figure S3 in S1). This is in agreement with the results of TEM analysis proving stability of Au NPs against sintering. Since K strongly affects catalyst performance (Figure 1), which does not, however, alter with time on stream, promoter leaching under reaction condition can be practically excluded.

Figure 1 shows  $CO_2$  and  $C_2H_4$  conversion (eq 2) at 473 and 523 K as well as propanol selectivity calculated with respect to each feed component (eq 3). We shall start with the discussion of conversion data. Au/SiO<sub>2</sub> showed some activity for CO<sub>2</sub> conversion only at 523 K (Figure 1a). The conversion increased when the catalyst was promoted with K; the higher the promoter content, the higher was the conversion (Figure 1a). The highest conversion of around 5% was obtained over  $4K-Au/SiO_2$  at 523 K. When comparing the above activity data with those previously reported for K-Au/TiO2 materials,<sup>8,9</sup> it becomes obvious that in contrast to Au/SiO<sub>2</sub>, the Kfree Au/TiO<sub>2</sub> catalyst converted CO<sub>2</sub> into CO and further into propanol but this activity decreased with rising K content. These results strongly suggest the importance of the interplay between the support, promoter, and Au NPs for CO<sub>2</sub> activation and propanol formation.

The conversion of  $C_2H_4$  over K-Au/SiO<sub>2</sub> decreased from 33% to 7% at 473 K and from 72% to 21% at 523 K with an increase in K loading from 0 wt % to 4 wt %, respectively (Figure 1c). A similar effect of the promoter was previously



**Figure 1.** Conversion of (a) CO<sub>2</sub> and (c) C<sub>2</sub>H<sub>4</sub> as well as selectivity to propanol calculated with respect to (b) CO<sub>2</sub> and (d) C<sub>2</sub>H<sub>4</sub> over K–Au/SiO<sub>2</sub> catalysts at 473 K (closed symbols) and 523 K (open symbols). Reaction conditions: CO<sub>2</sub>/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> = 1:1:1:1, 2 MPa, modified contact time of 45 g min l<sup>-1</sup>.

reported by us for K–Au/TiO<sub>2</sub> catalysts.<sup>8,9</sup> The latter materials showed, however, significantly higher conversion of  $C_2H_4$ .

Au/SiO<sub>2</sub> did not produce propanol, while this product was formed over all K-promoted catalysts. The highest alcohol selectivity with respect to CO<sub>2</sub> of 100% and 70% was obtained over 1K-Au/SiO<sub>2</sub> at 473 and 523 K, respectively, and slightly decreased with an increase in K loading. The propanol selectivity with respect to C<sub>2</sub>H<sub>4</sub> was lower because of high catalyst activity for nondesired  $C_2H_4$  hydrogenation to  $C_2H_6$ . This selectivity increased from 0 to 14% with an increase in K loading (Figure 1d). It is important to highlight that previously tested K-Au/TiO<sub>2</sub> materials<sup>8,9</sup> performed with significantly less selectivity; the selectivity did not exceed 4.2%. Fundamental origins of the support effect on propanol selectivity are thoroughly discussed in sections 3.4 and 3.5. To clarify the effect of the support and the loading on propanol formation and catalyst activity, we investigated interactions of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> with K-Au/SiO<sub>2</sub> and K-Au/TiO<sub>2</sub>. The results are presented and discussed in the following sections.

3.3. CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> Interaction with K–Au/SiO<sub>2</sub> and K– Au/TiO<sub>2</sub>. The type of  $CO_2$  and  $C_2H_4$  adsorption (reversible vs irreversible) was established from analysis of  $CO_2/Ar = 1:1$  and  $C_2H_4/Ar = 1:1$  pulse experiments at 473 K in the TAP reactor according to the approach described in literature.<sup>20</sup> The experimental data were transformed into a dimensionless form for discriminating between the pure diffusion process (the dimensionless Ar response) and reversible/nonreversible interactions of reactive gases. Figure 2 compares the dimensionless responses of CO<sub>2</sub> and Ar over K-Au/SiO<sub>2</sub> with 0-3 wt % K and K-Au/TiO<sub>2</sub> with 0-2 wt % K.<sup>8</sup> For  $Au/SiO_2$ , there is no visible difference between the  $CO_2$  and Ar responses (Figure 2a). In other words,  $CO_2$  does not practically interact with the catalyst but simply diffuses similarly to Ar. This statement agrees with the results of catalytic tests in Section 3.2, where no  $CO_2$  conversion was observed at 473 K.

