Combined transformations of carbon dioxide and ethanol in the presence of the intermetallic compound $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$, Pd/SiO_2, and Al_2O_3

M. V. Tsodikov, V. Ya. Kugel', E. V. Slivinskii, Yu. A. Egorov, and V. P. Mordovin*

A. V. Topchiev Institute of Pertochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

The influence of the composition of catalytic systems and the method for H_2 feed into the reaction area on the degree of conversion of CO_2 during its joint transformations with ethanol and on the selectivity of formation of liquid organic products (ethyl acetate, acetaldehyde, and hydrocarbons) was studied at p = 15 atm and T = 573 K. A noticeable conversion of CO_2 and ethanol into ethyl acetate and acetaldehyde was observed in the presence of only the intermetallic compound, its composition with a palladium-containing catalyst, and the whole ternary catalytic system. The selectivity of the reaction changed when the binary catalytic composition consisting of the intermetallic and γ-Al_2O_3 was used. In this case, the fraction of C_9—C_{14} alkanes and alkenes with normal and iso structures was mostly formed; its content was as high as 40%. The degree of conversion of CO_2 reached 30—36% and the selectivity to liquid products was 70—80% only when the hydrogen desorbed from the intermetallic was used.

Key words: intermetallic compound, hydrogen, carbon dioxide; CO_2 conversion; selectivity; absorption of hydrogen.

An important problem in the elaboration of energy- and resource-saving technologies is the development of catalytic processes for transformation of CO_2 into valuable products of petrochemical synthesis. Although numerous experimental studies and reviews have been devoted to the search for active heterogeneous and homogeneous catalysts for these reactions, the problem still remains topical.[1—4]

It has been reported that in the presence of the intermetallic compound $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ possessing high chemisorption capacity with respect to hydrogen, CO_2 is hydrogenated to CO or methane even at room temperature.[5] At higher temperatures (up to 623 K), the degree of conversion of CO_2 reaches 19%. An important feature of this system is that a high selectivity in the formation of CO (up to 80%) at 293—573 K was observed only when hydrogen was desorbed from the intermetallic structure. Hydrogenation with dihydrogen resulted in substantially increased amounts of gaseous C_1—C_4 hydrocarbons. No liquid products were detected upon the gas-phase transformation of CO_2.

Liquid carboxylation products, mono- and dicarboxylic acids, were produced in small amounts in the case of electrochemical activation of CO_2 in the presence of alkenes and butadiene.[6,7]

When CO_2 was hydrogenated in an autoclave using a heterogeneous catalyst Cu_3Zr_2Mn or palladium-containing homogeneous catalysts, solvents were found to have an effect on the formation of small amounts of esters and ethers.[8,9]

In this work, we studied joint transformations of CO_2 and ethanol in the presence of the intermetallic compound $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ and also in the presence of catalytic compositions consisting of this intermetallic compound, Pd/SiO_2, and γ-Al_2O_3.

Experimental

Catalytic experiments on the transformation of CO_2 were carried out using a flow-circulation type laboratory setup equipped with a dosing apparatus for the supply of the liquid reactant over a catalyst bed. In order to separate the gas and the liquid phases, the reactor outlet was connected to a cooled separating vessel. The total volume of the system was 0.75 L, that of the reaction area was 0.25 L. The intermetallic compound was charged in the reactor as the crushed 0.2—0.5 mm fraction (56 g). When compositions were used, the intermetallic compound was mixed with the 0.1—0.2 mm fraction of 0.5% Pd/SiO_2, which we had synthesized, and/or commercial γ-Al_2O_3 as beads weighing 3.0 g with a granule size of 1.5—2.0 mm. Hydrogenation was accomplished with hydrogen desorbed from the intermetallics, with a mixture of desorbed hydrogen and dihydrogen, or with dihydrogen alone. To identify the products of CO_2 transformations, the experiments were also carried out under purified N_2, CO, and with a small amount of ethylene added. Prior to each entry, a pressure test was carried out: the system was filled with dinitrogen under a pressure of 120—130 atm and kept for 24 h. Then dinitrogen

