

# Carbon Dioxide Hydrogenation on Au Nanoparticles Supported on TiO<sub>2</sub>, ZrO<sub>2</sub> and Sulfated ZrO<sub>2</sub> Under Supercritical Conditions

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**Abstract** Hydrogenation of CO<sub>2</sub> into CO and CH<sub>4</sub> was studied for the first time on Au and Au–Ni catalysts supported on ZrO<sub>2</sub>, TiO<sub>2</sub> and sulfated ZrO<sub>2</sub> under supercritical conditions. The extremely high selectivity to CO exceeding 96–98 % was found with a quite good stability of the catalytic activity. Surprisingly, almost no methanation reaction was observed, this reaction being typical for nickel-based catalysts.

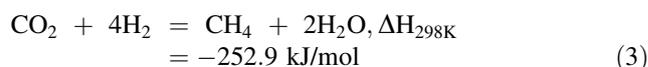
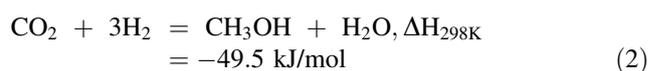
**Keywords** Carbon dioxide hydrogenation · Carbon monoxide · Supercritical CO<sub>2</sub> · Zirconia · Titania · Gold · Nickel · Bimetallic metal nanoparticles

## 1 Introduction

One of the partial solutions to the problem of CO<sub>2</sub> utilization is its conversion into intermediates that can be further easily transformed into high value-added products. The first option is CO<sub>2</sub> hydrogenation. Among the primary products of CO<sub>2</sub> hydrogenation, carbon monoxide, methane (synthetic natural gas) and methanol are the key intermediates that can be further transformed by the known technologies into aldehydes, ketones, higher alcohols, liquid hydrocarbon fuels or energy. The methanation reaction is known to proceed quite efficiently on Ni- or Ru-con-

taining catalysts, while Cu-based catalysts can transform CO<sub>2</sub> into methanol, with some other metals capable of converting carbon dioxide into CO [1–3]. Heterogeneous catalysts are more preferable compared to homogeneous counterparts in terms of stability, separation, handling, recyclization, reactor design to decrease CAPEX and OPEX costs for large-scale productions. Excellent reviews devoted to CO<sub>2</sub> reactions have been published recently [4–7].

The catalytic conversion of CO<sub>2</sub> to CO via reverse water gas shift reaction (1) is considered as the first step of CO<sub>2</sub> reduction with hydrogen, with the possibility of occurrence of methanol formation (2) as the second step, with the final product being methane (3).



The catalysts for CO<sub>2</sub> methanation have been reviewed in [8]. For instance, Ru-containing catalysts supported on a ceramic sponge (1 wt% Ru, Ru particle size 5–20 nm) were studied [9].

Martin et al. investigated Ni- and Ru-containing catalysts (5 wt%) in CO<sub>2</sub> hydrogenation at 350–400 °C, 1–20 bar, molar ratio of H<sub>2</sub>/CO<sub>2</sub> = 4:1, with a gas hourly space velocity 6000 h<sup>-1</sup> [10]. The Ru/ZrO<sub>2</sub> catalysts with a Ru particle size of 4 nm were found to be much more active as compared to Ni/ZrO<sub>2</sub> catalysts with a Ni particle size of 20–30 nm. The methane yields above 70 % were obtained at an ambient pressure, whereas at elevated pressures the yields increased to 93 % for Ni and 96 %

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for Ru with the methane selectivity exceeding 99.9 %. Zirconia-based Ru–Ni bimetallic nanoparticles (3–5 wt% of metals) were shown [11] to provide a complete CO<sub>2</sub> conversion at 300–400 °C, 10 bar, and space velocities up to 36,000 h<sup>-1</sup> with the selectivity to methane being 100 %. Noteworthy that the gas mixture was significantly diluted with H<sub>2</sub> and N<sub>2</sub> (a 4–7 times excess over CO<sub>2</sub>).