The dimensionless  $CO_2$  responses obtained in the experiments with K-free Au/TiO<sub>2</sub> and all K-doped catalysts are



Figure 2. Dimensionless responses of CO<sub>2</sub> and Ar after pulsing of a CO<sub>2</sub>/Ar = 1:1 mixture over (a) Au/SiO<sub>2</sub>, (b) 1K–Au/SiO<sub>2</sub>, (c) 3K–Au/SiO<sub>2</sub>, (d) Au/TiO<sub>2</sub>, (e) 1K–Au/TiO<sub>2</sub>, and (f) 2K–Au/TiO<sub>2</sub> at 473 K.

located below the corresponding Ar responses and cross them (Figure 2). This is an indication of reversible  $CO_2$  adsorption. One can see in Figure 2 that the  $CO_2$  response tailing (nonzero  $CO_2$  signal at high dimensionless times) increases with rising K loading in K-Au/SiO<sub>2</sub> and K-Au/TiO<sub>2</sub>. According to ref 20, this is due to the fact that (i) the strength of  $CO_2$  interaction or (ii) the number of  $CO_2$  adsorption sites increase with rising K loading. Importantly, the tailing is stronger for the K-Au/TiO<sub>2</sub> catalysts than for their SiO<sub>2</sub>-based counterparts. This difference between these two catalyst systems is explained by stronger  $CO_2$  adsorption over the former materials.

Compared with  $CO_2$ ,  $C_2H_4$  interacts with the catalysts significantly weaker, and the strength of this interaction does not practically depend on K loading. This conclusion was derived from the analysis of the dimensionless responses of  $C_2H_4$  and Ar; these responses do not significantly differ from each other (Figure S4 in SI).

Further insights into  $CO_2$  adsorption and reduction of adsorbed  $CO_2$  species to CO were derived from  $H_2$ -TPR experiments performed with catalysts, on which  $CO_2$  had been preadsorbed at 523 K. Irrespective of K loading,  $CO_2$  desorbed from K-Au/SiO<sub>2</sub> in three temperature regions (Figure 3); between 323 and 473 K, between 473 and 673 K, and above 673 K with a desorption maximum at around 743 K. The amount of desorbed  $CO_2$  increased with rising K loading (Figure 3a).  $CO_2$  on the surface of Au/SiO<sub>2</sub> was reduced to CO only above 673 K (Figure 3c), while CO was formed between 373 and 573 K over all K-Au/SiO<sub>2</sub> catalysts. The amount of formed CO increased with K loading, thus supporting the positive effect of K on  $CO_2$  conversion mentioned in section 3.2.

In coincidence with the results of transient and catalytic tests,  $K-Au/TiO_2$  catalysts accumulated significantly higher amounts of  $CO_2$  than  $K-Au/SiO_2$  (Figure 3a,b). The  $CO_2$  desorption from the former materials took place in three regions with maxima at around 383, 600, and 800 K. The amount of  $CO_2$  desorbed at the two latter temperatures significantly decreased upon impregnation of  $Au/TiO_2$  with 1 and 2 wt % K. When K loading was increased to 3 wt %, the most  $CO_2$  desorbed at 473



**Figure 3.** Temperature profiles of CO<sub>2</sub> desorption and CO production on as-prepared (a,c) K-Au/SiO<sub>2</sub> and (b,d) K-Au/TiO<sub>2</sub> catalysts doped with (gray —) 1 wt % K, (- - -) 2 wt % K, (- - -) 3 wt % K, (- - -) 4 wt % K or (- ) without K.

