TABLE 3. Effect of Space Velocity on Composition of Gas Mixture on Hydrogenation of CO_2 on Zr—Co—H Catalyst at 350°C

Space velocity, h^{-1}	CO_2 conversion, %	Composition, mole %				
		CO	CO_2	CH_4	H_2	H_2O
1000	94,7	0,2	2,3	30,4	11,4	55,7
8000	76,0	0,3	8,7	19,3	33,3	58,4
18400	65,6	0,5	9,1	18,5	39,9	32,2
26500	17,4	0,8	17,6	5,1	70,9	5,6

SUMMARY

1. Hydrides of the intermetallides Zr—Ni, Zr—Co, Hf—Ni, and Hf—Co are active in the synthesis of methane from CO_2 and H_2.

2. The compositions of the gas mixtures after hydrogenation of CO_2 in the interval 300-500°C at a space velocity of 1000 h^{-1} correspond well to equilibrium compositions derived from thermodynamic calculations.

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CARBONYLATION OF PROPYLENE WITH CARBON MONOXIDE IN THE PRESENCE OF $Ru_3(CO)_{12}$ CATALYSTS

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Carbonyl complexes of group VIII metals are active and selective catalysts for reactions that involve CO [1]. Ru complexes are active in olefin hydroformylation [2], water gas conversion [3, 4], CH_3COOH synthesis from methanol [5], and olefin carbonylation to yield esters of carboxylic acids [6].

The purpose of the present work was to study the effect of solvents, water concentration, and added salts on the catalytic activity of $Ru_3(CO)_{12}$ and derived complexes in the carbonylation of propylene with carbon monoxide to form the methyl esters of fatty acids.

The catalytic activity of ruthenium carbonyl (RC) depends on the solvent (Table 1). In the presence of methyl cellosolve or THF only traces of carbonylation products are formed. The selectivity for methyl butyrate is maximum and close to 100% in methanol or a methanol—hexane mixture. In benzene, dimethyl ether and other compounds are formed. The solvent also affects the ratio of products of normal and iso structure; in DMFA it is 1.9, in hexane 1.5,

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TABLE 1. Effect of Solvent on Propylene Carbonylation in Presence of $Ru_3(CO)_{12}$ (180°C, 5 h, 2 ml CH_3OH, 0.4 ml H_2O, 5 ml solvent, C_3H_6 pressure 8 atm, CO 20 atm)

Solvent	Total yield of $C_3H_7COOCH_3$, moles/mole RC	n: iso ratio
Benzene	540	1,0
Hexane	370	1,5
Methanol	280	1,0
DMFA	10	1,9

and in benzene and methanol 1.0.

Substantial variations in the yield of carbonylation products and the ratio of isomeric products in various solvents point to the possibility of replacing carbonyl ligands by solvent molecules, and the consequent variation of both activity and selectivity of the catalytic complex.

In the absence of water, in highly purified solvents, $Ru_3(CO)_{12}$ is inactive (Table 2). As the water content of methanol–water mixture increases from 0 to 100%, the methyl butyrate yield increases, and reaches a maximum (830 moles/mole RC) at 28.5 vol.% water. The yield of the butyric acids also increases with the water content, reaching its maximum (520 moles/mole RC) at 80% water. In pure water the yield of acids is 480 moles/mole RC. The maximum yield of carbonylation products (1010 moles/mole RC) is reached at 32.5% water. With increasing water content the n:iso ratio in the products increases, both for the butyrate esters (from 1.0 to 2.5) and the butyric acids (1.7 to 2.5).

In the methanol–hexane–water system (see Table 2), in contrast to the methanol–water system, the methyl butyrate yield passes through a maximum (1110 moles/mole RC) at 46.2% water. The yield of carbonylation products also passes through a maximum (1780 moles/mole RC). This is evidently related to the fact that ruthenium carbonyl passes into the hexane, in which it is readily soluble, so that its concentration in the methanol–water layer is drastically reduced.

