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An Innovative Approach for Highly Selective Direct Conversion of CO₂ into Propanol using C₂H₄ and H₂

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Multifunctional catalysts are developed for converting CO_2 with C_2H_4 and H_2 into propanol. Au nanoparticles (NP) supported on TiO₂ are found to facilitate this reaction. The activity and selectivity strongly depend on NP size, which can be tuned by the method of Au deposition and by promoting with K. The promoter improves the selectivity to propanol. Under optimized reaction conditions (2 MPa, 473 K, and $CO_2/H_2/C_2H_4$ = 1:1:1), CO_2 is continuously converted into propanol with

Introduction

Carbon-based compounds play a vital role in everyday life by fulfilling our needs for a wide range of household and commercial products. For their production, the chemical industry uses natural gas and oil. With rising energy costs caused by limited natural resources, the efficiency of current processes and the development of alternative routes have become a priority for modern and, particularly, future industry. In addition, the emission of CO₂ contributing to global warming has strongly increased since the industrial revolution.^[1] One way to circumvent both energy and ecological problems is to use plant-derived materials and CO₂ as feedstock.^[2] Biomass is already applied world-wide to produce fuels and allows for the generation of bulk chemicals.^[3] CO₂ also finds an application for the production of various chemicals, with technologies for CH₃OH and CH₄ synthesis being now commercially available.^[4] However, when these products are used as fuels they cannot contribute to long-term CO₂ fixation. In order to ensure the reduction of CO₂ emissions, it is highly desirable to develop processes/catalysts for converting CO₂ into products having a long lifecycle, for example, polymers, dyes, and resins. Such products are typically produced from ethylene and propylene.

Today, propene is mostly produced through the steam cracking of naphtha and liquid petroleum gas, or fluid catalytic cracking (FCC) of heavy fractions of crude oils. Since the existing production capacities cannot completely fulfill the continuously growing propene demand, two purpose-built processes were commercialized: non-oxidative propane dehydrogenation (DH)^[5] and metathesis of ethylene and 2-butenes.^[6] Alternative-

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a near-to-100% selectivity. Catalytic tests as well as mechanistic studies by in situ FTIR and temporal analysis of products with isotopic tracers allow the overall reaction scheme to be determined. Propanol is formed through a sequence of reactions starting with reverse water–gas shift to reduce CO_2 to CO, which is further consumed in the hydroformylation of ethylene to propanal. The latter is finally hydrogenated to propanol, while propanol hydrogenation to propane is suppressed.

ly, propene can be formed through dehydration of propanol. The latter is commercially produced in a two-step process involving the high-pressure homogeneous hydroformylation of ethylene over a Co- or Rh-containing catalyst and consecutive hydrogenation of the resulting propanal to propanol.^[7] Various heterogeneous catalysts were also applied for gas-phase hydroformylation of ethylene, resulting in propanal and propanol.^[8] However, all hydroformylation processes suffer from the usage of toxic CO. This drawback can be overcome when using CO₂ instead of CO. The idea behind our concept is to develop a multifunctional heterogeneous catalyst for CO₂ conversion with H₂ initially to CO via the reverse water–gas shift (RWGS) reaction, followed by C_2H_4 hydroformylation with CO to propanal and hydrogenation of the latter to propanol (Scheme 1). A similar concept was recently introduced to pro-

$$CO_2 + H_2 \xrightarrow{Cat.} CO + H_2O$$

$$= \frac{CO/H_2}{Cat.} \xrightarrow{H_2} O \xrightarrow{H_2} OH$$

Scheme 1. Schematic representation of concept for 1-propanol (propanol) formation from CO $_{2^\prime}$ H $_{2^\prime}$ and C $_2$ H_4.

duce carboxylic acids from CO₂, liquid olefins, and H₂ over a homogeneous [RhCl(CO)₂]₂ catalyst with iodine promoters.^[9] Immobilized Ru complexes in ionic liquids are also able to catalyze the hydroformylation of 1-hexene with CO₂ and H₂.^[10]

Developing multi-functional catalysts for production of propanol from CO₂, C₂H₄, and H₂ is a big challenge because the RWGS reaction runs above 573 K^[11] due to the thermodynamic constrains, while the hydroformylation requires lower temperatures.^[8a, 12] Possible side reactions like Fischer–Tropsch (FT) synthesis, methanation, and C₂H₄ hydrogenation to C₂H₆ should

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also be suppressed. According to literature data,^[8a,b,11a,c,12,13] Cu, Co, Rh, and Au are known to support either RWGS and/or hydroformylation reactions. However, supported Cu-containing materials do not catalyze the hydroformylation step,^[13d] while Co-based catalysts are active for the formation of hydrocarbons through FT synthesis^[14] and catalysts with supported Rh species tend to completely hydrogenate olefins,^[15] in our case C₂H₄ to C₂H₆. Supported Au-containing catalysts appear to be a good alternative as they catalyze the RWGS reaction at moderate temperature up to chemical equilibrium^[16] and are active and selective in the heterogeneous hydroformylation of olefins with CO.^[8a]

Based on this background, the main intention of the present study was to explore the potential of Au-containing catalysts for the direct conversion of CO_2 into propanol in presence of C_2H_4 and H_2 . For this purpose, we applied different methods for the deposition of Au nanoparticles (NP) on TiO₂ with the aim to tune their size. The monometallic supported catalysts were additionally doped with K to check if the promoter influences NP size and catalyst performance. To test their activity and selectivity in the target reaction, continuous-flow tests were performed between 473 and 523 K using reaction feeds with different ratios of $CO_2/H_2/C_2H_4$. We demonstrated that promoting Au/TiO₂ with K increases the selectivity for CO_2 conversion to propanol up to 100%. This positive effect was thoroughly elucidated by in situ FTIR analysis and transient experiments with isotopic tracers.

