# Carbon Oxide Hydrogenation over $GdBO_3$ (B = Fe, Mn, Co) Complex Oxides: Effect of Carbon Dioxide on Product Composition

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Received July 22, 2019; revised November 17, 2019; accepted January 9, 2020

**Abstract**—The catalytic properties of GdFeO<sub>3</sub>, GdCoO<sub>3</sub>, and GdMnO<sub>3</sub> perovskite-type complex oxides in carbon oxide hydrogenation are studied. A correlation between the composition and catalytic properties of the oxide is found. It is shown that carbon monoxide conversion increases in the following order: GdFeO<sub>3</sub> < GdMnO<sub>3</sub>  $\leq$  GdCoO<sub>3</sub>; carbon dioxide conversion increases in the reverse order. Differences in the catalytic characteristics of GdFeO<sub>3</sub>, GdMnO<sub>3</sub>, and GdCoO<sub>3</sub> are attributed to different forms of chemisorbed CO, CO<sub>2</sub>, and H<sub>2</sub> and the hydrogen mobility across the catalyst surface. The introduction of carbon dioxide into the reaction mixture suppresses the formation of olefins and causes an increase in methane yield. In the catalytic process, GdCoO<sub>3</sub> is partially decomposed into Gd<sub>2</sub>O<sub>3</sub>, Co, and Gd<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. It is assumed that carbon oxides are adsorbed by Gd<sup>3+</sup> ions (A site), while transition metal ions (B site) are responsible for the formation of atomic hydrogen. It is presumed that carbon sites formed on the surface differ in catalytic activity: some of them are responsible for the formation of unsaturated hydrocarbons, and the others are responsible for the formation of unsaturated hydrocarbons, and the others are responsible for the formation of paraffins.

*Keywords:* hydrogenation, carbon monoxide, carbon dioxide, perovskite **DOI:** 10.1134/S0965544120050114

Fischer–Tropsch synthesis is a catalytic process to convert synthesis gas to a broad range of hydrocarbons, the most important of which are light olefins (ethylene, propylene, and butylene) used for various chemical industries. A promising process for light olefin production is a modified Fischer–Tropsch synthesis involving  $CO_2$  [1–5]. Selectivity for particular products depends on the composition of the reaction mixture and the ratio of carbon oxides in it. For example, the authors of [6, 7] state that  $CO_2$  behaves as an inert component; however, the introduction of  $CO_2$ into the reaction mixture shifts the product distribu-

## tion toward $C_2^{=} - C_4^{=}$ [8].

Conventional carbon oxide hydrogenation catalysts are systems based on iron and cobalt [9, 10]; however, their main disadvantage is that they are prone to poisoning and coking. In addition, in the presence of conventional catalysts, the range of the resulting products is extremely broad. Therefore, the control of selectivity remains one of the most important and complex problems in the field of scientific research. Perovskite-type complex oxides ABO<sub>3</sub> (A is an alkali or rare-earth metal cation, B is a transition metal cation), which exhibit a mixed oxygen-ionic and electronic conductivity and a high stability, are used as catalysts for various processes, in particular, carbon oxide hydrogenation [11–13]. A variation in the cationic composition at A and B sites provides the formation of systems with a controlled yield and selectivity for target synthesis products [14–17].

This study is focused on the catalytic activity of complex oxides  $GdBO_3$  (B = Fe, Co, Mn) in carbon oxide hydrogenation and the determination of the effect of  $CO_2$  on the reaction product distribution and the olefin/paraffin ratio.

## **EXPERIMENTAL**

Complex oxides  $GdBO_3$  (B = Fe, Co, Mn) were synthesized by the sol-gel (citrate) method described in [18].