Kwak et al. studied the Ru particle size effect on the catalytic behavior of Ru/Al<sub>2</sub>O<sub>3</sub> [12]. The bimetallic catalysts (Ru–Ni/CeO<sub>2</sub>–ZrO<sub>2</sub>) demonstrated enhanced performance in methane formation [13].

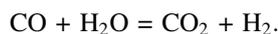
Copper-catalysts were also used in CO<sub>2</sub> reduction to CO. Liu et al. developed bimetallic Cu–Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for CO<sub>2</sub> hydrogenation [14]. Whereas Cu is beneficial for CO formation, Ni is effective in CH<sub>4</sub> formation. The selectivities to CO and CH<sub>4</sub> depend on the Cu/Ni ratio in the catalyst composition and vary in a wide range.

Cu/ZnO and Cu–Zn/Al<sub>2</sub>O<sub>3</sub> catalysts of methanol synthesis from CO to H<sub>2</sub> were also used for CO<sub>2</sub> reduction [15]. The highest activity was demonstrated by the system with the Cu/Zn ratio of 4:3 on alumina.

Chen et al. found that Cu/SiO<sub>2</sub> promoted with potassium showed the CO<sub>2</sub> conversion of 12.8 % at 600 °C. [16]. The selectivity to CO is rather high and approaches 100 % in the case of potassium-promoted samples. It was also demonstrated that the activity is improved upon modification of the catalyst with iron (0.3 wt% Fe added to 10 % Cu/SiO<sub>2</sub>) without decreasing the selectivity to CO of around 98–100 % [17, 18].

Gold catalysts became one of the most intriguing area of research in catalysis in recent 20 years. The majority of publications of supported gold nanoparticles are related to oxide- and carbon-supported systems, with certain research being carried out with zeolites as the supports. Since the early works by Haruta [19, 20] and the book of Bond et al. [21], it is well recognized that the gold particles with the size of 2–5 nm are most active in the catalytic reactions of different nature, including CO oxidation and other reactions.

The water–gas shift reaction is one of the most important processes from the view point of production of H<sub>2</sub>:



Gold catalysts were considered as a versatile system for this reaction [22]. Obviously the opposite reaction of CO<sub>2</sub> hydrogenation can also be catalyzed by gold nanoparticles. The reasons behind the high efficiency of gold catalysts in this particular reaction are still elusive, but, as in the case of other Au-catalyzed reactions, the activity should be accounted for by several factors, not just one, including, but not limiting the scope:

- The possibility to prepare and stabilize gold nanoparticles with a small and uniform size, which can be tuned in between 1–2 and 15 nm, with larger particles being less active,
- The specific characteristics of the electronic structure of such tiny metal nanoparticles, including the density of *d*-electrons near the Fermi level and the flexibility of the electronic configuration capable of transforming from Au<sup>0</sup> to Au<sup>δ-</sup>, Au<sup>δ+</sup>, Au<sup>+</sup> or Au<sup>3+</sup> states.

To the best of our knowledge, the use of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) in the CO<sub>2</sub> hydrogenation reaction was the focus of only a few recent publications [23–25].

Synthesis of *N,N*-dimethylformamide (DMF) from CO<sub>2</sub>, H<sub>2</sub>, and dimethylamine has been examined by several groups. Jessop et al. was the first who reported on the homogeneous RuCl<sub>2</sub>[P(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> catalyst for this reaction [26].

The only publication related to supercritical studies with heterogeneous catalysts is focused on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts and supercritical mixture of CO<sub>2</sub> and H<sub>2</sub>, with infrared spectra indicating the formation of surface species such as carbonate, formate, and CO [27]. However, no real catalytic tests were carried out in this work.