Results

Catalyst characterization by BET, ICP, and TEM

The Brunauer–Emmett–Teller specific surface areas (S_{BET}) of bare support and catalytic materials are listed in Table 1. These values are in the range of 52 to 67 m²g⁻¹. There is only a slight decrease in S_{BET} of the support after Au and/or K deposition, that is, the support morphology has persisted. Our inductively coupled plasma optical emission spectrometry (ICP-OES) analysis revealed that Au loading differs from the nominal one of 2 wt%. The exact loading was around 1.3 wt% for all catalysts with the exception for Au/TiO₂_c possessing only 0.5 wt%. The

Table 1. Catalysts and their selected physicochemical and catalytic properties. ^[a]										
Catalyst	Loadir Au	ng [wt%] K	d _{Au-NP} ^[b] [nm]	S_{BET} [m ² g ⁻¹]	X(CO₂) [%]	S(CO) [%]	S(oxo) ^[c] [%]	<i>r</i> _{Au} ^[d] [h ⁻¹]		
TiO ₂	-	_	-	58	-	-	-	-		
Au/TiO ₂ _a	1.3	-	7.5	52	3.6	83	18	0.39		
Au/TiO ₂ _b	1.3	-	22.5	67	0.5	100	0	0		
Au/TiO ₂ _c	0.5	-	2.5	50	0.2	66	34	0.63		
1K-Au/TiO ₂ _a	1.3	1.0	4.5	64	3.3	25	75	8.03		
2K-Au/TiO ₂ _a	1.4	2.1	7.0	65	1.2	0	100	2.76		
3K-Au/TiO ₂ _a	1.3	2.9	7.5 & 10.0	59	0.8	0	100	1.79		
[a] Reaction conditions: 2 MPa, 473 K, contact time of 45 g min L ⁻¹ , CO ₂ /H ₂ /C ₂ H ₄ = 1:1:1. [b] d_{Au-NP} was determined from HAADF-STEM (Figure S1). [c] S(oxo) stands for										

[a] Reaction conditions: 2 MPa, 473 K, contact time of 45 g min L⁻¹, CO₂/H₂/C₂H₄ = 1:1:1. [b] d_{Au-NP} was determined from HAADF-STEM (Figure S1). [c] S(oxo) stands for overall selectivity to propanol and propanal. [d] r_{Au} was calculated according to Equation (4) at close degrees of CO₂ conversion.

potassium content corresponded to the nominal loading (Table 1). The bimetallic catalysts are abbreviated as follows: XK-Au/TiO₂_a, where "X" stands for the K weight concentration.

The size of supported Au NP and their distribution were analyzed by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Representative images and the corresponding size distributions are shown in Figure 1 and Figure S1 respectively. The smallest Au NP of 2.5 nm in diameter were identified on the surface of Au/TiO₂_c, while the surface of Au/TiO₂ b is populated by significantly larger NP of approximately 22.5 nm. Au/TiO2_a possesses NP of around 7.5 nm. It is worth mentioning that promoting Au/TiO2_a with K influences the size of the Au NP. An average diameter decreases from 7.5 to 4.5 nm after adding 1 wt% K. The size distribution is also narrow compared to the unpromoted counterpart. Upon further increase in K loading, the NP become larger and their distribution broader: in case of 3K-Au/TiO2_a, differently sized Au NP with two size maxima at 7.5 nm and at 10 nm were identified (Table 1). Due to the low contrast between K and Ti, elemental energy dispersive X-ray analysis of selected regions of the images did not reveal where the promoter is located. However, considering the effect of K on the size of the Au NP, we can conclude that both these components are located close to each other.

Steady-state catalytic results

The activity and oxo-selectivity (propanol plus propanal) of monometallic Au-containing catalysts were elucidated under continuous-flow conditions at 2 MPa using reaction feeds with different ratios of $CO_2/H_2/C_2H_4$. Figure 2 shows the conversion of CO_2 and the selectivity to CO and propanol obtained over monometallic Au/TiO₂ catalysts using differently composed $CO_2/H_2/C_2H_4$ feeds.

The selectivity was calculated on CO_2 basis, that is, products originated from this feed component were taken into account. Irrespective of the feed composition, the highest CO_2 conversion was obtained over Au/TiO₂_a with Au NP of ca. 7.5 nm, while Au/TiO₂_b and Au/TiO₂_c with respectively larger or smaller NP were less active. As expected from the thermodynamics of the RWGS reaction, CO_2 conversion is positively influ-

> enced when operating at an excess of H₂ (Figure 2). Propanol formation was observed over Au/TiO2_ a and Au/TiO₂_c, whereas Au/TiO₂_b did not produce any oxygenates. It is worth mentioning that propanol was only formed when CO2, C2H4, and H2 were present in the feed, while CO and H₂O were the only products in the absence of C_2H_4 (Figure 2). Thus, propanol is formed from CO_2 and C_2H_4 and not through CO₂ hydrogenation. The presence of hydrogen is also highly important because propanol formation only from CO₂ and C₂H₄ is thermodynamically not possible. A reaction feed with equimolar amounts of CO₂, H₂, and C₂H₄ was identified as optimal to produce propanol. When we used a feed with an excess of hydrogen as required from the reaction stoichiometry, side ethylene hydrogenation to ethane

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Figure 1. HAADF-STEM images of (a) Au/TiO₂_a, (b) Au/TiO₂_b, (c) Au/TiO₂_c, (d) 1K-Au/TiO₂_a, (e) 2K-Au/TiO₂_a, and (f) 3K-Au/TiO₂_a.

strongly dominated. The highest oxo-selectivity of 34% with the optimized feed was obtained over Au/TiO₂_c followed by Au/TiO₂_a with 18%. However, the former catalyst showed significantly lower CO₂ conversion. Unfortunately, all catalysts also hydrogenated C₂H₄ to C₂H₆ with the selectivity being always above 95%. Au/TiO₂_a, Au/TiO₂_b, and Au/TiO₂_c revealed an ethylene conversion of 46, 18, and 30%, respectively. However, ethane is not a waste product and can be converted to ethylene in a cracker.