The phase composition of the catalysts was determined by X-ray powder diffraction analysis (Rigaku MiniFlex II instrument). The surface morphology of the samples was studied by scanning electron microscopy on Zeiss EVO®40 and Carl Zeiss Supra 40VP microscopes. Data on specific surface area were calculated by the Brunauer–Emmett–Teller (BET) method



Fig. 1. X-ray diffraction patterns of complex oxides: (1)  $GdFeO_3$ , (2)  $GdCoO_3$ , and (3)  $GdMnO_3$ .

from nitrogen adsorption isotherms (Quantachrome Nova 4200e instrument). The oxidation state of iron, cobalt, and manganese was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were conducted on a Thermo Fisher Scientific Escalab 250Xi instrument (Al $K_{\alpha}$ ,  $\lambda = 0.1541$  nm).

The catalytic activity in carbon monoxide hydrogenation was tested in a U-shaped flow quartz reactor with a fixed catalyst bed composed of a 0.1-g weighed portion of the catalyst diluted with silica. The reactor was placed in a temperature-controlled furnace; temperature was measured/controlled using a K-type thermocouple placed into the center of the catalyst bed without direct contact. The process temperature was increased from 523 to 708 K. Carbon oxide hydrogenation was run at atmospheric pressure and a gas mixture flow rate of 1.5 L/h (CO + CO<sub>2</sub>/H<sub>2</sub> = 1/2). In all tests, the samples without prereduction were used. Analysis of the reaction mixture above the catalyst surface was conducted on a Kristall 5000.2 gas chromatograph equipped with a stainless steel column filled with the Porapak Q sorbent and thermal conductivity and flame ionization detectors.

Reaction product formation rate (specific catalytic activity) R (mol/(h g)) was determined from the constancy of chromatographic peaks. Carbon oxide conversions  $(X_i, \%)$ , product formation rates  $(R_i, mmol/(h g))$ , and olefin selectivity  $(S_i, \%)$  were calculated by the equations given in [19].

## **RESULTS AND DISCUSSION**

According to X-ray diffraction analysis, the synthesized GdBO<sub>3</sub> oxides (B = Fe, Co, Mn) are singlephase materials and do not contain impurity phases (Fig. 1); the diffraction peaks are consistent with the PDF2 database: #01-070-9906 (GdFeO<sub>3</sub>), #00-025-1057 (GdCoO<sub>3</sub>), and #01-070-9190 (GdMnO<sub>3</sub>). As evidenced by scanning electron microscopy, all the samples have a porous structure. The particle morphologies are slightly different: the GdFeO<sub>3</sub> sample consists of agglomerated elongated particles with a diameter of 30-60 nm and a length of about 200 nm, whereas GdCoO<sub>3</sub> and GdMnO<sub>3</sub> consist of spherical particles with a diameter of about 100 and 200 nm, respectively.

X-ray photoelectron spectroscopy showed that, in all the studied compounds, gadolinium is in the 3+ state; the Gd 4*d* energy is ~143.5 eV<sup>1</sup>. In the GdFeO<sub>3</sub> compound, the Fe  $2p_{3/2}$  binding energy is 710.9 eV; this value suggests that iron is in the 3+ state [20, 21]. The XPS results show that the main Co  $2p_{3/2}$  peak is broad and consists of a peak at 779.89 eV and a satellite peak at 789.5 eV; this finding is consistent with the published data for Co<sub>3</sub>O<sub>4</sub> [20, 21] and indicates the presence of cobalt atoms in the heterovalent state (+3 and +2). According to the published data<sup>1</sup>, the  $2p_{3/2}$ peak localized at an energy of 641.48 eV indicates the presence of manganese in heterovalent states of 2+ and 3+.

In the case of carbon monoxide hydrogenation at a  $CO: H_2$  ratio of 1 : 2 in the presence of GdFeO<sub>3</sub>, GdMnO<sub>3</sub>, and GdCoO<sub>3</sub>, the CO conversion was 50-70%, respectively (Fig. 2). The lowest CO conversion (about 55%) was observed for gadolinium ferrite. Up to a temperature of 673 K, gadolinium manganite exhibited the highest activity in carbon monoxide conversion. At temperatures above 623 K, an abrupt increase in the CO conversion was observed in the case of using gadolinium cobaltite as a catalyst: in the temperature range of 648-673 K, the carbon monoxide conversion achieved almost 90%; in addition, the formation of  $CO_2$  was observed; in the presence of gadolinium cobaltite, the amount of carbon dioxide increased with increasing temperature and significantly exceeded the amount of CO<sub>2</sub> formed in the presence of manganite and ferrite (Fig. 2).

