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Two-Stage Conversion of Carbon Dioxide to Methanol on Co-Pd-Containing Catalysts Based on Aluminosilicates at Atmospheric Pressure

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Article info	ABSTRACT
Received:	A two-stage process for CO_2 conversion into methanol under continuous flow and
20 November 2024	atmospheric pressure conditions is proposed, using a bimetallic cobalt-palladium catalyst supported on a Siral-type aluminosilicate (Co-Pd/Siral). In the first stage,
Received in revised form:	CO_2 is hydrogenated to methane at 473–523 K according to the reaction: CO_2 + $4H_2$
16 January 2025	\rightarrow CH ₄ + 2H ₂ O, carried out in the first reactor. After removing the water formed, the second stage involves the conversion of methane, unreacted CO ₂ , and H ₂ into
Accepted:	methanol in a second reactor at 573 K. The introduction of 0.5 wt.% palladium into
19 February 2025	the 10 wt.% Co/Siral catalyst was shown to promote methanol formation, with a maximum yield of 3.3% observed at 573 K. It is suggested that the catalytically active sites for CO_2 hydrogenation to methane are nanosized Co, COO_x particles,
Keywords:	while methanol is formed through the oxidation of methane over nanosized PdO
Carbon dioxide conversion	particles, following the reaction: PdO + $CH_4 \rightarrow Pd$ + CH_3OH . Methane is oxidized
Pd-Co-containing catalysts	by PdO, and the Pd–PdO redox cycle is sustained by carbon dioxide through the
Methane	reaction: $Pd + CO_2 \rightarrow PdO + CO$. In addition, cobalt oxides (CoO_x) contribute to CO_2
Methanol	activation, significantly facilitating the catalytic cycle.

1. Introduction

Catalytic hydrogenation of carbon dioxide (CO_2) is one of the most important reactions in heterogeneous catalysis, which has attracted considerable attention due to its wide application in the fields of environmental protection and energy (such as CO_2 emission control, CO_2 processing into methanol, dimethyl ether, urea, hydrocarbons, synthesis gas) [1-3]. The involvement of carbon dioxide in chemical syntheses is currently also considered as one of the possible options for replacing oil (fossil) raw materials with non-oil (alternative) ones. In this regard, expanding the scope of using carbon dioxide as a starting reagent for chemical processes is an urgent task aimed at both solving issues of environmental safety and rational use of CO_2 [4-8]. One of the promising and important methods of CO_2 utilization is its hydrogenation into methanol [9, 10].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \Delta H = -49.5 \text{ kJ/mol},$$

$$\Delta G = 3.48 \text{ kJ/mol}$$
(1)

From a thermodynamic point of view, low temperature and high pressure favor the hydrogenation of CO_2 to methanol. In addition to methanol, this reaction is also accompanied by the formation of carbon monoxide:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \Delta H = 41.2 \text{ kJ/mol},$$

$$\Delta G = 28.6 \text{ kJ/mol}$$
(2)

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Since the rate of CO_2 conversion is very low at low temperatures, achieving high conversion and selectivity at the same time becomes problematic.