Having generated the potentially propanol-forming Au/TiO₂_a catalyst, we turned our attention to optimizing its selectivity. To this end, it was doped with different amounts of K, which is an important promoter for CO₂-FT catalysts.^[17] Doping Au/TiO₂_a with 1 wt% K resulted in an increase in oxoselectivity from 18 to 78% with the related decrease in CO selectivity (Figure 3). CO₂ conversion did not change and was ap-

proximately 3.3%, while the conversion of C_2H_4 to mainly C_2H_6 increased from 46 to 62%. The latter non-desired reaction was suppressed to 35% upon increasing K loading to 3 wt% with a coincident decrease in CO_2 conversion to 0.8% (Figure 3). Simultaneously, the oxo-selectivity increased to 100% on 2K- and 3K-Au/TiO₂_a. This result is very promising from a practical viewpoint because propanol and propanal can be easily separated from the non-reacted feed components, which are further recycled. Doping with K also strongly influenced the rate of propanol formation. The highest Au-related rate of 8.03 h⁻¹ was obtained over 1K-Au/TiO2_a. Upon a further increase in K loading, the rate decreased but was higher than over the non-promoted counterparts (Table 1). It is also worth mentioning that our catalysts showed high on-stream stability under different reaction conditions over 250 h on stream (Figure S2). Taking this information into account together with the fact that the carbon balance was not worse than 99%, we propose that carbon deposition does not play any significant role in our approach.

To elucidate mechanistic aspects of CO_2 transformation to oxygenates, we performed tests at different degrees of CO_2 con-

version by varying contact time (τ) from 5 to 45 g min L⁻¹. Figure 4 demonstrates the effect of τ on the selectivity to CO, propanal, propanol, and propane over the K-Au/TiO₂_a catalysts. The corresponding data for CO₂ conversion are shown in Figure S3. As expected, the degree of conversion increased with an increase in τ . CO selectivity over Au/TiO₂_a, however, decreased from 97 to 80% in the investigate rage of τ , while propanol selectivity accordingly increased from 2 to 17%. Traces of propane were observed at τ of 30 and 45 g min L⁻¹. Propanal was not detected at any contact time. Doping of Au/ TiO₂_a with K strongly influenced CO selectivity in the whole τ range. Similarly to Au/TiO2_a, this selectivity decreased over 1K-Au/TiO₂_a from 80 to 29% upon increase in τ from 5 to 45 g min L^{-1} . The propanol selectivity increased from 20 to 70%. However, propane was not detected, while the selectivity to propanal passed over a maximum with rising τ (Figure 4b).

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Figure 2. Conversion of CO₂ and selectivity (*S*) to CO and propanol on Au/ TiO₂_a (dark grey bar), Au/TiO₂_b (grey bar), and Au/TiO₂_c (light grey bar) against various reaction feeds. *x:x:x* represents the ratio of CO₂/H₂/C₂H₄ in the feeds. Reaction conditions: 2 MPa, 473 K, contact time of 45 g min L⁻¹.



Figure 3. Selectivity to CO (blue bar), propanal (yellow bar), and propanol (green bar) against K content on Au/TiO₂–a. Reaction conditions: 2 MPa, 473 K, contact time of 45 g min L⁻¹, CO₂/H₂/C₂H₄/N₂ = 1:1:1:1.

For catalysts with K loading of 2 and 3 wt%, CO and propane were not detected at any contact time (Figure 4c-d). Propanol and propanal were the only products formed from



Figure 4. Effect of τ on selectivity to CO (•), propanal (•), propanol (•), and propane ($_{\odot}$) over (a) Au/TiO₂_a, (b) 1K-Au/TiO₂_a, (c) 2K-Au/TiO₂_a, and (d) 3K-Au/TiO₂_a at 2 MPa and 473 K using a CO₂/H₂/C₂H₄ = 1:1:1 feed.

CO₂, with the former being the main oxygenate in the whole range of τ tested. In agreement with Au/TiO₂_a and 1K-Au/ TiO₂_a, propanol selectivity increased but started from around 80% at the shortest τ of 5 g min L⁻¹. The selectivity to propanal decreased correspondingly. The relationship between selectivity and contact time shown in Figure 4 is further analyzed in the discussion section together with the results presented in the following section to develop a mechanistic scheme of CO₂ conversion into propanal and propanol in the presence of C₂H₄ and H₂.