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was replaced by dihydrogen, and the surface of the intermetallics was treated with the latter for 8 h at atmospheric pressure and 100 °C, and then the system was cooled to 20 °C, and the H_2 pressure was increased to 120—130 atm. When the pressure in the system decreased as a result of absorption of the hydrogen by the intermetallics, H_2 was supplied again, and this was repeated to saturation. The amount of absorbed H_2 was estimated using a standard manometer; then dihydrogen was replaced by CO_2 at a pressure of 15 atm. When the CO_2 pressure became constant, a circulating pump was turned on, and the temperature of the reaction mixture was quickly increased to 300 °C. The turnover number for CO_2 circulation through the heterogeneous system was 5 L h^{-1}. When a specified temperature had been attained, ethanol was supplied onto the catalyst bed at a rate of 10—12 cm^3 h^{-1}. Each experiment lasted for 3 h. After the experiment, the setup was cooled, and the volume of gas in the system was determined with the standard manometer at ~20 °C.

The initial gas and that formed during hydrogenation were analyzed for H_2, CO, CH_4, and CO_2 by GC using a "Biokhrom" chromatograph (TC detector, a 150×0.4 cm column, SKT 0.25—0.50 mm, Ar as the carrier gas). The composition of gaseous hydrocarbons was determined using an LKhM-8 MD chromatograph (flame-ionization detector, a 150×0.4 cm column, 0.25—0.50 mm α-Al_2O_3 modified with 5% squalane, He as the carrier gas).The contents of the gas components were calculated by comparison with standard mixtures.

The degree of conversion of CO_2 was determined by the manometric method using the following procedure. After conducting an experiment and cooling the system to ~20 °C, the total gas volume in the system was determined from the manometer reading; the concentration of CO_2 in the gaseous reaction products was found by GC; and the amount of CO_2 converted during the reaction (ΔCO_2) was calculated; the degree of conversion was found as follows: $\alpha(\% \ v/v) = [\Delta CO_2(L)/CO_{2,init.}(L)] \cdot 100\%$. After that, the concentrations and volumes (in liters) of the gas components formed during the reaction were found. Since ethane and ethylene were also formed from ethanol, the experiments were carried out under identical conditions; CO_2 was replaced by nitrogen. Based on the quantities of converted CO_2 and the gaseous products formed, the amount of CO_2 spent for gas formation was determined. The rest of the converted CO_2 (% v/v) was characterized as the selectivity with respect to the formation of liquid products

$$S = [\Sigma \Delta CO_2(L) - \Delta CO_{2,\text{into gases}}(L) / \Sigma \Delta CO_2] \cdot 100\%.$$

The data of GC analysis were also used to determine the amount of H_2 desorbed from the intermetallics during the experiment at 573 K.

The composition of liquid products was studied by GC/MS using a Kratos MS 25RF mass spectrometer (a 200×0.4 cm packed column filled with polyethylene glycol). The composition of liquid products was also determined by GLC on a "Khrom-5" chromatograph (flame-ionization detector, a 200×0.4 cm packed column, Celite 545 modified with 5% polypropylene glycol sebacinate).

The palladium-containing catalyst was prepared using the alkoxo method. $PdCl_2$ and tetraethoxysilane (TES) were used as initial reactants. Methanol (10 cm^3) and several drops of glacial acetic acid were added to TES (10 g) with stirring. Palladium chloride (0.17 g) was dissolved in water (2.4 g) containing several drops of concentrated HCl (d = 1.18 g cm^{-3}) and mixed with methanol (3 cm^3). A solution of palladium chloride in aqueous ethanol was slowly added with intense stirring to the mixture of TES with ethanol, then the resulting sol was thoroughly stirred for an additional 30 min and allowed to stand in the dark. The gel was formed over a period of 2 days. The freshly prepared gel was evacuated at 180—200 °C and the resulting powder was heated for 6 h at 500 °C. The concentration of Pd in the resulting catalyst was determined by atomic-absorption spectroscopy using a Perkin—Elmer 400 spectrometer.

According to analysis, the concentration of palladium in the Pd/SiO_2 samples was 0.45—0.53%.

Results and Discussion

It can be seen in Table 1 that the reaction with the hydrogen contained in the intermetallics in the atmosphere of H_2 affords acetaldehyde [AcH], ethyl acetate [EtOAc], and a slight amount of *n*-butanol. In an atmosphere of dinitrogen, AcH and EtOAc are not produced; however, traces of *n*-butanol are detected; therefore, it is difficult to draw definite conclusions concerning participation of CO_2 in the formation of this compound.