Earlier we have also studied this reaction in the gas phase using microwave activation of the catalysts (Fe- and Au-containing catalysts, LaNi<sub>5</sub> intermetallide) [28]. Also, we have revealed a synergy between gold and nickel in different reactions in our previous publications [29–33]. It was worth trying to study the Au–Ni catalyst of the already optimized composition and exhibiting the synergetic behavior in the new reaction of CO<sub>2</sub> hydrogenation.

Thus, the present paper is devoted to the first study of the CO<sub>2</sub> hydrogenation under supercritical CO<sub>2</sub> conditions on a series of monometallic (Au) and bimetallic (Au–Ni) catalysts prepared using ZrO<sub>2</sub>, SO<sub>4</sub>/ZrO<sub>2</sub>, and TiO<sub>2</sub> as supports.

## 2 Experimental

The monometallic (Au) and bimetallic (Au–Ni) catalysts were prepared by combination of deposition–precipitation and impregnation techniques as described in [29–33]. First gold was supported using an alkaline solution of HAuCl<sub>4</sub> × nH<sub>2</sub>O (Sigma-Aldrich, Au = 41 wt%) with ZrO<sub>2</sub>, 5 wt% SO<sub>4</sub>/ZrO<sub>2</sub> (Magnesium Electron, S = 120 m<sup>2</sup>/g, 0.2 mm grains) and TiO<sub>2</sub> (Degussa, 50 m<sup>2</sup>/g, 6.0 IEP, 0.5 mm grains) followed by calcination at 623 K in air for 3 h. Next, bimetallic Au–Ni catalysts were prepared by incipient wetness impregnation of the Au/support material with an aqueous solution of Ni(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O (Sigma-Aldrich, 98–99 % pure) followed by calcination at 623 K in

air for 3 h. The content of the supported metals in the catalysts was measured by atomic absorption spectroscopy using a ThermoCE 3000 AA spectrometer as described in [30]. The actual gold and nickel contents were 0.21–0.06 wt%, respectively, that corresponds to the desired equimolar Au/Ni ratio.

The sulfated zirconia was prepared by incipient wetness impregnation of Zr hydroxide (MEL) with ammonium sulfate with further calcination at 600 °C. The content of sulfate groups on the surface of zirconia was 5 wt%.

The reaction of CO<sub>2</sub> with H<sub>2</sub> was studied under supercritical conditions in a plug-flow reactor. The H<sub>2</sub>:CO<sub>2</sub> ratio was equal to 1:1 or 2:1. The catalyst loading in the reactor was 2 cm<sup>3</sup>. The reaction temperature was ranged from 300 to 450 °C. Carbon dioxide was supplied with a syringe pump under the pressure of 80 atm, hydrogen was fed via a mass flow controller. The pressure in the reactor was maintained at 80 atm using a back pressure valve. Analysis of products was performed with a Crystallux-5000 gas chromatograph with a thermal conductivity detector and Porapack Q and zeolite CaA packed columns. The conversions of CO<sub>2</sub> and H<sub>2</sub> were determined by the formula:

$$C = (n_{in} - n_{out})/n_{in} \times 100$$

$n_{in}$  and  $n_{out}$ —are the quantities of CO<sub>2</sub> or H<sub>2</sub> at the inlet and outlet of the reactor.

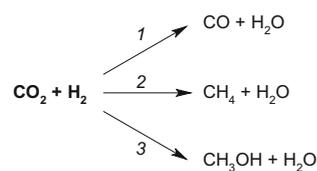
$$n = c \times V,$$

$c$  is the concentration and  $V$  is the gas flow rate. The carbon balance was closed at 99–100 %. The hydrogen conversion was calculated on the basis of the CO<sub>2</sub> conversion and selectivities to all the products:

$$C_{calc}(H_2) = C(CO_2) \times (S(CO) + 4 \times S(CH_4) + 3 \times S(CH_3OH) + 7 \times S(C_2H_6))/100.$$