Effect of doping of Au/TiO $_2_a$ with K on CO $_2$ and H $_2$ adsorption

To clarify the effect of K doping on CO₂ conversion, we analyzed the interaction of CO2 with K-Au/TiO2_a by means of in situ FTIR spectroscopy and CO₂-pulse experiments in the TAP (temporal analysis of products) reactor. Figure 5 shows the FTIR spectra recorded after CO₂ adsorption on Au/TiO₂_a, 1K-Au/TiO₂_a, and 3K-Au/TiO₂_a at 473 K. Carboxylate species (1550 and 1446 cm⁻¹) were identified on the surface of Au/ TiO2_a. Doping this catalyst with 1 wt% K influenced CO2 adsorption in such a way that bidentate carbonates (1581 and 1326 cm⁻¹) were additionally formed. The strength of CO₂ interaction with K-Au/TiO₂_a further increases with K loading as concluded from the fact that, besides the bidentate carbonate species, ionic carbonates (1390 cm⁻¹) were also identified on the surface of 3K-Au/TiO2_a after its reaction with CO2. To study the stability of surface CO2-containing species, we analyzed their reduction by H_2 at 473 K. For this purpose, H_2 was fed to the CO2-treated catalyst at the same temperature (473 K), followed by purging with He. The results obtained are summarized in Figure 6. Carboxylate species on the surface of Au/TiO2_a were easily destroyed after reaction with H2 but were again formed after exposure to a $CO_2/H_2/C_2H_4 = 1:1:1$ feed (Figure 6a). In the case of the K-doped catalysts, bidentate and ionic carbonate species were only partly decomposed

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Figure 5. FTIR spectra of CO₂ adsorbed on (a) Au/TiO₂_a, (b) 1K-Au/TiO₂_a, and (c) 3K-Au/TiO₂_a at 473 K.



Figure 6. FTIR spectra after reacting (i) CO_{2r} (ii) H_{2r} and (iii) $CO_2/H_2/C_2H_4 = 1:1:1$ with (a) Au/TiO₂_a, (b) 1K-Au/TiO₂_a, and (c) 3K-Au/TiO₂_a at 473 K.

after reaction with H₂. These species also dominate the surface of 1K-Au/TiO₂_a and 3K-Au/TiO₂_a under the $CO_2/H_2/C_2H_4$ = 1:1:1 reaction conditions.

Thus, promoting of Au/TiO_2 with K increases the strength of CO_2 adsorption. This conclusion was additionally supported

by CO₂-pulse experiments in the TAP reactor. In the latter experiments, a CO2/Ar=1:1 mixture was pulsed over the K-Au/ TiO₂_a catalysts at 473 K in vacuum. The height-normalized responses of CO₂ are shown in Figure S4. Normalization was performed for accurate comparison of their shape. One can clearly see that these responses exhibit a broad tailing (non-zero concentration at high times). According to the theory of the TAP reactor,^[18] this tailing means that CO₂ adsorbs and desorbs. However, these processes occur with different rates depending on K loading. Since the tailing increases with rising concentration of K in K-Au/TiO₂_a, we can safely conclude that the ratio of the rates of adsorption to desorption increases correspondingly. From a chemical viewpoint, the K effect is related to reducing the acidity of the TiO₂ surface while simultaneously increasing its basicity. Owing to the acidic properties of CO₂, its adsorption is favored in presence of basic sites.

Since H₂ is required for the conversion of CO₂ and C₂H₄ into C₃-oxygenates, we also investigated mechanistic aspects of activation of gas-phase H₂ on the surface of K-Au/TiO₂_a catalysts. Two types of experiments were performed in the TAP reactor: i) single pulsing of an H₂/Ne = 1:1 mixture and ii) simultaneous pulsing of H₂/Ne = 1:1 and D₂/Ar = 1:1 mixtures. We shall start with the description of the first experiments. The type of H₂ interactions with supported Au NP was elucidated as suggested by Gleaves et al.^[18] To this end, the experimental responses of H₂ and Ne were transformed into a dimensionless form. The modified response of Ne characterizes the solely diffusion process and is called the standard diffusion curve. Such a transformation of experimental data helps to discriminate between reversible and irreversible adsorption of H₂ pulsed together with Ne. In Figure 7 (a–b) the dimensionless responses of Ne and H₂



Figure 7. Dimensionless responses after pulsing of (a, b) $H_2/Ne = 1:1$ and (c, d) $H_2/Ne = 1:1$ and $D_2/Ar = 1:1$ over (a, c) Au/TiO_2_a and (b, d) 1K- Au/TiO_2_a a at 473 K. HD signal in (d) is multiplied by a factor of 10 for better illustration.

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after pulsing of an $H_2/Ne = 1:1$ mixture over Au/TiO₂_a and 1K-Au/TiO₂_a at 473 K are compared. The corresponding results for 2K-Au/TiO2_a are shown in Figure S5. Irrespective of K loading, the H₂ response crosses the Ne response and is located below it. This means that H₂ reacts reversibly. To derive further insights into the H₂ adsorption, that is, whether it is dissociative or non-dissociative, we also investigated H/D exchange by means of $H_2/Ne = 1:1$ and $D_2/Ar = 1:1$ pulse experiments. HD was detected only in traces over Au/TiO₂_a, while significant amounts of HD were observed over the K-containing counterparts (Figure 7 c-d and Figure S5 b). It should be especially highlighted that Au-free 2K/TiO₂ did not show any activity for H/D exchange (Figure S6). Therefore, the presence of HD on K-Au/TiO2_a indicates that K promotes dissociation of H2 and D₂ on the surface of Au NP to yield adsorbed H species, which can recombine to HD.