The results of a number of studies published over the past two decades [11, 12] show that catalysts with an oxide, zeolite base at low temperatures <573 K and atmospheric pressure hydrogenate CO₂ to methane. In [13] it was shown that cobalt-containing catalysts based on aluminum oxide and aluminosilicate of the Siral type hydrogenate CO₂ to methane $(CO_2 + H_2 = CH_4 + H_2O)$ with almost 100% selectivity at a temperature of ≤573 K and at higher temperatures - with the formation of small amounts of CO. Analysis shows that from a thermodynamic point of view, the conversion of CO₂ to methane is preferable compared to its conversion to methanol. Therefore, in the present work an attempt was made to use a two-stage scheme for the reaction of hydrogenation of CO₂ to methanol – hydrogenation of CO₂ to methane in the first stage and methane to methanol in the second stage. The results of studies on the direct selective oxidation of methane to methanol with hydrogen peroxide, nitrous oxide, and also the oxygen anion radical O- under atmospheric conditions are well known. The formation of this type of active oxygen forms is characteristic, for example, of palladium oxide PdO, silver Ag₂O. In order to generate such highly reactive oxygen species and use them for direct oxidation of methane to methanol, we modified cobalt-containing catalyst samples based on aluminum oxide and aluminosilicate with palladium. To our knowledge, finding the most efficient conditions for combining the hydrogenation reaction of CO_2 to methane ($CO_2 + 4H_2 =$ $CH_4 + 2H_2O$) and methane to methanol ($CH_4 + CO_2$) = $CH_3OH + CO$) at atmospheric pressure has not yet been systematically studied. The most studied catalyst for selective oxidation of CH₄ in the gas phase is molybdenum oxide supported on SiO2. One of the earliest studies was published by Liu et al. using 1.7 wt.% Mo/SiO₂ catalyst with N_2O as an oxidizer [14]. Overall selectivity for methanol and formaldehyde of 84.6% was achieved at 8.1% methane conversion when steam was fed together with the reactants at 833 K. Surface forms of the oxygen anion radical O-, formed by the interaction of N₂O with Mo⁵⁺ ions, were identified by the EPR method and were considered as active centers for the cleavage of methane with the formation of methyl radicals [15].

Currently, methanol is produced on an industrial scale by processing synthesis gas on Cu-ZnO-Al₂O₃ catalysts at 493–573 K and 5–10 MPa [16]. Copper catalysts based on zirconium demonstrate the best

catalytic properties in the hydrogenation of CO_2 to methanol [17, 18]. At the same time, the search for catalytic systems for the hydrogenation of CO_2 to methanol under atmospheric conditions remains in the area of increased interest [19, 20]. This paper presents the results of CO_2 conversion into methanol at atmospheric pressure using cobalt-palladium-containing catalysts based on aluminosilicate of the Siral type (Co-Pd/Siral) and a stepwise reaction scheme – hydrogenation of CO_2 into methane at the first stage and oxidation of methane into methanol at the second stage.

2. Experimental

Samples of cobalt-palladium-containing catalyst were obtained by applying hexa-aqua cobalt(II) nitrate $Co(NO_3)_2 \cdot 6H_2O$ and palladium(II) chloride PdCl₂ (ammonia solution) to aluminosilicates of the Siral type from SASOL (Germany) with an Al₂O₃/SiO₂ ratio of 99:1, 90:10, 60:40, followed by oxidation at 773 K for 4 hours in an air flow and reduction in a hydrogen flow at 723 K for 1 h of treatment. Preliminary reduction of the catalyst was carried out directly in the reactors at a temperature of 723 K in a hydrogen flow (V_{H2} = 40 ml/min).

The synthesized cobalt-palladium-containing catalysts were tested in the carbon dioxide hydrogenation reaction in a flow mode in two sequentially connected quartz reactors with a diameter of 20 mm with a fixed catalyst bed in each reactor at atmospheric pressure in the range of temperatures 473– 773 K with chromatographic analysis of the reaction products in the online mode. The reactors were separated by a trap for freezing the water formed in the reaction of CO₂ hydrogenation to methane in the first reactor. Figure 1 shows the catalytic installation diagram used for CO₂ hydrogenation.

Carbon dioxide (CO₂) from the cylinder (1) passes through the pressure regulator along line (I) and enters the manometer (3). It then flows into the rotameter (4), which measures the amount of CO₂. The CO₂ exiting the rotameter (4) moves along line (II) and, through the tee connector (5), enters the first reactor (8). Hydrogen from the hydrogen generator (6) is regulated by the pump (7) and enters the first reactor (8) through the tee connector along line (III). The reactor (8) is a hollow stainless steel tube wrapped with a nichrome heating coil (9) and equipped with a thermocouple pocket (10) and a thermocouple (11), which regulates the temperature throughout the catalyst bed. Inside the reactor, hydrogen mixes with carbon dioxide.



Fig. 1. Diagram of the laboratory experimental setup for the carbon dioxide hydrogenation process: $1 - CO_2$ cylinder; 2 – pressure regulator; 3 – manometer; 4 – rotameter; 5 – tee connector; 6 – hydrogen generator; 7 – pump; 8 – first and second reactors; 9 – nichrome catalyst winding; 10 – thermocouple pocket; 11 – thermocouple; 12 – grid; 13 – catalyst; 14 – dryer; 15 – frizer; 16 – receiving vessel; 17 – flow meter; 18 – gas chromatograph (GC).