K, whereas the peak at 383 K completely disappeared. Based on our previous FTIR studies,<sup>8</sup> such changes in CO<sub>2</sub> desorption behavior with rising K loading can be result of formation of ionic bidentate carbonates over  $3K-Au/TiO_2$ . The highest amount of CO formed over this catalyst was observed at around 650 K. The K-Au/TiO<sub>2</sub> catalysts with 1 and 2 wt % K produced CO at 433 and 503 K, respectively. The shift in the temperature of maximal CO formation indicates a decrease in the rate of CO generation with rising K loading, thus supporting the results of catalytic steady-state tests (Figure 1). **3.4. Effect of Support and Promoter on CO<sub>2</sub> Conversion.** Our previous mechanistic studies with  $TiO_2$ based catalysts showed that CO<sub>2</sub> adsorbed on the support in the vicinity of Au NPs is reduced to CO by hydrogen surface species.<sup>8</sup> Gas-phase H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are activated on Au NPs. As a consequence, propanal/propanol formation takes place over such particles, too. The same mechanistic picture should be valid for K-Au/SiO<sub>2</sub> as discussed below. The fact that the CO<sub>2</sub> conversion was zero over Au/SiO<sub>2</sub> at 473 K but increased upon doping with K proves that CO<sub>2</sub> adsorption takes place on basic sites created by the promoter homogeneously distributed on the surface of catalysts. As C<sub>2</sub>H<sub>4</sub> was hydrogenated over both nondoped and doped Au/SiO<sub>2</sub>, Au NPs should be responsible for activation of this olefin.

Despite the above similarities between K–Au/TiO<sub>2</sub> and K–Au/SiO<sub>2</sub> with respect to activation of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, these two catalytic systems differ in the effect of K loading on propanol formation. Importantly, the K–Au/TiO<sub>2</sub> catalysts converted CO<sub>2</sub> to propanol in the absence of the promoter but lost their activity with rising K content. In contrast, Au/SiO<sub>2</sub> did not produce propanol, but the activity strongly increased with rising K loading. Such different behavior should be related to the catalyst ability for CO<sub>2</sub> reduction to CO with the latter being required for ethylene hydroformylation to propanal, which is the precursor of propanol.<sup>8–10</sup>

The above difference between K-Au/TiO<sub>2</sub> and K-Au/SiO<sub>2</sub> can be explained when assuming that promoting Au/SiO<sub>2</sub> with K results in formation of K<sub>2</sub>SiO<sub>3</sub>, which does not decompose to K<sub>2</sub>O upon calcination<sup>12</sup> and cannot be converted to K<sub>2</sub>CO<sub>3</sub> under reaction conditions due to thermodynamic reasons. This process would explain the negative effect of promoter on the  $S_{\text{BET}}$  of K-Au/SiO<sub>2</sub> (Table 1). Such silicate cannot be formed on the surface of K-Au/TiO<sub>2</sub>, where K is stabilized as K<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub>. Indeed, our in situ FTIR studies revealed formation of different carbonate species upon catalyst contact with reaction feeds.<sup>8</sup> Thus, basic properties of K<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>O/K<sub>2</sub>CO<sub>3</sub> should determine the activity of K-Au/SiO<sub>2</sub> and K-Au/TiO<sub>2</sub> for CO<sub>2</sub> conversion to CO with the latter reacting with C2H4 to propanal in a separate step. However, our XRD analysis did not reveal any crystalline K<sub>2</sub>SiO<sub>3</sub> phase (Figure S5 in SI).

To verify the hypothesis about the effect of potassium silicate on catalytic performance, we prepared three additional 3K–  $Au/TiO_2$  catalysts using a mixture of KNO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub> for impregnation of  $Au/TiO_2$ . Importantly, all these catalysts possessed 3 wt % of K, but the ratio of  $KNO_3/K_2SiO_3$  was varied to achieve 10%, 50%, or 100% of the promoter from the silicate. To distinguish between the different K sources in these catalysts, we call them as XK-YK(Si)- $Au/TiO_2$ , where "X" and "Y" stand for the particular weight concentration of K from  $KNO_3$  and  $K_2SiO_3$  respectively. The  $S_{BET}$  of these catalysts is around 46 m<sup>2</sup> g<sup>-1</sup> (Table 1). The representative images and the size distribution profiles of Au NPs are shown in Figure S6 (SI).