Discussion

The results of the steady-state catalytic tests (above) are discussed to elaborate a mechanistic scheme of CO_2 conversion with C_2H_4 to propanal/propanol in the presence of H_2 . The relationships between products selectivity and CO_2 conversion over Au/TiO₂_a and 1K-Au/TiO₂_a in Figure 4 show that CO_2 is initially reduced to CO followed by consecutive CO reaction with C_2H_4 to yield propanal with the latter being further hydrogenated to propanol (Scheme 2). The absence of propanal is

Scheme 2. Reaction pathways of CO_2 conversion to propanal/propanol in presence of C_2H_4 and $\text{H}_2.$

related to its rapid hydrogenation to propanol as a result of the high hydrogenation activity of Au NP as supported by the formation of propane, which is the end product of such a hydrogenation process. Since CO was the only product when using a $CO_2/H_2/N_2/=1:1:2$ feed (Figure S2), the absence of CO over 2K-Au/TiO₂_a and 3K-Au/TiO₂_a in presence of C₂H₄ and H_2 (Figure 4c-d) is strong evidence for its reaction with C_2H_4 to propanal, which was observed over these catalysts with high selectivity at low contact times. From a kinetic viewpoint, the hydroformylation reaction appears to be faster than the RWGS reaction over the K-promoted catalysts but not over the K-free counterpart. It is worth mentioning that the selectivity to propanal decreases with rising τ , while the selectivity to propanol increases and approaches almost 100% at τ of 45 g min L⁻¹, implying that propanol is formed through consecutive propanal hydrogenation. Thus, promoting Au/TiO₂_a with K does not change the overall scheme of CO₂ conversion into propanol shown in Scheme 2. We put forward that the presence of K strongly increases the kinetics of hydroformylation of C₂H₄ with CO formed initially from CO₂. This statement is supported by the reaction rate of oxygenate formation determined at a close degree of CO₂ conversion, that is, at a similar partial CO pressure. The corresponding values are given in Table 1. One can clearly see that the presence of K strongly increases this reaction rate. Importantly, propanol hydrogenation to propane is also suppressed over K-containing catalysts.

Based on our results and previous literature on the RWGS reaction^[11c] and C₂H₄ hydroformylation with CO,^[8a,b] we suggest the following mechanistic scheme of propanol formation from CO₂ and C₂H₄ under consideration of TiO₂ surface free of Au NP. CO₂ adsorbs reversibly over the support, while H_2 and C_2H_4 are activated on Au NP.^[19] The oxidation state of Au under reaction conditions is supposed to be zero as concluded from our X-ray diffraction analysis of used catalysts and previous literature studies.^[11c, 20] For thermodynamic reasons, we do not expect formation of metallic potassium. Surface hydrogen species formed on Au NP from gas-phase H₂ reduce CO₂ adsorbed in the vicinity of Au NP to yield CO and H₂O. From a reactivity viewpoint, carboxylate species, which are only present on the surface of K-free TiO₂, are more easily converted to CO than bidentate and ionic carbonates, which are formed on the catalysts promoted with high (>1 wt%) K loading. This is a reason for the low CO_2 conversion over K-Au/TiO₂_a catalysts with 2 and 3 wt% K (Table 1). Since the rate of CO formation was not influenced by C₂H₄ presence, we propose that the RWGS reaction and ethylene activation run independently on each other. The former reaction probably takes place on the edge of the NP while ethylene hydroformylation to propanal and hydrogenation to ethane compete for the same active sites located on the surface of NP. Both of these ethylene transformations are initiated by the formation of a surface ethyl species through addition of one H atom to adsorbed ethylene.^[8a] This intermediate species can react with either another H species to yield undesired ethane or with gas-phase CO to result in an adsorbed CH₃CH₂CO.^[8a,b] The latter species was observed in our FTIR experiments and is characterized by a typical carbonyl band at approximately 1700 cm⁻¹ (Figure S7). In heterogeneous $\mathsf{C}_2\mathsf{H}_4$ hydroformylation with $\mathsf{CO}^{_{[8a,b]}}$ an adsorbed ethyl species is formed very rapidly, while reaction of CH₃CH₂CO with surface H species limits the formation of propanal.^[8a] Bearing this in mind, we suggest that promoting Au/TiO₂_a with K accelerates the latter reaction through an increased generation of adsorbed H species as proven by H/D exchange (Figure 7 and Figure S5). Importantly, doping with K simultaneously increases the strength of adsorbed CO2 species, thus lowering the rate of formation of CO required for the hydroformylation step. Therefore, an optimal loading is required to achieve high activity to the target product.

In addition to the effect of K, the size of Au NP has a manifold effect on the catalyst activity for both CO_2 conversion to propanal/propanol and ethylene hydrogenation to ethane. First of all, an appropriate size of NP was necessary to make catalysts active for the target reaction. Au/TiO₂_b with the 20 nm NP was not able to support the propanal synthesis, while Au/TiO₂_c with the smallest NP of 2.5 nm showed significantly lower activity for the formation of oxygenates than the catalyst possessing NP of 7.5 nm. Furthermore, the size of Au NP controls the C₂H₄ conversion to C₂H₆ as shown in Figure 8; the conversion passes over a maximum for Au NP of ca. 5 nm.

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Figure 8. Effect of size of Au NP on C_2H_4 conversion to mainly C_2H_6 over different catalysts at 2 MPa and 473 K using a $CO_2/H_2/C_2H_4 = 1:1:1$ feed.

The lower activity of smaller NP is in a good agreement with a previous study on selective hydrogenation of acetylene in excess of ethylene over Au/Al_2O_3 .^[21] In that paper, Au NP of 3 nm were found to be unable to hydrogenate C_2H_4 .