Carbon monoxide undergoes both molecular adsorption to form linear and bridge species and dissociative adsorption;  $CO_2$  can be formed owing to the interaction of  $CO_{ads}$  with either perovskite surface oxygen ( $O_S$ ) or oxygen released during the dissociative adsorption of carbon monoxide:  $CO_{ads} + O_S \rightarrow CO_2$ [22]. Higher carbon monoxide conversions in the presence of GdMnO<sub>3</sub> can be attributed to different heats of adsorption of CO and H<sub>2</sub> on the metal surface and the difference in these values. According to [23], the difference in the surface adsorption energies of CO and H<sub>2</sub> decreases in the following order: Mn > Fe >

<sup>&</sup>lt;sup>1</sup> J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data (Physical Electronics Division, PerkinElmer, 1992).

Co; these energies are not extremely high; therefore, the energy barrier to the reaction of adsorbed CO and  $H_2$  will be small. The Me–CO binding energy increases in the same order: Mn < Fe < Co. These values correlate well with the observed CO conversions.

In the case of cohydrogenation of CO and CO<sub>2</sub> at a mixture : hydrogen ratio of 1 : 2, the carbon monoxide conversions in the presence of GdMnO<sub>3</sub> and GdCoO<sub>3</sub> were comparable with the values obtained in the hydrogenation of pure CO (Fig. 3). At the same time, in the presence of GdFeO<sub>3</sub>, a significant decrease in X(CO) was observed; it can be attributed to the desorption of carbon monoxide formed during the dissociative adsorption of carbon dioxide at lower temperatures. With respect to CO<sub>2</sub> conversions, an opposite tendency was observed: the lowest values (<50%) were obtained in the case of using GdCoO<sub>3</sub> as a catalyst, and the highest values (80-100%) were observed in the presence of GdFeO<sub>3</sub>. However, at temperatures above 648 K, the  $X(CO_2)$  conversions began to decrease. This process was particularly pronounced in the presence of gadolinium ferrite; this fact can be apparently attributed to a more intense occurrence of the Boudouard reaction to form active carbon:  $2CO \rightarrow CO_2 + C$ .

The introduction of carbon dioxide into the reaction mixture in amounts not exceeding 11% (CO:  $CO_2 = 2:1$ ) hardly affected the CO conversion in the reaction over GdFeO<sub>3</sub> (Fig. 4). However, an increase in the CO<sub>2</sub> content to an amount equimolar with that of CO led to a significant decrease in the CO conversion. At a temperature of 648 K, it was as low as 20%. A decrease in CO conversions with an increase in the CO<sub>2</sub> content in the feed mixture can be associated with the desorption of carbon monoxide formed during the dissociative adsorption of carbon dioxide at initial reaction temperatures. A further increase in temperature (catalytic region) leads to an increase in the carbon dioxide content in the mixture, which is most probably attributed to the further chemisorption of both CO and CO<sub>2</sub> on active surface sites released during catalysis. However, it is not improbable that Boudouard and Bosch side reactions can occur:  $2CO \rightarrow C + CO_2$  and  $CO_2 + 2H_2 \rightarrow C + 2H_2O_2$ , respectively.

At the same time, for a mixture with excess  $CO_2$ (22%, CO :  $CO_2 = 1$  : 2), an increase in CO conversions was observed; the conversions achieved 80%, which is higher than the values obtained in the hydrogenation of pure carbon monoxide. The data on the reaction in the presence of GdFeO<sub>3</sub> and excess carbon dioxide in the reaction mixture indicate an intensification of dissociative chemisorption  $CO_2 \rightarrow CO + O$  and the possible occurrence of carbon monoxide disproportionation to form active carbon:  $2CO \rightarrow CO_2 + C$ ; it is these factors that lead to a significant increase in carbon monoxide conversions. The authors of [24]



**Fig. 2.** Temperature dependences of CO conversions and  $CO_2$  content in the case of the reaction at a CO : H<sub>2</sub> ratio of 1 : 2 in the presence of (1, 4) GdFeO<sub>3</sub>, (2, 5) GdCoO<sub>3</sub>, and (3, 6) GdMnO<sub>3</sub>.