Figure 4a shows that the conversion of  $CO_2$  in propanol synthesis tests increases with an increase in  $K_2SiO_3$  content. However, the number of  $CO_2$  adsorption sites decreased with this content as concluded from  $CO_2$  desorption tests (Figure S7 in SI). On the basis of these two results, we suggest that replacing  $K_2O$  by  $K_2SiO_3$  inhibits formation of ionic potassium carbonates under reaction conditions and consequently the catalyst activity for  $CO_2$  conversion increases because  $CO_2$ activated over less basic potassium silicate can be easily reduced



**Figure 4.** Conversion of (a,b)  $CO_2$  and (c,d) its selectivity to propanol over (a,c) K-K(Si)-Au/TiO<sub>2</sub> and (b,d)  $K-Au/TiO_2-K_2SiO_3$  at 473 K (closed symbols) and 523 K (open symbols). Reaction conditions:  $CO_2/H_2/C_2H_4/N_2 = 1:1:1:1, 2$  MPa, modified contact time of 45 g min  $l^{-1}$ .

to CO in the presence of hydrogen species formed from gasphase H<sub>2</sub> over Au NPs. It is also worth mentioning that the selectivity to propanol with respect to CO<sub>2</sub> did not practically depend on the content of K<sub>2</sub>SiO<sub>3</sub> and was around 100% and between 40% and 60% at 473 and 523 K, respectively (Figure 4c). Owing to high CO<sub>2</sub> conversion, the obtained propanol yield of 3.5% is higher than 2.4% previously reported by us for K–Au/TiO<sub>2</sub> catalysts prepared without K<sub>2</sub>SiO<sub>3</sub><sup>8,9</sup>

For further analyzing the collective influence of potassium silicate and oxide, we synthesized three additional catalysts as follows. Initially, TiO<sub>2</sub> was impregnated with  $K_2SiO_3$  to gain a support containing 1 wt % K. Hereafter, the modified support TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub> was loaded with Au using an aqueous solution of HAuCl<sub>4</sub>. So-prepared Au/TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub> was additionally doped with KNO<sub>3</sub> (1, 3, or 5 wt % K). According to our ABF-STEM analysis, the silicate covers the surface of TiO<sub>2</sub> as a thin layer (about 1 nm), where Au NPs are located (Figure 5). Histograms of Au NPs for the corresponding catalysts are in Figure S8.

Analogously to K–Au/SiO<sub>2</sub>, the conversion of CO<sub>2</sub> over K– Au/TiO<sub>2</sub>–K<sub>2</sub>SiO<sub>3</sub> increased with K loading (Figure 4b). This effect is particularly pronounced for tests at 523 K. It is important to highlight that the conversion values are higher than those obtained over K–Au/TiO<sub>2</sub> loaded with the same amount of K.<sup>8,9</sup> This is due to the fact that CO<sub>2</sub> is weaker adsorbed on K<sub>2</sub>SiO<sub>3</sub> than on K<sub>2</sub>O and therefore easily reduced to CO on Au NPs, which are actually located on the silicate (Figure 5). However, in contrast to K–Au/TiO<sub>2</sub>, the selectivity to propanol over K–Au/TiO<sub>2</sub>–K<sub>2</sub>SiO<sub>3</sub> decreased from 80% to 25% at 473 K and passed over maximum of 45% at 523 K with an increase in K loading from 1 wt % to 5 wt % (Figure 4d). Nevertheless, the propanol yield over K–Au/TiO<sub>2</sub>–K<sub>2</sub>SiO<sub>3</sub> was

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**Figure 5.** ABF- and HAADF-STEM images of (a,c,d) 1K-Au/TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub> and (b) 3K-Au/TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub>. A thin layer of K<sub>2</sub>SiO<sub>3</sub> on TiO<sub>2</sub> surface is indicated by black arrows. Images (c,d) illustrates Au NPs located on K<sub>2</sub>SiO<sub>3</sub>.

higher than over K-Au/TiO<sub>2</sub> as a result of easier CO<sub>2</sub> activation on the former catalysts. A possible reason for the negative effect of K loading on propanol selectivity is given in the following section after discussing the factors affecting ethylene activation.

**3.5. Mechanistic and Kinetic Origins of the Effect of Support and Promoter on C<sub>2</sub>H<sub>4</sub> Hydrogenation.** It is in general accepted that the activity of various Au-containing catalysts for hydrogenation of olefins and aldehydes increases with a decrease in the size of supported Au NPs.<sup>13,22,23</sup> This effect is ascribed to facilitated adsorption and activation of hydrogen (i.e., smaller NPs have higher number of lowcoordinated Au atoms on edges and corners). Such atoms adsorb and dissociate H<sub>2</sub> easier than Au atoms on terraces.<sup>13,24,25</sup> Alternatively, the size of Au NPs influences their electronic structure, viz., narrowing of the d-band and its shift closer to the Fermi level.<sup>23,26</sup> As a consequence of this electronic effect, molecules like H<sub>2</sub>, CO, and O<sub>2</sub> dissociate easier.