Conclusions

Heterogeneous C_2H_4 hydroformylation with CO_2 to propanal/ propanol was for the first time demonstrated over TiO_2 -supported Au-containing catalysts in a single continuous-flow reactor. Since propanol can be easily dehydrated to propene, our concept opens a new way for production of this important building block of chemical industry. Another important feature of this concept is its sustainability because it functionalizes CO_2 with C_2H_4 , which can be produced from bioethanol.

Our thorough kinetic and mechanistic studies enabled us to develop an overall reaction scheme of products formation. CO_2 adsorption takes place on bare and K-modified TiO_2 , while H_2 and C_2H_4 are activated on Au NP. In a first step, CO_2 adsorbed in vicinity of Au undergoes reduction to CO through reverse water–gas shift reaction. So in situ generated CO is further used for classical hydroformylation of ethylene to propanal with the latter being finally hydrogenated to propanol.

Doping of Au/TiO₂ with K resulted in a 100% oxo-selectivity with respect to CO₂ conversion at 2 MPa and 473 K using a $CO_2/H_2/C_2H_4 = 1:1:1$ feed. The promoter was established to influence the size of supported Au NP and the strength of CO₂ adsorption. The former catalyst property, which can also be controlled by the method of gold deposition on TiO₂, determines the activity of catalyst for non-selective ethylene hydrogenation to ethane: too small (< 3 nm) and too large (> 15 nm) NP show low activity to activate C_2H_4 . The positive effect of K on oxo-selectivity is of a kinetic nature as doping strongly increases the rate of ethylene hydroformylation owing to an accelerated formation of adsorbed H species required for propanol formation from adsorbed CH₃CH₂CO. Besides the improvement of oxo-selectivity, K doping lowers CO₂ conversion because CO₂ is strongly adsorbed on basic sites to yield ionic carbonates, which only slowly decompose to the CO required for the hydroformylation step.

Experimental Section

Monometallic Au-containing catalysts with the nominal metal loading of 2 wt% were synthesized according to the methods previously described in literature using ammonia,^[22] urea,^[22] and ammonia/ magnesium citrate^[23] as reducing agents. Briefly, Au/TiO₂_a was prepared by deposition-precipitation of gold hydroxide from HAuCl₄ (41.1 wt% Au, Chempur) on TiO₂ (Anatase, BASF) calcined at 773 K for 8 h. Ammonia solution (25%, Roth) was added to the suspension of TiO₂ in water solution of HAuCl₄ until a pH value of 11 was reached. For preparation of Au/TiO₂_b, the deposition-precipitation of gold hydroxide was done with a urea solution (\geq 99%, Roth) instead of ammonia. Au/TiO2_c was synthesized similarly to Au/TiO2_a additionally using a saturated magnesium citrate solution (>95.0%, Fluka). All catalysts were filtrated, washed, and finally dried at 373 K. K-Au/TiO₂ a catalysts were prepared by incipient wetness impregnation of dried Au/TiO₂ a with a KNO₃ solution (>99%, Merck). The K loading was amounted to 1, 2, and 3 wt%. All catalysts were finally calcined in air at 473 K for 4 h and then pressed and sieved to yield a fraction of 250-450 µm.

The weight concentration of Au and K in calcined catalysts was determined by ICP-OES using a Varian 715 emission spectrometer.

Nitrogen adsorption-desorption isotherm was collected at 77 K on BELSORP-mini II (BEL Japan, Inc.). The specific surface area was calculated from the adsorption applying the Brunauer, Emmett and Teller equation for the N₂ relative pressure range of $0.05 < P/P_0 < 0.30$.

HAADF-STEM investigations were performed using an aberrationcorrected JEM-ARM200F microscope operated at 200 kV and equipped with a JED-2300 energy-dispersive X-ray spectrometer (EDXS, JEOL) for elemental analysis. The Cs-corrector CESCOR (CEOS) was used for scanning transmission (STEM) applications. Samples were deposed on a holey carbon-supported copper grid (mesh 300). To estimate size distribution of supported Au NP, at least 100 particles were counted.

The insitu FTIR measurements were carried out in transmission mode using a Thermo Scientific Nicolet 6700 spectrometer equipped with an in-house-developed reaction cell with CaF2 windows connected to a gas-dosing system. The sample powders were pressed into self-supporting wafers with a diameter of 20 mm and a weight of 50 mg. All spectra were recorded with a resolution of 4 cm⁻¹ and 64 scans according to the following protocol. Before FTIR measurements, each sample was heated in a He flow (50 mL min⁻¹) up to 473 K for 30 min. After this treatment, the cell was flushed in CO₂ (10 mLmin⁻¹ CO₂ plus 60 mLmin⁻¹ He) for 5 min at the same temperature and then closed for 60 min. Subsequently, He was fed to the cell for 10 min to remove gaseous species followed by feeding H_2 (10 mLmin⁻¹ H_2 plus 60 mLmin⁻¹ He) for 5 min. Again, the cell was closed for 60 min. After this reductive treatment, the catalyst was flushed in a He flow for 10 min and then exposed to a $CO_2/H_2/C_2H_4/He = 1:1:1:4$ mixture with a total flow of 70 mLmin $^{-1}$ for 5 min. The catalyst was treated in this mixture under static conditions for 60 min followed by flushing with He for 10 min. FTIR spectra were recorded after each specific treatment and removal reactive gas-phase species by He. In separate experiments with fresh samples, propanal (97%, Sigma Aldrich) was adsorbed at 473 K after pretreatment of the catalysts in a He flow (50 mLmin⁻¹) at 473 K for 30 min followed by feeding H₂ for 60 min and flushing with He for 10 min. Propanal was dosed using a saturator (ambient temperature) and a gas flow of CO₂ (10 mLmin^{-1}) and He (60 mLmin⁻¹). The adsorption procedure was the same as described above. Background-subtracted adsorbate spectra were obtained by subtraction of the spectrum after pre-

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treatment from the spectrum after propanal adsorption and He flushing.