**Fig. 3.** Temperature dependences of CO and CO<sub>2</sub> conversions in the reaction at ratios of (CO : CO<sub>2</sub> = 1 : 1) : H<sub>2</sub> = 1 : 2 in the presence of (1, 4) GdFeO<sub>3</sub>, (2, 5) GdCoO<sub>3</sub>, and (3, 6) GdMnO<sub>3</sub>.



**Fig. 4.** Dependence of CO conversions on the  $CO_2$  content in the reaction mixture of carbon oxides in the presence of (1) GdFeO<sub>3</sub>, (2) GdCoO<sub>3</sub>, and (3) GdMnO<sub>3</sub>.



Fig. 5. Dependence of (a) the olefin/paraffin ratio at 648 K and (b) olefin selectivity on the  $CO_2$  content in the reaction mixture: (1) GdFeO<sub>3</sub>, (2) GdCoO<sub>3</sub>, and (3) GdMnO<sub>3</sub>.

believe that two active phases— $Fe^0/Fe$  carbides and iron oxides ( $Fe_3O_4$ )—are simultaneously present on the iron surface. The carbide phase is active in the dissociation of CO and the formation of hydrocarbons, while the oxide phase adsorbs CO by the associative mechanism.

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Unlike GdFeO<sub>3</sub>, in the case of GdMnO<sub>3</sub> and GdCoO<sub>3</sub>, the presence of CO<sub>2</sub> had hardly any effect on CO conversion: regardless of the CO<sub>2</sub> content, carbon monoxide conversions were comparable to those obtained in the hydrogenation of pure CO (Fig. 4).

In either case—the hydrogenation of pure CO and the cohydrogenation of CO and  $CO_2$ —the reaction products were  $C_1$ — $C_6$  hydrocarbons, among which methane, ethylene, and propylene were dominant. A variation in the CO/CO<sub>2</sub> ratio in the reaction mixture led to a change in the quantitative ratio of hydrogenation products. An increase in the carbon dioxide content suppressed the formation of unsaturated hydrocarbons and caused a decrease in the olefin/paraffin ratio (Fig. 5).

It should be noted that, in the case of using  $GdMnO_3$  as a catalyst, at an equimolar content of CO and  $CO_2$  in the reaction mixture, an anomalous increase in olefin selectivity was observed.

The ratio between saturated and unsaturated hydrocarbons in hydrogenation products is mostly determined by the amount of atomic hydrogen capable of migrating from some active surface sites to other and by the structure of these sites [25, 26]. Differences in the catalytic activity of the samples can be associated with different rates of hydrogen diffusion across the catalyst surface (the spillover effect). Hydrogen is known to undergo mostly molecular adsorption on the manganese surface and dissociative adsorption in the atomic form on the surface of iron and cobalt [27]. The high rates of formation of paraffins (in particular, methane) in the presence of GdFeO<sub>3</sub> and GdCoO<sub>3</sub> (Table 1) are apparently attributed to both a larger amount of atomic hydrogen on the surface and its higher diffusion rate across the surface. On the manganese surface, the formation of  $CH_x$  radicals and their subsequent recombination to olefins are observed.

On the other hand, the catalyst activity and selectivity in this synthesis are also determined by the mechanism of CO and CO<sub>2</sub> adsorption the magnitude of which exceeds the adsorption of hydrogen by an order of magnitude; in addition, CO can be adsorbed on both metal and oxide components of the catalyst [28, 29]. The adsorption by the dissociative mechanism increases in the following order: Co, Fe, Mn; the Me–CO binding energy decreases and, as noted above, the difference in the adsorption energy of CO and H<sub>2</sub> on the catalyst surface increases in the same order.