### 3 Results and Discussion

According to the previous XPS, XAS, TEM and IR studies [29–33], 100 % of nickel species on the surface of the Au–Ni catalysts exist as 3–4 nm NiO particles. Gold species are presented in two forms:  $\approx 20$  % of gold species on the surface of the Au–Ni catalysts exist as isolated 12–16 nm Au<sup>0</sup> particles, whereas  $\approx 80$  % of gold species exist as small 4–5 nm Au<sup>δ+</sup> clusters anchored to NiO particles. The difference between the Au–Ni/ZrO<sub>2</sub> and Au–Ni/TiO<sub>2</sub> catalysts is related to the size of Au nanoparticles: for the zirconia-based system the particles are somewhat smaller (around 4 nm) compared to the titania-containing sample (5–6 nm) [29–33].

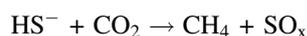


**Scheme 1** Main reactions occurring in the CO<sub>2</sub> + H<sub>2</sub> system

In a general case, the interaction between CO<sub>2</sub> and H<sub>2</sub> occurs with the formation of several products, with CO, methanol, and methane being the main products (Scheme 1):

The catalytic data on the gas mixture compositions and the conversions and selectivities to the main products on the Au-containing catalysts are presented in Tables 1 and 2. The yield of methanol is negligible (less than 1 vol%).

In the case of the Au/ZrO<sub>2</sub>–SO<sub>4</sub> catalyst, some amount of methanol is formed at  $T = 220$ – $300$  °C. The selectivity to methanol ranges from 9 to 15 % at the conversion of CO<sub>2</sub> increasing from 6 to 15 %. When the reaction temperature rises from 300 to 450 °C, methane starts to form with the selectivity increasing from 11 to 28 % in this temperature interval. Such an increase in the CH<sub>4</sub> selectivity in this particular case of the sulfated gold catalyst containing no nickel, which is known to catalyze the methanation reaction of CO<sub>2</sub>, can be explained by possible participation of reduced sulfur species in the entire process. It is known that sulfur in sulfated zirconia starts to be reduced to H<sub>2</sub>S at temperatures higher than 350 °C. Perhaps, the reduced surface forms of sulfur participate in CO<sub>2</sub> reduction thus competing to H<sub>2</sub> via, for instance, the reaction:



The dependence of the conversion and selectivity to the main products for this particular catalyst is presented in Fig. 1.

The non-sulfated catalysts, Au–Ni/TiO<sub>2</sub> and Au–Ni/ZrO<sub>2</sub>, behave pretty much differently compared to the sulfated catalyst. First these two catalysts are less active than the sulfated counterpart. Second, the formation of methanol and methane is severely suppressed on the Au–Ni catalysts, with the selectivity to either of these products hardly exceeding 5–7 %. The comparison of the CO<sub>2</sub> conversion versus temperature for the Au–Ni catalysts is presented in Fig. 2.

The interaction of CO<sub>2</sub> and H<sub>2</sub> on both Au–Ni catalysts results mainly in the formation of CO by the reverse water–gas shift reaction. The selectivity to CO is 95–100 %, with methane being the second abundant product (0–5 %). No clear dependences were observed of the catalyst activity/

**Table 1** Composition of gas mixtures in the course of CO<sub>2</sub> hydrogenation on Au-containing catalysts (80 atm)