The hydrogenation reaction products-methane, water vapor, carbon monoxide, and unreacted CO_2 and H_2 -exit the first reactor and pass through a column filled with activated aluminum oxide. The dried gas mixture (CH_4 , H_2 , CO_2) then enters the second reactor. The reaction products formed in the second reactor flow into a condenser (15) cooled by water. The condensed water vapor collects in the receiving vessel (16), which has graduated markings to measure the amount of condensate formed. The gases from the reaction pass through the flow meter (17), which determines the gas quantity. After passing through the flow meter, the gases are analyzed using gas chromatography (18).

In the experiments, high-purity H_2 and CO_2 (\geq 99.99%) were used at a 1:4 ratio. The gas-phase products from the first reactor – CH_4 , CO_2 , H_2 , and CO- entered the second reactor after water removal. Activated aluminum oxide, chosen for its high efficiency and ease of use, effectively removed water from the gas mixture. The gas stream was passed through an activated aluminum oxide column, ensuring that the dried gas mixture (CH_4 , H_2 , CO_2) proceeded to the second reactor.

The water removal efficiency was approximately 99.5%, which was considered sufficient to prevent

moisture from affecting the target reaction in the second stage. The removal of water formed in the first-stage reaction $(CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O)$ was necessary because the presence of water in the gas mixture reduced the selectivity of the methane oxidation reaction to methanol. The composition of the gases $(CH_4 + CO + CO_2 + H_2)$ entering the second reactor varied depending on the reaction temperature in the first reactor (Table 1). No oxygen was supplied to the reactors.

The reactor was loaded with 1.5 cm³ of catalyst (fraction 1–2 mm) mixed with 3.5 cm³ of quartz. The CO₂ hydrogenation reactions were carried out at atmospheric pressure and a gas space velocity of 120 h⁻¹ at a temperature of 473, 573, 673 and 773 K. The experiments were carried out for 60–70 h, with chromatographic analysis of the composition of the gas-phase reaction products at the reactor outlet every 30 min. Conversion was determined as the proportion of converted CO₂ relative to the initial amount:

$$X_{CO2} = (nCO_{2init} - nCO_{2con}/nCO_{2init}) \times 100\%$$

where: nCO_{2init} is the initial amount of CO_2 , nCO_{2con} is the remaining amount of CO_2 , in moles.

Product selectivity (S) was determined by the formula

$$Si = (n_i/nCO_{2reagent}) \times 100\%$$

where: n_i is the number of moles of the target product CH₄ or CH₃OH, $nCO_{2reagent} = nCO_{2init} - nCO_{2con}$ is the amount of CO₂ that has entered into the reaction.

For methane: $S_{CH4} = (nCH_4/nCO_{2reagent}) \times 100\%$. For methanol: $S_{CH3OH} = (nCH_3OH/nCO_{2reagent}) \times 100\%$. The yield of the product (Y) was determined by the formula: $Y_i = (n_i/nCO_{2initial}) \times 100\%$.

For methane: $Y_{CH4} = (nCH_4/nCO_{2initial}) \times 100\%$.

For carbon monoxide: $Y_{CO} = (nCO/nCO_{2initial}) \times 100\%$.

For methanol: $Y_{CH3OH} = (nCH_3OH/nCO_{2initial}) \times 100\%$. The content and distribution of cobalt and palladium in the catalysts were determined by X-ray fluorescence analysis using an energy-dispersive X-ray spectrometer (XGT 7000, Horiba, Japan). Textural characteristics, including specific surface area and total pore volume, were measured via low-temperature nitrogen adsorption on a Belsorp Mini II device (BEL Japan Inc.). The specific surface area was calculated using the BET (Brunauer-Emmett-Teller) method, while the pore volume was determined by the BJH (Barrett-Joyner-Halenda) method at a relative pressure of $P/P_0 = 0.95$. Prior to analysis, the samples were degassed under vacuum at 473 K for 4 hours. X-ray diffraction (XRD) analysis was carried out on an XRD 3500 TD diffractometer (China) with monochromatic CuKα radiation. Electron paramagnetic resonance (EPR) spectra were recorded at 300 K using an EMXmicro spectrometer (Bruker, Germany) operating at 9.8 GHz (X-band) with a modulation frequency of 100 kHz.