The amounts of AcH and EtOAc substantially increased when a catalytic composition consisting of the intermetallics, Pd/SiO_2, and γ-Al_2O_3 was used (see Table 1).

As has been noted previously,[6,7] a slight amount of oxygen-containing carboxylation products can be formed upon interaction of CO_2 with alkenes.

We found that addition of a slight amount of ethylene (up to 0.075%) into the reaction mixture results in a sharp decrease in the degree of CO_2 conversion during the subsequent experiments and appearance of ethane in gaseous reaction products; the ethane is likely to be formed upon hydrogenation of ethylene on the surface of the activated intermetallic compound (see Table 1, entry *13*). Therefore, alumina was added to the catalyst, so that ethylene could be formed *in situ* on its surface.

In view of the known ability of some palladium-containing systems to accomplish catalytic activation of CO_2, we used the Pd/SiO_2 system.[1–3,7,8]

The composition of liquid reaction products obtained with a binary system comprising the intermetallics and Pd/SiO_2 is close to that obtained in entries *1* and *2* (see Table 1). However, the concentration of oxygen-containing compounds is higher than that in entry *1* in which only the intermetallic compound was used as the heterogeneous catalyst and lower than that in entry *2* (see Table 1) in which the ternary composition consisting of the intermetallics, Pd/SiO_2, and γ-Al_2O_3 was used.

The composition of the products changes considerably in the presence of the binary intermetallics—γ-Al_2O_3 composition (see Table 1, entry *4*). With the overall degree of CO_2 conversion α = 34% and the selectivity S = 77%, the liquid products of the synthesis contain large proportions of alkanes and alkenes (up to 40%), the content of branched isomers being as high as ~40%.

Table 1. Products of hydrogenation of CO_2 with ethanol in the presence of an intermetallic compound ($TiFe_{0.95}Zr_{0.03}Mo_{0.02}$); Pd/SiO_2, and γ-Al_2O_3 (p = 15 atm, 573 K)

Entry	Catalytic composition	Reactant	α_{CO_2}	S	Product composition	
			(% v/v)		gaseous (% v/v)	liquid[e] (% w/w)
1	Intermetallic compound	CO_2, H_2,[a] ethanol	24.0	89	CO 1.7, CH_4 0.85, C_2—C_4 0.44[c]	AcH 1.5, EtOAc 6.7, MeOH 1.4, BuOH 4.0
2	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	CO_2, H_2,[a] ethanol	36.0	80	CO 1.0, CH_4 2.5 C_2—C_4 2.5[c]	AcH 7.9, EtOAc 14.0, BuOH 1.8, DEE 7.0
3	Intermetallic compound, Pd/SiO_2	CO_2, H_2,[a] ethanol	26.0	67	CH_4 3.0 C_2—C_4 0.9[c]	AcH 3.2, EtOAc 9.6, BuOH 1.7, DEE 2.0
4	Intermetallic compound, γ-Al_2O_3	CO_2, H_2,[a] ethanol	34.0	77	CH_4 0.35 C_2—C_4 0.92[c]	alkanes + alkenes (normal) 23.8, (*iso*) 17.0 BuOH 1.7, DEE 8.2
5	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	CO_2, H_2,[a] H_2,[b] ethanol	35.0	50	CH_4 6.0 C_2—C_4 4.4[c]	EtOAc 2.0, BuOH 2.0 DEE 2.0
6	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	CO_2, H_2,[b] ethanol	20.0	0	CH_4 10.0 C_2—C_4 5.0[c]	BuOH 2.0, DEE 1.5
7	Intermetallic compound	CO_2, H_2,[b] ethanol	15.0	0	CO 2.5, CH_4 7.5 C_2—C_4 2.7[c]	BuOH traces
8	Intermetallic compound, γ-Al_2O_3	CO_2, H_2,[b] ethanol	10.0	~5	CH_4 0.5 C_2—C_4 4.0[c]	alkanes + alkenes (normal + *iso*) 2.0 DEE 7.0
9	Intermetallic compound	N_2, H_2,[a] ethanol	—	—	CH_4 0.05, C_2H_4 2.0 C_2H_6 5.0[d]	DEE traces
10	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	N_2, H_2,[a] ethanol	—	—	CH_4 0.1, C_2H_4 traces, C_2H_6 6.6[d]	DEE 10.0
11	Intermetallic compound, Pd/SiO_2	N_2, H_2,[a] ethanol	—	—	CH_4 0.12, C_2H_4 traces, C_2H_6 5.5[d]	BuOH traces DEE 2.3
12	Intermetallic compound, γ-Al_2O_3	N_2, H_2,[a] ethanol	—	—	CH_4 0.01, C_2H_4 7.2 C_2H_6 5.7[d]	BuOH traces DEE 15.0
13	Intermetallic compound	CO_2, H_2,[a] EtOH	<1.0	—	CH_4 traces, C_2H_4 1.7 C_2H_6 0.4[c]	—
14	Intermetallic compound, γ-Al_2O_3	CO, H_2,[a] EtOH	19.0	0	CH_4 0.53, C_2—C_4 0.95 CO_2 0.25[c]	BuOH traces BuOEt 2.0 DEE 10.0
15	Intermetallic compound	CO_2, H_2[a]	11.5	0	CO 7.8, CH_4 1.8 C_2—C_4 1.9[c]	—
16	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	CO_2, H_2[a]	18.0	0	CH_4 4.1, C_2—C_4 7.2[c]	—
17	Intermetallic compound, Pd/SiO_2, γ-Al_2O_3	CO_2, H_2[a]	25.0	0	CH_4 8.2, C_2—C_4 4.7[c]	—