To take into account the effect of Au NPs size on catalyst activity for ethylene conversion, we calculated an apparent turnover frequency (TOF) of ethylene consumption over K-Au/SiO<sub>2</sub> and K-Au/TiO<sub>2</sub> catalysts. To this end, an overall concentration of surface Au atoms in these catalysts was estimated from the size of Au NPs as suggested by Abe et al.<sup>19</sup> for Ru/TiO<sub>2</sub> catalysts. The TOF values obtained at 473 and 523 K are presented in Figure 6. The activity of K-Au/SiO<sub>2</sub> strongly decreased with rising K loading, while for K-Au/TiO<sub>2</sub> it was practically independent of the promoter content at 473 K and slightly decreased with K content at 523 K. Because K-Au/SiO<sub>2</sub> catalysts possessed similarly (4–5 nm) sized Au NPs (Table 1), the promoter should directly influence particle activity. As demonstrated in our recent study on Cs-Au/TiO<sub>21</sub> the promoter is even located on the Au NPs.<sup>10,11</sup> On the basis of the chemical similarity between K and Cs, we suggest that K



**Figure 6.** Turnover frequencies of  $C_2H_4$  conversion as a function of K content in K–Au/TiO<sub>2</sub> (squares) and K–Au/SiO<sub>2</sub> (circles) catalysts at 473 K (closed symbols) and 523 K (open symbols). Reaction conditions:  $CO_2/H_2/C_2H_4/N_2 = 1:1:1:1$ , 2 MPa.

also interacts with Au NPs, thus affecting their performance. The most likely explanation for the K effect might be a repulsion of electronic densities between the promoter and the  $\pi$ -bonding of ethylene, thus resulting in inhibition of ethylene adsorption.

The discrepancy between the K-Au/SiO<sub>2</sub> and K-Au/TiO<sub>2</sub> systems in terms of K effect on the TOF values could be explained by the fact that the promoter influences not only ethylene adsorption but also activation of hydrogen on Au NPs. Our previous study on H/D exchange demonstrated that promoting Au/TiO<sub>2</sub> with K accelerates generation of adsorbed H species,<sup>8</sup> whereas such an effect was not observed over the K-Au/SiO<sub>2</sub> catalysts tested in the present study. From a kinetic viewpoint, the rate of ethylene hydrogenation depends on the coverages by ethylene and hydrogen species. Bearing this in mind, the independence of C<sub>2</sub>H<sub>4</sub>-TOF on K loading in K-Au/TiO<sub>2</sub> can be explained as follows. The negative effect of K on ethylene adsorption is compensated by the positive K effect for generating hydrogen species. Because such a positive effect of K was not determined for the K-Au/SiO2 catalysts, the TOF values of ethylene conversion over these materials decreased with K loading due to the negative effect of the promoter on ethylene adsorption (Figure 6).

Another important conclusion from Figure 6 is the effect of the supporting material on the TOF values for ethylene conversion; K-Au/TiO2 catalysts showed significantly higher activity than their SiO<sub>2</sub>-based counterparts. Because the activity of Au/SiO<sub>2</sub> was at least 2 times lower than that of Au/TiO<sub>2</sub>, it can be concluded that, in addition to K, the support also influences the intrinsic activity of surface Au atoms. The importance of the kind of support for hydrogenation activity of Au NPs is further illustrated by the results shown in Figure 7. This figure shows the conversion of ethylene and the selectivity to propanol over K–Au/TiO<sub>2</sub>–K<sub>2</sub>SiO<sub>3</sub> and K–K(Si)-Au/TiO<sub>2</sub> catalysts differing in the location of K2SiO3 and Au NPs. As discussed in section 3.4, TiO2 in K-Au/TiO2-K2SiO3 is covered by a layer of K<sub>2</sub>SiO<sub>3</sub>, and Au NPs are situated on this layer; contrarily, the nanoparticles are located on the surface  $TiO_2$  and decorated by  $K_2SiO_3$  in K-K(Si)-Au/TiO<sub>2</sub> materials. One can see in Figure 7a,b that the K-K(Si)-Au/TiO<sub>2</sub> catalysts have a higher hydrogenation activity than K-Au/TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub>. On the basis of these results, one can assume that