Catalyst	T (°C)	Concentration in the gas mixture after the reaction (vol%)					
		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>3</sub> OH
Au/ZrO <sub>2</sub> -SO <sub>4</sub> H <sub>2</sub> /CO <sub>2</sub> = 1:1	150	49.1	0.0	0.0	50.9	0.0	0.0
	220	49.2	1.2	0.0	46.0	1.5	0.4
	260	48.4	5.2	0.1	44.3	6.0	0.5
	300	44.9	6.5	0.9	42.3	9.2	0.9
	350	43.7	8.3	2.2	41.1	12.6	0.0
	400	37.9	11.5	3.1	41.5	17.7	0.0
	450	35.5	12.3	4.8	39.2	21.8	0.0
Au-Ni/TiO <sub>2</sub> H <sub>2</sub> /CO <sub>2</sub> = 1:1	350	47.2	0.8	0.0	41.2	0.8	0.0
	380	44.1	3.6	0.1	41.4	3.8	0.0
	400	44.4	6.0	0.1	40.1	6.2	0.0
	420	41.9	8.3	0.2	35.2	8.8	0.0
	450	40.5	11.3	0.4	35.3	12.1	0.0
Au-Ni/ZrO <sub>2</sub> H <sub>2</sub> /CO <sub>2</sub> = 1:1	280	43.6	0.0	0.0	44.8	0.0	0.0
	300	44.4	1.1	0.0	43.0	1.2	0.0
	320	46.6	1.8	0.1	40.9	2.0	0.0
	350	40.1	7.2	0.3	40.9	7.9	0.0
	400	40.3	13.9	0.3	36.9	14.6	0.2
	450	34.0	18.8	0.6	37.9	19.9	0.0
Au-Ni/ZrO <sub>2</sub> H <sub>2</sub> /CO <sub>2</sub> = 2:1	320	57.6	0.0	0.0	28.9	0.0	0.0
	350	58.2	1.6	0.0	28.5	1.6	0.0
	380	55.7	4.9	0.1	25.9	5.4	0.4
	400	55.5	8.0	0.1	23.9	8.5	0.4
	420	54.1	10.8	0.2	21.6	11.2	0.0
	450	53.2	14.2	0.4	20.6	15.0	0.0

selectivity on the H<sub>2</sub>:CO<sub>2</sub> ratio and of the selectivity on the reaction temperature in the temperature range studied (180–450 °C). The higher activity of the zirconia-based catalyst in comparison with the titania sample can be explained by the smaller particle size (and thus better dispersion) of the bimetallic nanoparticles in the case of the Au–Ni/ZrO<sub>2</sub> catalyst (about 4 vs. 5–6 nm for Au–Ni/TiO<sub>2</sub>) [29–33].

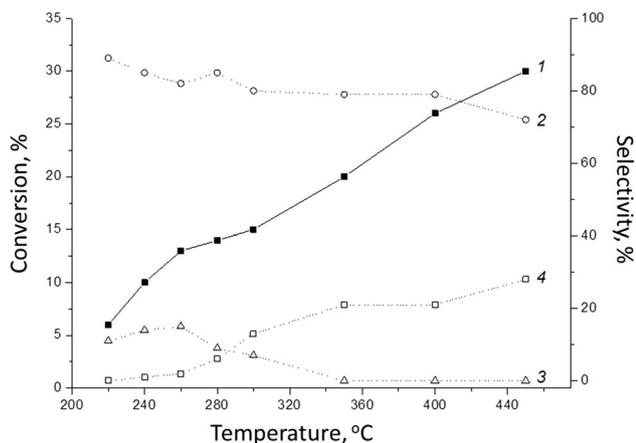
The stability of the operation was studied for the Au–Ni/ZrO<sub>2</sub> and Au–Ni/TiO<sub>2</sub> catalysts at T = 450 °C. The activity of both catalysts was kept quite constant within 7 h (Fig. 3). The sulfated catalyst was tested at a lower temperature (300 °C) because of hydrogen sulfide evolutions at higher temperatures. The seeming “oscillation” of the conversion versus time on stream for the Au–Ni/ZrO<sub>2</sub> catalyst may be the result of the fluctuation of the supercritical CO<sub>2</sub> flux. Therefore 3–4 % variations in the conversion is rather the data spread than a kind of a dependence. The same seems to be true with the sulfated zirconia catalyst and the observed insignificant increase of the activity can be neglected and the catalyst performance can be treated as stable.