[a] Hydrogen was supplied from the catalyst structure. [b] Gaseous H_2. [c] The rest was CO_2 and H_2. [d] The rest was N_2 and H_2. [e] The rest was ethanol.

The transformations of ethanol under N_2 in the presence of catalytic compositions containing the palladium catalyst supported on γ-Al_2O_3 and SiO_2 yield substantial amounts of diethyl ether (DEE), ethylene, and ethane and traces of methane, whereas in the presence of only the intermetallic compound possessing no acidic properties, no DEE was detected (see Table 1, entries *9*—*12*).

The introduction of gaseous H_2 as a reactant into the system markedly decreases the selectivity of transformation of CO_2 into liquid oxygen-containing products and enhances gas formation. In the presence of only H_2, CO_2, or EtOH, the selectivity in the formation of oxygen-containing liquid products drops almost to zero (see Table 1, entries *5*—*7*).

The use of dihydrogen in the reaction catalyzed by the intermetallics—γ-Al_2O_3 binary composition decreases the selectivity from 75 to ~5%; however, the composition of the hydrocarbon fraction remains virtually the same as observed with hydrogen desorbed from the intermetallic compound. The use of dihydrogen results in increased hydrogenating activity, and, hence, in a higher proportion of CO_2 consumed for gas formation (see Table 1, entry *8*).

It has been found previously[5] that hydrogenation of CO_2 alone gives CO with high selectivity. Therefore, it can be suggested that liquid organic products are produced with participation of CO, formed intermediately from CO_2. This scheme of formation of liquid products is more likely to be realized with the intermetallics—Al_2O_3 binary composition, because in this case, the liquid products contain a hydrocarbon fraction, which is usually obtained in the syntheses based on CO and H_2 in the presence of iron-containing catalysts.[10] Therefore, we carried out an experiment in which CO_2 was replaced by CO. It can be seen from Table 1 (entry *14*) that hydrogenation of CO in the presence of the intermetallic compound yields gaseous C_1—C_4 hydrocarbons as the major products; among the liquid products, butyl ethyl ether and traces of butanol were detected in addition to the DEE present as the major component. The degree of conversion of CO was 17%, of which up to 16% was consumed for the formation of gaseous products.

At the stage of chemisorption, 1 mole of the intermetallic compound absorbed 0.95—1.0 moles of H_2, which corresponds to a hydride of the empirical formula $TiFe_{0.95}Zr_{0.03}Mo_{0.02}H$. During experiments at 573 K, 0.5—0.6 moles of H_2 was evolved into the system over a period of 3 h, and 0.4—0.5 moles remained in the structure of the intermetallics. This result was confirmed by the quantity of hydrogen absorbed repeatedly during the second cycle of saturation with the same quantity of the heterogeneous catalyst. The amount of hydrogen absorbed in the second cycle per mole of the intermetallics decreased approximately twofold.