3. Results and discussion

Table 1 shows the results of CO₂ conversion on palladium-containing catalysts Co-Pd/Siral.

Table 2 also shows the results of CO_2 hydrogenation on samples of catalysts based on Siral-1,10,40, containing only cobalt in an amount of 10 wt.% in terms of CoO.

The results of catalytic tests (Table 1) show that the maximum yield of methanol (3.3%) is achieved at a reaction temperature of 573 K. The activity of the Co-Pd/Siral-1(10) catalyst is significantly higher compared to the catalyst with Co-Pd/Siral-40, indicating a noticeable effect of the SiO₂/Al₂O₃ ratio on their catalytic properties in the reactions of CO₂ hydrogenation to methane and methane oxidation to methanol. In the case of Co-containing catalysts at a temperature of T≤573 K, i.e. under conditions of maximum methanol yield for Co-Pd/Siral catalysts, methanol was not observed in the reaction products. Thus, it can be clearly stated that the introduction of palladium into the composition of the Co/ Siral catalyst stimulates the formation of methanol.

Table 1. P	roducts of two-stag	e conversion of t	he mixture (CO ₂	+ H ₂) on catalys	sts Co-Pd/Siral-1,	10, 40 (P = 0	0.1 MPa,
$CO_2:H_2 = 1$.:4, vol. W - 120 h ⁻¹)						

Catalysts	Т, К	Conversion CO ₂ , %	Selectivity, %						
			CH_4		CO		CH₃OH		
			select	yield	select	yield	select	yield	
Co-Pd/Siral-1	473	49	98.8	48.4	1.2	0.6	-	-	
	573	54	91.1	49.2	6.7	3.6	2.2	1.2	
	673	56	75.5	42.3	21.8	15.5	2.7	1.5	
	773	64	63.6	40.7	34.7	16.9	1.7	11	
Co-Pd/Siral-10	473	54	98.5	53.2	1.5	0.8	-	-	
	573	58	78.1	45.3	16.2	9.4	5.7	3.3	
	673	62	70.0	43.4	26.8	18.9	3.2	2.0	
	773	69	55.7	38.4	42.7	17.9	1.6	1.1	
Co-Pd/Siral-40	473	41	99.2	40.7	0.8	0.3	-	-	
	573	43	96.3	41.4	1.1	1.1	2.6	1.1	
	673	44	91.8	40.4	5.9	2.6	2.3	1.0	
	773	45	79.1	35.6	19.8	8.9	1.1	0.5	

*Chromatographic analysis was performed every 30 minutes

Catalysts	Т, К	Conversion	Selectivity, %						
		CO ₂ , %	CH_4		С	CO		CH₃OH	
			select	yield	select	yield	select	yield	
Co/Siral-1	473	51	10	51	-	-	-		
	573	55	100	55	-	-	-	-	
	673	52	98.7	51.3	1.3	0.7	-	-	
	773	41	97.8	40	2.2	1.0	-	-	
Co/Siral-10	473	38	100	38	-	-	-	-	
	573	41	100	41	-	-	-	-	
	673	37	97.3	36	2.7	0.99	-	-	
	773	28	96.8	27.1	3.6	1.1	-	-	
Co/Siral-40	473	29	100	29	-	-	-	-	
	573	33	100	33	-	-	-	-	
	673	28	96.4	27	3.6	0.98	-	-	
	773	25	98.8	24.7	4.2	1.05	-	-	

Table 2. Products of two-stage conversion of the mixture $(CO_2 + H_2)$ on catalysts Co/Siral-1, 10, 40 (P = 0.1 MPa, CO₂:H₂ = 1:4, vol. W - 120 h⁻¹)

*Chromatographic analysis was performed every 30 minutes

A comparison of the data presented in Tables 1 and 2 shows that, despite the addition of the highly active hydrogenating metal (Pd), CO_2 conversion slightly decreases at 473–573 K compared to pure Co. The decrease in CO_2 conversion upon the addition of Pd – for example, to Co/Siral-1 – is most likely due to a change in the reaction pathway (methanation shunting):

- Co/Siral-1 directs CO₂ almost entirely toward methane (CH₄) formation,

– The addition of Pd opens alternative reaction pathways, which become more pronounced at 573 K: $CO_2 \rightarrow CO$ (reverse water-gas shift reaction); $CO_2 \rightarrow CH_3OH$ (partial reduction).