The advantage of the catalytic experiments under supercritical conditions is the high throughput, i.e. the productivity of the catalyst expressed in terms of grams of CO<sub>2</sub> passed or converted per gram of the catalyst per hour. Most gas-phase experiments described in the literature were performed in diluted gas mixtures, with H<sub>2</sub> or N<sub>2</sub> serving as diluents, including one of the best result obtained by Martin et al. who tested the Ni- and Ru-containing catalysts (5 wt%) in CO<sub>2</sub> reduction with H<sub>2</sub> at 350–400 °C, 1–20 bar, molar ratio of H<sub>2</sub>/CO<sub>2</sub> = 4:1, with a gas hourly space velocity 6000 h<sup>-1</sup> [10]. Also, the productivity was quite limited (about 0.2 g/g h). In our tests, the productivity reached 1.54 g/g h, which is about 7–8 times higher compared to the literature data.

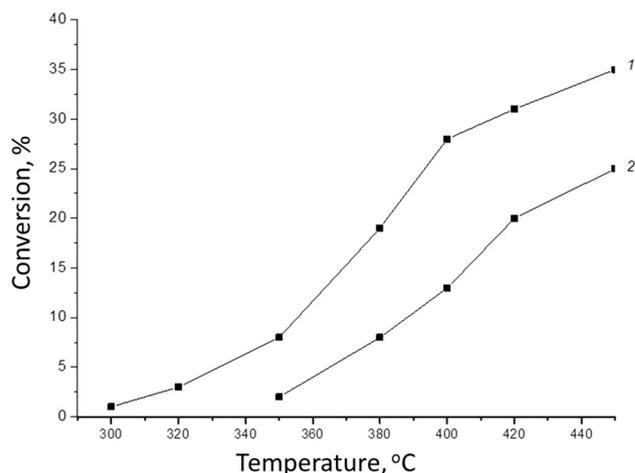
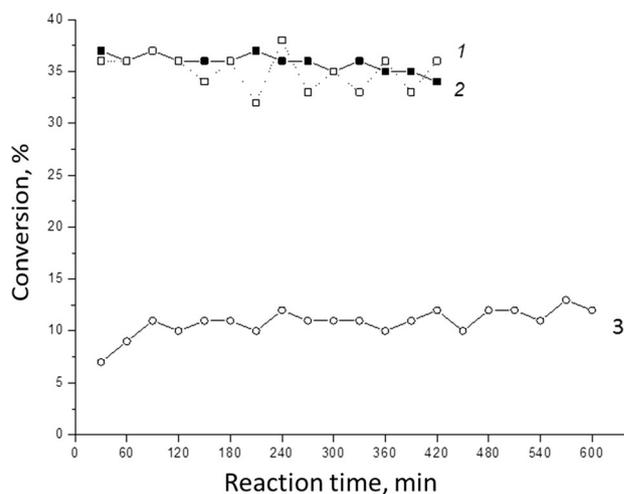
Thus, the gold-based catalysts can be used effectively for reverse water gas shift reaction (CO<sub>2</sub> hydrogenation). This process, even though does not provide a means for complete utilization of industrial wastes of CO<sub>2</sub> because of the huge scale of CO<sub>2</sub> released to the environment, does serve as a step forward to produce high added-value products via further CO conversion. The reaction of CO<sub>2</sub> hydrogenation is only slightly endothermic ( $\Delta H_{298K} =$