Thus, the obtained results suggest that CO_2 participates in the formation of liquid organic products in the reaction with ethanol occurring on the surface of the intermetallic compound during desorption of hydrogen from it. The molecules of the major oxygen-containing products (AcH, EtOAc) contain the same numbers of C—C bonds as the ethanol molecule. Nevertheless, high degrees of conversion of CO_2 including its conversion into liquid products are observed. This might imply that CO_2 reacts with unstable products resulting from thermolysis of ethanol. The rate of dehydration of ethanol increases in the presence of γ-Al_2O_3 or SiO_2. Apparently, the latter is the reason for the increase in the concentration of unstable decomposition products, whose interaction with CO_2 can yield ethyl acetate and acetaldehyde. This can account for the fact that in the presence of catalytic compositions 2 and 3, the yields of acetaldehyde and ethyl acetate (see Table 1) are higher than those obtained with the intermetallic compound alone.

The process selectivity markedly changes in the presence of the intermetallics—γ-Al_2O_3 composition. In this case, mostly C_9—C_{14} alkanes and alkenes with a high content of isomers (~40%) are formed at a relatively high degree of conversion of CO_2 (α = 34%). The formation of 40% alkanes and alkenes in the liquid products correspond to extensive transformations of ethanol (~50%) and CO_2 (22.8%, or 67% based on the consumed reactant). As should be expected, the concentration of DEE in the liquid product is rather high (8.2%), which is not associated with participation of CO_2.

It should be noted that the use of desorbed hydrogen results in a substantially lower yield of hydrogenation products compared to that attained in the experiments with gaseous H_2.

Iron—titanium systems saturated with hydrogen are known to be thermodynamically less stable (H_f° = −29 kJ mol^{-1}) than titanium hydride (H_f° = −126 kJ mol^{-1}).[11] Destruction of bonds in the hydride phase and, correspondingly, virtually complete hydrogen desorption from the intermetallic compound under the experimental conditions occurs at 623 K. However, according to our results, this does not rule out the possibility that some of the hydrogen is desorbed at lower temperatures down to room temperature. It can be assumed that at lower temperatures, hydrogen is bound to the intermetallic surface, which apparently accounts for its smooth addition to liquid intermediates.

The change in the process selectivity in those cases where large amounts of dihydrogen are used can be explained by assuming that dihydrogen is activated on the surface of metal-containing catalysts, and this accelerates exhaustive hydrogenation of CO_2 to hydrocarbon gases.

A small amount of an alkene added to the system as a reactant before the experiment is apparently largely chemisorbed on the intermetallics surface in competition with CO_2 and thus blocks the sites of its transformation on the surface. This can account for the fact that in this case, the degree of conversion of CO_2 into gaseous products is low and that ethane resulting from hydrogenation of ethylene is the major gaseous product (see Table 1).

The results obtained suggest that EtOAc is produced *via* intermediate formation of acetic acid, as a result of reaction of hydrogen-activated CO_2 with intermediate products of ethanol decomposition, followed by its esterification with excess ethanol. The formation of AcH can be rationalized by partial hydrogenation of the intermediate.

The effect of the intermetallics—γ-Al_2O_3 binary composition, which promotes the formation of the alkane—alkene fraction, is apparently due to the intense condensation of the ethylene formed *in situ* on the surface of Al_2O_3. The fact that, in this case, only DEE, ethylene, ethane, and traces of methane are formed in the atmosphere of N_2 suggests that the high degree of conversion of CO_2 is due its incorporation in the intermediate hydrocondensation products.

In the experiments in which the setup was pressurized with nitrogen at a high pressure (>100 atm) prior to the saturation of the intermetallics structure with hydrogen, mass spectra of the liquid products of the synthesis exhibit intense peaks with *m/z* 44, which are known to correspond to nitrogen-containing compounds such as amines. However, in the experiments carried out at a pressure of N_2 equal to 15 atm, no nitrogen-containing organic compounds were found among the liquid products.

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