These pathways are less thermodynamically favorable at 473–573 K, resulting in a portion of the CO_2 being "lost" midway, which reduces the overall conversion to CH_4 .

Under reaction conditions, the catalysts exhibit the following behaviors:

– Hydride formation and surface passivation of Pd – At lower temperatures, Pd actively forms PdH_x hydrides, which diminishes the overall efficiency of CO_2 methanation.

– Surface poisoning of Pd by water and CO – Intermediate products (water and CO) remain on the Pd surface longer at temperatures below 600 K, which leads to: a) blockage of active sites, and b) hindered desorption, causing part of the CO_2 to remain unreacted.

Table 3 shows the values of the specific surface area and specific pore volume of Co-Pd-containing catalysts on Siral-1, 10, and 40 aluminosilicates, pre-calcined at 823 K in an air flow and then reduced in a hydrogen flow at 723 K for 1 hour.

Table 3. Values of the specific surface area and specific pore volume of 10% Co, 0.5% Pd-containing aluminosilicatesSiral-1, 10, 40

Catalysts	SiO ₂ , mas. %	Specific area, m²/g	Specific volume of pore, cm ³ /g	*Specific area of Co particles, m ² /g	*Specific area of CoO particles, m ² /g
Co-Pd/Siral-1	1	242	0.36	5.25	8.14
Co-Pd/Siral-10	10	298	0.45	4.27	6.62
Co-Pd/Siral-40	40	355	0.56	3.57	5.54

*The values of the specific surface area of cobalt particles and cobalt oxide were estimated using the ratio S=6/($\rho_{Co,CoO}$)d and S_{catalyst} = w(Co,CoO) · S(Co,CoO) + w(AlSi) · S(AlSi) under the condition of 10% reduction of cobalt oxides to metallic cobalt, where ρ Co,CoO is the density of metallic cobalt and cobalt oxide, d is the particle size estimated from X-ray diffraction patterns and FMR spectra, w is the contributions of the indicated phases to the total specific surface area of the catalyst.



Fig. 2. X-ray diffraction patterns of catalysts (a) – 10% Co and (b) – 10% Co, 0.5% Pd based on Siral-10 support, reduced in a hydrogen stream at 723 K for 1 hour.

Figure 2 (a, b) shows X-ray diffraction patterns of 10% Co and 10% Co, 0.5% Pd catalyst samples based on Siral-10, pre-calcined in an air stream at 823 K for 4 hours and then reduced in a hydrogen stream at 723 K for 1 hour.

40

Co-Pd-containing catalysts with the Siral aluminosilicate base reduced in a hydrogen flow are poorly crystallized systems with γ -Al₂O₃ and CoO_x oxides (most likely, CoO and Co₃O₄) and metallic nanosized palladium particles characteristic of γ -Al₂O₃ [21, 22]. By comparing the experimental X-ray diffraction pattern with the calculated one, the phase composition of the 10% Co, 0.5% Pd catalyst based on the Siral-10 support, reduced in a hydrogen flow at 723 K for 1 h, was determined. Calculations have shown that the best agreement between the experimental and calculated X-ray diffraction patterns is found with a composition comprising crystalline phases of Co₃O₄ (5%) and CoO (5%), metallic palladium (~0.5%), crystalline and amorphous gamma-aluminum oxide (30 and 50%, respectively) and amorphous SiO_2 (~10%), considering that the size of the Co₃O₄ phase is 30–35 nm, the CoO phase is 10–15 nm, metallic palladium is 3-5 nm, and gamma-aluminum oxide and silicon dioxide are 15–20 nm. The X-ray diffraction pattern calculated using the Monte Carlo method clearly reflects the complex distribution of amorphous components, characteristic of systems with no long-range order.