**Table 2** Performance of the Au catalysts in CO<sub>2</sub> reduction with H<sub>2</sub>

Catalyst	T (°C)	CO <sub>2</sub> conversion (%)	Selectivity (vol%)			
			CO	CH <sub>4</sub>	CH <sub>3</sub> OH	
Au/ZrO <sub>2</sub> -SO <sub>4</sub>	150	0	—	—	—	
H <sub>2</sub> /CO <sub>2</sub> = 1:1	220	3	75	0	25	
	260	12	89	2	9	
	300	16	78	11	11	
	350	20	79	21	0	
	400	26	79	21	0	
Au-Ni/TiO <sub>2</sub>	350	2	100	0	0	
	H <sub>2</sub> /CO <sub>2</sub> = 1:1	380	8	98	2	0
		400	13	98	2	0
		420	20	97	3	0
450	25	97	3	0		
Au-Ni/ZrO <sub>2</sub>	280	0				
	H <sub>2</sub> /CO <sub>2</sub> = 1:1	300	3	96	4	0
		320	5	95	5	0
		350	16	96	4	0
		400	28	97	2	1
450	34	97	3	0		
Au-Ni/ZrO <sub>2</sub>	320	0				
	H <sub>2</sub> /CO <sub>2</sub> = 2:1	350	5	100	0	0
		400	26	95	1	4
		420	34	98	2	0
450	41	97	3	0		

H<sub>2</sub>/CO<sub>2</sub> = 1:1 or 2:1, P = 80 atm**Fig. 1** Dependence of the CO<sub>2</sub> conversion (1) and selectivity to CO (2), CH<sub>3</sub>OH (3) and CH<sub>4</sub> (4) versus the reaction temperature for CO<sub>2</sub> hydrogenation on the Au/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst, H<sub>2</sub>:CO<sub>2</sub> = 1:1 (mol), catalyst loading 2 cm<sup>3</sup>

41.2 kJ/mol), therefore, the energy expenses for the CO<sub>2</sub> utilization may be expected to be covered by the value of the target products. Among the target products of further CO processing, one should consider first formic acid and

**Fig. 2** CO<sub>2</sub> conversion in the CO<sub>2</sub> + H<sub>2</sub> reaction on the Au-Ni/ZrO<sub>2</sub> (1) and Au-Ni/TiO<sub>2</sub> (2) catalysts, H<sub>2</sub>:CO<sub>2</sub> = 1:1, pressure 80 atm, catalyst loading 2 cm<sup>3</sup>**Fig. 3** Dependence of the CO<sub>2</sub> conversion on the time of stream for CO<sub>2</sub> hydrogenation: (1) Au-Ni/ZrO<sub>2</sub> (450 °C), (2) Au-Ni/TiO<sub>2</sub> (450 °C), (3) Au/ZrO<sub>2</sub>-SO<sub>4</sub> (300 °C). H<sub>2</sub>:CO<sub>2</sub> = 1:1, V = 2 cm<sup>3</sup>

its derivatives, hydroformylation and alkoxyformylation products and other organic compounds. Nevertheless, simple conversion of CO into fuel components and petrochemical products via Fischer-Tropsch synthesis and methanol production may be of immediate interest.

## 4 Conclusions

Thus, the use of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) in the CO<sub>2</sub> hydrogenation reaction is quite a new approach. Actually CO<sub>2</sub> hydrogenation reaction was studied here in the supercritical conditions for the first time. Only the synthesis of formamide was the focus of recent publications

devoted to supercritical tests starting, for instance, from CO<sub>2</sub>, H<sub>2</sub>, and dimethylamine [23–26] using homogeneous catalysts that are known to demonstrate very often poor recyclability. Gold nanoparticles supported on sulfated zirconia turned out to be most active, though the selectivity was inferior to the bimetallic Au–Ni/ZrO<sub>2</sub> and Au–Ni/TiO<sub>2</sub> catalysts. The latter demonstrated the CO selectivity close to 100 % (95–100 %) in the entire temperature range of 180–450 °C. All the studied gold-containing catalysts exhibited a rather good stability originating in the case of the Au–Ni supported catalysts from high selectivity towards CO. The main advantage of the process under supercritical conditions is the enhancement of the space–time yield due to the use of the high-density media. The productivity in supercritical CO<sub>2</sub> reached 1.54 g/g h, which is about 7–8 times higher compared to the known literature data.

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