Catalytic tests were performed at 2 MPa between 473 and 623 K in an in-house developed setup consisting of 51 continuous-flow fixed-bed reactors operating in parallel. Reactants are CO₂ (4.5, Air Liquide), H₂ (5.0, Air Liquide), C₂H₄ (3.0, Linde), and N₂ (5.0, Air Liquide). 300 mg of catalyst (fraction of 250–450 µm) were placed in stainless-steel tube reactors (i.d. 4 mm) with threefold amount of SiC for dilution and heated up to 523 K in a N_2 flow (6.67 mL min⁻¹ per reactor). Subsequently, the N₂ flow was replaced by a flow (6.67 mLmin⁻¹ per reactor) of $CO_2/H_2/C_2H_4/N_2 = 4:2:1:1$ reaction feed for 24 h. Then, various $CO_2/H_2/C_2H_4/N_2$ feeds were sequentially fed to the reactors at 473 K and 523 K. In order to derive insights into the effect of CO₂ conversion on product selectivity using a $CO_2/H_2/C_2H_4/N_2 = 1:1:1:1$ feed, the modified contact time was varied from 5 to 45 $gminL^{-1}$. Steady-state data were collected after at least 10 h stabilization under each condition. 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&Molsieve 5A). The conversion of C₂H₄ and CO₂ was calculated from their inlet and outlet concentrations [Eq. (1)]. The selectivity and yield to propanol, propanal, propane, and CO were calculated on CO₂ basis using Equations (2) and (3), respectively, taking into account that one C3-hydrocarbon/oxygenate molecule is formed from one CO₂ and one C_2H_4 . Calculation of C_2H_6 yield was performed on C₂H₄ basis.

$$X_{\rm f} = \frac{\dot{n}_{\rm f,0} - \dot{n}_{\rm f}}{\dot{n}_{\rm f,0}} \tag{1}$$

$$Y_{i} = \frac{\dot{n}_{i} - \dot{n}_{i,0}}{\dot{n}_{f,0}}$$
(2)

$$S_{i} = \frac{Y_{i}}{X_{f}}$$
(3)

where $\dot{n}_{\rm f}$ and $\dot{n}_{\rm i}$ stand for mole flows of feed components and reaction products, respectively. Subscript 0 is used for inlet mole flows.

The Au-related reaction rate was calculated using Equation (4)

$$r_{Au} = \frac{x_{Propanol} \cdot F \cdot M_{Au}}{V_{m} \cdot m_{Au}} \tag{4}$$

where x_{Propanol} is the mole fraction of propanol in the outlet feed and V_{m} the molar volume. m_{Au} represents the amount of gold on the corresponding catalyst and *F* is the total feed flow.

Mechanistic aspects of CO₂ and H₂ interaction with TiO₂, Au/TiO₂_a, 1K-Au/TiO₂_a and 2K-Au/TiO₂_a were investigated in the temporal analysis of products (TAP-2) reactor, a time-resolved technique with a resolution of approximately 100 µs. The TAP reactor system has been described in detail elsewhere.^[18,24] The catalysts (70 mg) were packed into the quartz tube reactor (internal diameter=6 mm, length = 40 mm) as a thin layer between two layers of quartz particles (sieve fraction of 250-350 µm) within the isothermal zone of the reactor. Before starting pulse experiments, the catalysts were pretreated at ambient pressure in a flow of 5 vol % H₂ in Ar (20 $mL\,min^{-1})$ at 523 K with a ramp of 10 $K\,min^{-1}.$ Hereafter, the reactor was evacuated to ca. 10⁻⁵ Pa and cooled down to 473 K in vacuum. Tree types of experiments were performed: (i) single pulsing of a $H_2/Ar = 1:1$ mixture, (ii) single pulsing of a $CO_2/Ar = 1:1$ mixture, and (iii) simultaneous pulsing of $H_2/Ne = 1:1$ and $D_2/Ar = 1:1$ mixtures. A fresh sample was used for each experiment. The pulse size of Ar or Ne was around 10¹⁵ molecules. Under such conditions (Knudsen diffusion regime), any collisions between gas-phase species are minimized and therefore, pure heterogeneous reaction steps were analyzed.

The reaction mixtures were prepared using Ar (5.0), Ne (5.0), CO_2 (4.5), H₂ (5.0), and D₂ (2.7, Messer Griesheim) without additional purification. A quadrupole mass spectrometer (HAL RC 301 Hiden Analytical) was applied for quantitative analysis of feed components and reaction products. The following AMUs (atomic mass units) were used for mass-spectrometric identification of different compounds: 44 (CO₂), 4 (D₂), 3 (HD), 2 (H₂), 20 (Ne, Ar), and 40 (Ar). Pulses were repeated 10 times for each AMU and averaged to improve the signal-to-noise ratio. The concentration of feed components and reaction products were determined from the respective AMUs using standard fragmentation patterns and sensitivity factors.