Figure 3 shows the EPR spectra recorded at room temperature for the catalyst samples reduced in a hydrogen stream at 723 K for 1 h: a) Co/Siral-10, b) Co-Pd/Siral-10, and c) the simulated EPR spectrum based on the assumption of a bimodal log-normal distribution of CoOx particles with size modes of 10–15 nm and 30–35 nm in the Co-Pd/Siral-10 sample.

The signals with a width of over 100 mT shown in Fig. 3, a, b, belong to nanosized superpara/ferromagnetic particles formed in the samples of these catalysts during their high-temperature treatment in a hydrogen flow. In the Co-Pd/Siral-10 samples calcined at 773 K and subsequently reduced in a hydrogen stream at 723 K, palladium is reduced to the zero-valent state and is likely stabilized as nanosized particles dispersed within the surface layer, interacting with ferromagnetic cobalt oxide particles. The size of the superparamagnetic/ferromagnetic CoOx particles, estimated by comparing theoretical



Fig. 3. EPR spectra recorded at room temperature for catalyst samples calcined at 773 K and subsequently reduced in a hydrogen stream at 723 K for 1 h: (a) – Co/Siral-10; (b) – Co-Pd/Siral-10; (c) – simulated spectrum assuming a bimodal log-normal distribution of CoO_x particles with modes at 30–35 nm and 10–15 nm, calculated based on the Landau-Lifshitz-Gilbert equations.

spectra (calculated using the Landau-Lifshitz-Gilbert equation) with experimental EPR data for Co/Siral-10 and Co-Pd/Siral-10, was found to be 20–23 nm and 15–18 nm, respectively. This suggests that the introduction of palladium into the Co/Siral-10 catalyst can significantly influence the size of CoO_x particles during thermal reduction, thereby affecting their magnetic properties.

The histogram in Fig. 4 (a, b) shows the distribution of nanosized CoOx particles in the catalyst structure, fitted with two separate log-normal distributions, each characterized by its own mean and variance. A corresponding 3D representation is also provided.

 Co_3O_4 is not a ferrimagnet, although it crystallizes in the magnetite structure. It is a normal spinel, with Co^{3+} ions occupying the B sites. The Co^{3+} ions exhibit zero net magnetic moment due to the splitting of the 3d levels by the octahedral crystal field. At 40 K, Co_3O_4 undergoes a transition to an ordered antiferromagnetic state. This magnetic structure arises from antiferromagnetic ordering of spins at the A sites, where each Co^{2+} ion is surrounded by four nearest neighbors with oppositely directed spins. This A–A interaction is significantly stronger-by about an order of magnitude-than expected. The exchange mechanism is believed to involve indirect exchange via a tightly bound octahedral complex surrounding the Co^{3+} ion [23, 24].

At the nanometer scale, CoO can crystallize in either the cubic rock-salt phase (space group Fm_3m) or the hexagonal wurtzite-type structure (space group $P6_3mc$) [25]. Anomalous magnetic behavior has been reported in rock-salt-type CoO nanoparticles, including ferromagnetic ordering in nanocrystals smaller than 10–20 nm. In contrast, bulk face-centered cubic CoO exhibits antiferromagnetic behavior, with a well-established Néel temperature of approximately 292 K [26].

The EPR spectra shown in Fig. 3b were calculated under the assumption of pseudo-Voigt signal shapes for CoO_x particles (Co_3O_4 and CoO), using g-factor values of 2.1 and a signal width of 0.78 T for one type of CoO_x particles, and g-factor values of 4.3 with a signal width of 0.62 T for the second type. The calculations were performed using the Landau-Lifshitz-Gilbert equations for EPR spectra [27]. The resulting spectrum assumes that the number of CoO_x particles with a g-factor of 2.1 is 1.2 times greater than those with a g-factor of 4.3.