To determine the energy barrier to the reaction path, the experimental data were reduced to the linear coordinates of the Arrhenius equation (Table 1). For all the studied catalysts, the introduction of  $CO_2$  into the reaction mixture leads to a decrease in the apparent activation energies for methane formation.

For GdFeO<sub>3</sub> and GdCoO<sub>3</sub>, at an equimolar ratio of CO and CO<sub>2</sub> in the feed reaction mixture, the effective activation energies for methane formation and the pre-exponential factor logarithms are almost identical to the values obtained in the hydrogenation of pure carbon monoxide. For GdMnO<sub>3</sub>, the introduction of CO<sub>2</sub> into the reaction mixture leads to a significant decrease in  $E_a$ (CH<sub>4</sub>); i.e., an increase in the fraction of paraffins in the hydrogenation products is apparently attributed to the energy factor. In this case, for all the catalysts, the pre-exponential factor logarithm with respect to ethylene, which indirectly characterizes the number of active surface sites, decreases.

Catalyst systems based on lanthanides can form carbonate complexes with carbon oxides [30–33]. The formation of a metal phase and the presence of  $Gd_2O_2CO_3$  play an important role for the hydrogenation reaction, because it was found that the resulting  $Gd_2O_3$  is an active site for the adsorption of CO and  $CO_2$  in this process. Earlier, in studying the adsorption

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Mixture composition	Methane formation rate, mmol/(h g)	Olefin selectivity, %	Kinetic parameters of the formation processes			
			$CH_4$		C <sub>2</sub> H <sub>4</sub>	
			activation energy, kJ/mol	pre-exponential factor of the rate constant, $\ln K_0$	activation energy, kJ/mol	pre-exponential factor of the rate constant, $\ln K_0$
GdFeO <sub>3</sub>						
CO	2.54	27	70	5.70	65	3.49
$CO + CO_2 = 1 : 1$	1.26	7	68	5.39	60	2.65
GdCoO <sub>3</sub>						
CO	37.42	65	50	5.32	65	3.49
$CO + CO_2 = 1 : 1$	27.34	3	54	5.40	28	-2.54
$GdMnO_3$						
CO	0.51	35	136	23.48	45	6.15
$CO + CO_2 = 1 : 1$	4.29	33	43	14.75	60	2.60

Table 1. Comparative characteristics of the studied samples in carbon oxide hydrogenation reactions at T = 648-708 K

of carbon oxides on GdFeO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> [34], the existence of two molecular forms of carbon monoxide adsorption on the perovskite surface was revealed. It was shown that carbon dioxide undergoes molecular adsorption to form carbonate–carboxylate complexes and dissociative adsorption with recombination during desorption in CO<sub>2</sub>. It can be assumed that the formation of carbonate complexes occurs on Gd<sup>3+</sup> ions (A site), whereas transition metal ions (B site) are responsible for the formation of atomic hydrogen.

Thus, our results suggest the following: if the introduction of  $CO_2$  into the reaction mixture contributes to an increase in saturated hydrocarbon yields and causes the suppression of olefin formation reactions, then the carbon sites formed on the surface during the process most probably differ in catalytic activity: some of the sites, which are assumed to arise from the dissociative adsorption of CO, are responsible for the formation of unsaturated hydrocarbons, while the other sites, which possibly arise from the interaction of  $CO_2$ with catalytic surface sites in accordance with the mechanism proposed in [35], are responsible for the formation of paraffins.

## ACKNOWLEDGMENTS

The physicochemical studies were conducted using the equipment of the Thermogravimetric and Calorimetric Research Center, the Center for X-ray Diffraction Studies, the Center for Physical Methods of Surface Investigation, and the Interdisciplinary Resource Center for Nanotechnology of the St. Petersburg State University Research Park.

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### FUNDING

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This work was supported by the Russian Foundation for Basic Research (project no. 17-03-00647). The publication has been prepared with the support of the RUDN University Program 5-100.

#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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Translated by M. Timoshinina