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Keywords: carbon dioxide \cdot gold \cdot hydroformylation \cdot reverse water–gas shift \cdot tap reactor

- C. Federsel, R. Jackstell, M. Beller, Angew. Chem. 2010, 122, 6392-6395; Angew. Chem. Int. Ed. 2010, 49, 6254-6257.
- [2] a) M. He, Y. Sun, B. Han, Angew. Chem. 2013, 125, 9798–9812; Angew. Chem. Int. Ed. 2013, 52, 9620–9633; b) W. Wang, S. Wang, X. Ma, J. Gong, Chem. Soc. Rev. 2011, 40, 3703–3727.
- [3] P. Y. Dapsens, C. Mondelli, J. Pérez-Ramírez, ACS Catal. 2012, 2, 1487– 1499.
- [4] a) G. A. Olah, Angew. Chem. Int. Ed. 2013, 52, 104–107; Angew. Chem.
 2013, 125, 112–116; b) G. Centi, S. Perathoner, ChemSusChem 2010, 3, 195–208; c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, Angew. Chem. Int. Ed. 2011, 50, 8510; Angew. Chem. 2011, 123, 8662; d) E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, J. Pérez-Ramírez, Energy Environ. Sci. 2013, 6, 3112–3135.
- [5] K. J. Caspary, H. Gehrke, M. Heinritz-Adrian, M. Schwefer in *Handbook of Heterogeneous Catalysis, Vol. 7* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3206–3229.
- [6] J. C. Mol, P. W. N. M. van Leeuwen in Handbook of Heterogeneous Catalysis, Vol. 7 (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, 2008, pp. 3240–3256.
- [7] A. J. Papa in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2000.
- [8] a) X. Liu, B. Hu, K. Fujimoto, M. Haruta, M. Tokunaga, Appl. Catal. B 2009, 92, 411–421; b) N. Sivasankar, H. Frei, J. Phys. Chem. C 2011, 115, 7545–7553; c) N. Navidi, J. W. Thybaut, G. B. Marin, Appl. Catal. A 2014, 469, 357–366.
- [9] T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 2013, 52, 12119–12123; Angew. Chem. 2013, 125, 12341–12345.
- [10] K.-i. Tominaga, Catal. Today 2006, 115, 70-72.
- [11] a) C.-S. Chen, W.-H. Cheng, S.-S. Lin, *Appl. Catal. A* 2004, 257, 97–106;
 b) L. Wang, S. Zhang, Y. Liu, *J. Rare Earths* 2008, 26, 66–70; c) R. Burch, *Phys. Chem. Chem. Phys.* 2006, 8, 5483–5500.
- [12] T. Hanaoka, H. Arakawa, T. Matsuzaki, Y. Sugi, K. Kanno, Y. Abe, Catal. Today 2000, 58, 271–280.
- [13] a) T. A. Kainulainen, M. K. Niemelä, A. O. I. Krause, *Catal. Lett.* **1998**, *53*, 97–101; b) D. Y. Murzin, A. Bernas, T. Salmi, *AIChE J.* **2012**, *58*, 2192–2201; c) T. Kim, F. Celik, D. Hanna, S. Shylesh, S. Werner, A. Bell, *Top.*

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Catal. **2011**, *54*, 299–307; d) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A* **1995**, *104*, 17–85.

- [14] Y. Zhang, G. Jacobs, D. E. Sparks, M. E. Dry, B. H. Davis, *Catal. Today* **2002**, *71*, 411–418.
- [15] M. Guerrero, N. T. Than Chau, S. Noel, A. Denicourt-Nowicki, F. Hapiot, A. Roucoux, E. Monflier, K. Philippot, *Curr. Org. Chem.* **2013**, *17*, 364–399.
- [16] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, Chem. Commun. 1997, 271-272.
- [17] a) R. W. Dorner, D. R. Hardy, F. W. Williams, H. D. Willauer, *Appl. Catal. A* 2010, *373*, 112–121; b) R. W. Dorner, D. R. Hardy, F. W. Williams, H. D. Willauer, *Catal. Commun.* 2011, *15*, 88–92; c) M. Niemelä, M. Nokkosmäki, *Catal. Today* 2005, *100*, 269–274; d) Y. Yang, H.-W. Xiang, Y.-Y. Xu, L. Bai, Y.-W. Li, *Appl. Catal. A* 2004, *266*, 181–194.
- [18] J. T. Gleaves, G. S. Yablonskii, P. Phanawadee, Y. Schuurman, Appl. Catal. A 1997, 160, 55–88.

- [19] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, J. Catal. 1999, 188, 176–185.
- [20] A. Goguet, R. Burch, Y. Chen, C. Hardacre, P. Hu, R. W. Joyner, F. C. Meunier, B. S. Mun, D. Thompsett, D. Tibiletti, J. Phys. Chem. C 2007, 111, 16927–16933.
- [21] J. Jia, K. Haraki, J. N. Kondo, K. Domen, K. Tamaru, J. Phys. Chem. B 2000, 104, 11153 – 11156.
- [22] N. D. Tran, M. Besson, C. Descorme, *New J. Chem.* 2011, *35*, 2095–2104.
 [23] D. A. H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota, M. Haruta, *J. Catal.* 1998, *177*, 1–10.
- [24] J. Pérez-Ramírez, E. V. Kondratenko, Catal. Today 2007, 121, 160-169.

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FULL PAPERS

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An Innovative Approach for Highly Selective Direct Conversion of CO₂ into Propanol using C₂H₄ and H₂ CORPCE IN CARLON CONTROL CONTR

A flowing conversion: CO_2 can be continuously converted into propanol with a near 100% selectivity through H₂-assisted coupling with C_2H_4 over K-promoted Au/TiO₂ in a single continuousflow reactor. Thorough kinetic and mechanistic studies reveal the overall reaction scheme of products formation. The activity and selectivity strongly depend on nanoparticle size, which can be tuned by the method of Au deposition and by doping with K.