EPR spectra of nanosized Pd particles were not detected at room temperature. Although signals characteristic of nanosized palladium particles have been observed in other studies [28, 29], we were unable to register them. To confirm nanosized palladium particles in the hydrogen-reduced samples, 1,3,5-trinitrobenzene (TNB) was used. Its adsorption onto the samples resulted in the appearance of TNB anion radicals in the EPR spectra, indicating electron-donor centers. These anion radicals form through electron transfer from donor centers in the catalyst to molecular TNB [30]. It is noteworthy that the concentration of TNB anion radicals is significantly higher in the 0.5% Pd/Siral-10 sample compared to 0.5% Pd/Siral-40. In the reduced Pd-containing catalysts, these electron-donor centers are palladium atoms, clusters, or particles. Each TNB molecule captures one electron from such a center, forming an anion radical. The concentration of these radicals, which can be accurately quantified from the EPR spectra, reflects the number of electron-donor centers - i.e., the number of palladium species – in the samples.



Fig. 4. (a) Histogram and (b) 3D representation of the log-normal distribution of CoO_x particles in the Co-Pd/Siral-10 catalyst sample, showing two dominant size modes: 10–15 nm and 30–35 nm, within the overall particle size range of 2–100 nm. The distribution accounts for a 1.2 time higher number of CoO_x particles in the 30–35 nm range compared to those in the 10–15 nm range.

Note that in the Co-Pd/Siral-10 samples calcined at 773 K and subsequently reduced in a hydrogen stream at 723 K, palladium is most likely reduced to the zero-valent state and stabilized as nanosized particles. These particles disperse ferromagnetic cobalt oxide species in the surface layer of the catalyst. As a result, the catalyst comprises nanosized palladium and cobalt oxide CoO_x particles supported on an aluminosilicate base.

We propose that the formation of methanol on Co-Pd-containing catalysts proceeds via a two-stage mechanism. In the first stage, CO_2 is hydrogenated to methane over cobalt-containing centers. In the second stage, methane is oxidized to methanol via reaction with PdO particles ($CH_4 + PdO \rightarrow CH_3OH + Pd$). It is likely that metallic palladium and nanosized cobalt oxide particles serve as the catalytically active centers in the hydrogenation of carbon dioxide to methanol.

4. Conclusion

This study demonstrates that palladium-containing oxide systems show promise as catalysts for CO₂ hydrogenation to methanol. Incorporating metal components such as palladium into oxide matrices is a viable strategy for enhancing catalytic activity in this reaction. However, the precise nature of the active centers and the underlying mechanism remains to be fully understood. Co-Pd-containing catalysts based on Siral-type aluminosilicate were proposed, and a two-stage conversion scheme under atmospheric conditions was developed: first, hydrogenation of CO₂ to methane over cobalt centers, followed by the oxidation of methane to methanol over palladium oxide PdO particles. The introduction of palladium not only alters the structural and magnetic properties of the catalyst but also generates active sites capable of facilitating the selective oxidation of methane to methanol. Upon reduction, the catalysts form nanosized metallic and oxide particles of cobalt and palladium, which exhibit enhanced reactivity toward CO₂, CH₄, and H₂. EPR spectroscopy confirmed that the Co,Pd-containing catalysts exhibit superparamagnetic or ferrimagnetic behavior, with cobalt oxide particles predominantly in the 10–30 nm range. These nanostructured features are associated with increased catalytic activity. Methanol formation at temperatures ≤573 K may proceed through surface CH₃O* intermediates, with methanol desorption occurring before further hydrogenation to methane. The data suggest that cobalt oxides may facilitate the oxidation of Pd to PdO, which then participates in the selective oxidation of methane to methanol. Overall, the results highlight the importance of catalyst design in steering CO_2 hydrogenation pathways and confirm that a two-reactor flow system with intermediate water removal is optimal for directing the reaction toward methanol production at atmospheric pressure and temperatures above 573 K.

Direct catalytic hydrogenation of CO_2 to methanol is limited by thermodynamic and kinetic barriers, especially under atmospheric pressure. Low yields, catalyst deactivation by water, and competition with side reactions hinder industrial application. However, advances in catalyst design – such as using In_2O_3 , CoPd, NiGa, and systems with oxygen vacancies – offer promising solutions. Improving water resistance, employing bifunctional or integrated systems, and exploring alternative approaches like photocatalysis or electrochemistry can enhance methanol production without increasing pressure. While challenges remain, these strategies bring the process closer to practical, sustainable CO_2 utilization.

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