Figure 7. Conversion of  $C_2H_4$  and selectivity to propanol on (a,c)  $3K-Au/TiO_2$  containing mixed source of dopants and (b,d)  $K-Au/TiO_2-K_2SiO_3$  at 473 K (closed symbols) and 523 K (open symbols). Reaction conditions:  $CO_2/H_2/C_2H_4/N_2 = 1:1:1:1, 2$  MPa, modified contact time of 45 g min  $l^{-1}$ .

the presence of potassium silicate layers on  $TiO_2$  appreciably reduces  $C_2H_4$  hydrogenation ability of Au NPs.

Thus, the location of K<sub>2</sub>SiO<sub>3</sub> (i.e., between Au NPs and TiO<sub>2</sub> vs on or at Au NPs) appears to be an important factor governing the hydrogenation activity of Au NPs. This conclusion is supported by the fact that K-Au/TiO<sub>2</sub>-K<sub>2</sub>SiO<sub>3</sub> catalysts lose their activity with rising K loading in a similar way as determined for K-Au/SiO<sub>2</sub> (Figure 1). Moreover, for these both catalytic systems, propanol selectivity increases with the dopant loading (Figure 7d and Figure 1d), thus further stressing the effect of support on selective and nonselective ethylene transformations, which can be explained as follows. According to Fujitani et al.,<sup>27</sup> Hartfelder et al.,<sup>28</sup> and Panayotov et al.,<sup>29</sup> an irreducible support like alumina or silica is less prone to accommodate the resulting electrons compared to reducible supports like titania. As a consequence, Au NPs on irreducible supports show in general low activity for generation of adsorbed hydrogen species from gas-phase H<sub>2</sub>.

In summary, the present study revealed that the interplay between Au NPs, support, and the source of K promoter are the key parameters for developing new catalysts for CO<sub>2</sub> conversion into propanol in the presence of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. When taking into account the fact that nondesired C<sub>2</sub>H<sub>4</sub> hydrogenation to C<sub>2</sub>H<sub>6</sub> in the present study was suppressed without losing propanol productivity when comparing with previous literature data,<sup>8-10</sup> it is expected that catalytic performance can be further improved by a proper catalyst design. To this end, deep understanding of factors governing the kinetics of CO<sub>2</sub>, H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> activation is still required.

# 4. CONCLUSIONS

K–Au/SiO<sub>2</sub> catalysts were demonstrated to efficiently produce propanol from CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the presence of H<sub>2</sub>. They outperform previously developed K–Au/TiO<sub>2</sub> in terms of propanol yield and propanol selectivity with respect to ethylene. Compared with TiO<sub>2</sub>, Au NPs supported over SiO<sub>2</sub> reveal lower intrinsic activity for the undesired C<sub>2</sub>H<sub>4</sub> hydrogenation to C<sub>2</sub>H<sub>6</sub>. This catalyst property is additionally affected by K promoter in the K–Au/SiO<sub>2</sub> catalysts; the higher the loading, the lower the Au-related TOF values. Support redox and promoter basic properties were suggested to influence this catalyst performance.

It was also established that the promoter affects the rate of CO<sub>2</sub> reduction to CO and thus indirectly propanol production. In contrast to the  $TiO_2$ -based catalysts, promoting the Au/SiO<sub>2</sub> catalysts with K facilitates CO<sub>2</sub> conversion. The main reason for the distinctive effect of the promoter on this catalyst property is related to the kind of compound, which is formed from the promoter under reaction conditions. K is present mainly as potassium carbonate species on the surface of K-Au/TiO<sub>2</sub>. Their reduction to CO by hydrogen species formed upon activation of gas-phase H<sub>2</sub> on Au NPs is inhibited with an increase in K loading because of formation of stable ionic carbonates. Due to thermodynamic reasons, in addition to K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SiO<sub>3</sub> species are stabilized on the surface of K-Au/ SiO<sub>2</sub>, which adsorb CO<sub>2</sub> less strongly. As a consequence, the conversion of CO<sub>2</sub> to CO increases with rising promoter loading because the concentration of such sites increases.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00590.

HAADF-STEM images and Au NPs distributions, selected catalytic data, results of  $CO_2$  desorption tests, and XRD data (PDF)

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# Notes

The authors declare no competing financial interest.

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