These experiments agree with the concept of intermediate formation of metal hydrocarbonyls during carbonylation. The hydrogen atoms for ruthenium hydrocarbonyl formation are apparently obtained from water by substitution [7, 8]. The absence of catalytic activity in abs. methanol confirms this supposition.

In connection with the acceleration of the reaction by the addition of salts to Group VIII catalysts [9–11], we studied the catalytic properties of $Ru_3(CO)_{12}$–MCl_n systems, where M is a metal of Groups I-III, VI, or VIII, and n = 1-6 (Table 3), in propylene carbonylation with carbon monoxide. Na, K, and Cu(I) chlorides increased the yield of carbonylation products to 410-490 moles/mole RC. The largest methyl butyrate yield was obtained with $Ru_3(CO)_{12}$–$CuCl_2$ (930 moles/mole RC). $MgCl_2$ and $SrCl_2$ had practically no effect, and $CaCl_2$ reduced the yield of carbonylation products.

$AlCl_3$ and $PrCl_3$ increased the activity of the system, while $LaCl_3$ and $DyCl_3$ reduced it. The maximum yield of methyl butyrates (1160 moles/mole RC) was obtained with $Ru_3(CO)_{12}$–$MoCl_5$. Addition of $FeCl_3$ reduced the yield of butyrate esters, evidently due to partial decomposition of $Ru_3(CO)_{12}$ to metallic Ru.

The effect of the metal chloride additives is evidently the result of their reaction with $Ru_3(CO)_{12}$, as confirmed by UV spectroscopic data for the model system of acetone containing 30 vol.% water. A solution of $Ru_3(CO)_{12}$ in this medium has an absorption maximum in the 333 nm region that is stable in an Ar atmosphere. When aqueous MCl_n is added, another absorption maximum appears, which is evidence of a reaction between MCl_n and $Ru_3(CO)_{12}$ (Table 4). The maxima of the absorption bands that form when equimolar amounts interact are independent of the nature of the added cation. This may be due to replacement of one or several (for different added salts, the same amount of one molar ratio) coordinated CO molecules by

TABLE 2. Effect of Water Concentration on Propylene Carbonylation in the Presence of $Ru_3(CO)_{12}$ (180°C, 5 h, C_3H_6 pressure 8 atm, CO 20 atm)

Water content, vol.%	Total yield of $C_3H_7COOCH_3$, moles/mole RC	n: iso ratio	Total yield of C_3H_7COOH, moles/mole RC	n: iso ratio	Total yield of carbonylation products, moles/mole RC
		CH_3OH-H_2O *			
0	0	–	0	–	0
2,0	140	1,0	0	–	140
9,1	260	1,0	Traces	–	260
21,7	540	1,1	55	1,7	595
28,5	830	0,9	130	1,0	960
32,5	710	1,1	300	5,6	1010
44,4	540	2,1	90	2,1	630
61,5	390	2,0	–	–	390
80,0	30	2,4	520	2,5	550
100,0	0	–	480	2,3	480
		$CH_3OH-n-C_6H_{14}-H_2O$ †			
0	0	–	0	–	0
5,4	250	1,0	0	–	250
12,5	340	1,5	Traces	–	340
22,2	320	2,5	310	5,9	630
46,2	1110	2,0	670	2,3	1780
53,3	40	1,2	260	1,5	300
66,7	20	3,5	580	2,5	600
100,0	0	–	60	1,1	60

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*CH_3OH 10 ml.

†$CH_3OH:n-C_6H_{14}$ = 8:1.

TABLE 3. Effect of Salts Added to $Ru_3(CO)_{12}$ on Propylene Carbonylation (180°C, 5 h, 10 ml CH_3OH, 1.1 ml H_2O, C_3H_6 pressure 8 atm, $3.1 \cdot 10^{-6}$ mole $Ru_3(CO)_{12}$, ∿2 mg MCl_n)

Group of periodic table	MCl_n	Total yield of $C_3H_7COOCH_3$, mole/mole RC	n: iso ratio	Group of periodic table	MCl_n	Total yield of $C_3H_7COOCH_3$, mole/mole RC	n: iso ratio
–	–	280	1,0	III	$AlCl_3$	490	0,9
I	NaCl	490	0,9		$LaCl_3$	210	0,8
	KCl	480	0,9		$PrCl_3$	670	1,0
	Cu_2Cl_2	410	0,8		$DyCl_3$	260	1,0
	$CuCl_2$	930	0,9	VI	$MoCl_5$	1160	0,9
II	$MgCl_2$	280	1,2	VIII	$FeCl_3$	70	0,7
	$CaCl_2$	140	1,0				
	$SrCl_2$	290	0,7				

TABLE 4. Absorption Maximum of Products of Reaction of Ruthenium Carbonyl Solution with Metal Chloride Solution

Added salt	ν, nm, at $MCl_n:Ru_3(CO)_{12}$ molar ratio				Added salt	ν, nm, at $MCl_n:Ru_3(CO)_{12}$ molar ratio			
	1:1	2:1	3:1	5:1		1:1	2:1	3:1	5:1
NaCl	395	430	–	–	$MgCl_2$	395	–	–	420
Cu_2Cl_2	395	440	430	430	$AlCl_3$	395	430	430	430
$CuCl_2$	395	430	430	430	$PrCl_3$	395	430	450–475	430

chloride ions to form $[Ru_3(CO)_{12-n}Cl_n]^n$, which is stabilized by the cation of the salt. Replacement of one or two CO is most probable, because at 1:1 molar ratio, the same absorption band is observed at 395 nm in all cases, and at 2:1 ratio and higher, at 430 nm. Evidently as the $MCl_n:Ru_3(CO)_{12}$ ratio increases, the replacement of Co by Cl^- goes further, so that disubstituted isomers of ruthenium carbonyl chloride are formed.

Such an interpretation of the spectra permits an explanation of the different activities of Ru catalysts with different degrees of stabilization of carbonylchloride anion by the metal cation, and different degrees of CO replacement by Cl^-.

EXPERIMENTAL

$Ru_3(CO)_{12}$ was obtained according to the procedure of [12] by carbonylation of $RuCl_3$. The latter was obtained by reduction of $Ru(OH)Cl_3$ in abs. ethanol in a current of dry HCl until the appearance of the dark red color that is typical of Ru(III) compounds.

The tests were carried out in a titanium autoclave of 80 cm^3 volume, into which were placed $3.1 \cdot 10^{-6}$ mole (1.8 to 2.2 mg) of ruthenium carbonyl, 5-10 ml of methanol, 0.4-10 ml of water, and 2-3 mg of the Group I-III, VI, or VIII metal salt. The autoclave was purged with propylene, then filled with the gases. It was agitated in a pendulum type rocker and was heated electrically. The liquid products were analyzed by GLC on an LKhM-8M chromatograph (column 5 m × 2 mm, 20% SE-30 on Chromosorb W 30-60 mesh, temperature 70°C for esters, 150°C foracids, flame-ionization detector, He carrier gas).

Spectra were obtained in a Specord UV-VIS UV spectrophotometer at ∿20°C in 0.1-2.0 cm quartz cuvets. The cuvets were filled both in an Ar atmosphere and in air; the $Ru_3(CO)_{12}$ and MCl_n solutions were mixed directly in the cuvet.

CONCLUSIONS

1. In the carbonylation of propylene with carbon monoxide in the presence of ruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, the solvent affects the yield and the isomeric composition of the product.

2. The addition of salts of Group I-III, VI, or VIII metals to $Ru_3(CO)_{12}$ affects the activity of the complex. The maximum yield of carbonylation products is obtained by adding $MoCl_5$.

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