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THE HOMOLOGATION OF METHANOL. THE MODIFICATION OF COBALT CATALYST BY DIPHOSPHINES

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Cobalt iodide modified by α,ω-bis(diphenylphosphino)alkane (PCnP; n=1-6) efficiently catalyzes the homologation of methanol to ethanol. The ethanol selectivity as high as 89% was achieved by using PC6P as the ligand.

Recently, the catalytic homologation of methanol to ethanol with syngas has been of interest to many workers.[1-4] The cobalt catalyzed reaction has produced ethanol in low yield, with acetaldehyde, acetic acid, methyl acetate, and propanol accompanied as major by-products.[1] In 1976, Slaugh proposed that the cobalt iodide catalyst modified by the tertiary phosphines such as tributylphosphine, 9-eicosyl-9-phosphabicyclo[4,2,1]nonane or 9-eicosyl-9-phosphabicyclo[3,3,1]nonane, can improve the selectivity of ethanol and its precursors.[3] Phosphorus ligands increased the ethanol selectivity and the catalyst stability. In this letter, we wish to describe the first example of the modification of cobalt iodide by diphosphines in the homologation of methanol; the ethanol selectivity up to 89% was achieved.

The typical reaction procedure is as follows: methanol (10 ml), benzene (20 ml), cobalt iodide (4 mmol), and α,ω-bis(diphenylphosphino)alkane (PCnP: n=1-6) (4-6 mmol) were placed in a 100 ml stainless steel autoclave with or without water. After purging air with nitrogen, carbon monoxide (60 kg/cm^2) and hydrogen (120 kg/cm^2) were pressurized at room temperature. The temperature was raised to 200°C within 20 min. After 2hr, the autoclave was cooled quickly with cold water to room temperature. The gas and liquid phases were analyzed by gas chromatography. Table shows some results.

The reaction was highly promoted by using diphosphine as the ligand of cobalt iodide. The chain length of diphosphine exhibited significant effects on the selectivities of ethanol and acetaldehyde. Excellent selectivity of ethanol, over 80%, was achieved by using the PCnP(n=1,4-6) ligands. High phosphorus/cobalt ratio improved the ethanol selectivity although the conversion was low. The best value of the ethanol selectivity was 89% in the case of PC6P. Acetaldehyde and its precursors were involved less than 6% in the products. On the other hand, the ethanol selectivity was low by using the PC2P and PC3P ligands. Particularly, acetaldehyde and its acetals, *i.e.*, 1-1-dimethoxyethane, and 1-ethoxy-1-methoxyethane, were the major products in the case of PC2P. Acetic acid and methyl acetate, the carbonylation products, were produced less than 2% except for PC2P. Propanol, the homologation product of ethanol, was found below 2%: the reactivity of ethanol was low under the present conditions. Methane was also observed in the gas phase, especially for the PCnP(n=1-3) ligands.

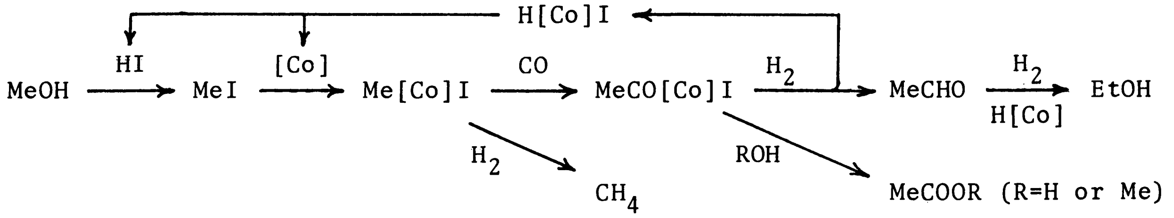
The addition of water increased the ethanol selectivity in the case of PC2P. However, little improvement was found by using diphosphines other than PC2P.

In the homologation of methanol, methyl iodide probably takes the roles of an

Table The Homologation of Methanol Catalyzed by Cobalt iodide-Diphosphine Complexes

No.	Phosphine (P/Co)[a]		H_2O (ml)	Conversion (%)[b]	Products Distribution (mol%)					Selectivity[c] (%)	
					EtOH	AcH + Acetals	AcOH + MeOAc	PrOH	Methane	EtOH	AcH
1	None	-	5	73.8	13.0	11.1	1.6	0.6	12.0	18.6	13.0
2	PC1P	3	5	44.9	77.5	5.2	0.6	1.8	10.1	80.9	5.4
3	PC2P	2	-	79.5	7.9	31.5	4.2	0.1	21.8	14.0	38.7
4	PC2P	2	5	70.4	30.5	10.7	2.4	0.5	22.4	34.5	11.4
5	PC2P	3	-	65.5	26.3	20.1	1.2	0.5	17.2	41.8	25.7
6	PC2P	3	5	64.9	50.3	14.9	1.9	1.0	14.2	58.4	16.3
7	PC3P	3	5	43.6	58.0	14.3	0.6	1.2	13.1	62.9	15.6
8	PC4P	2	5	39.5	76.3	4.8	0.6	1.9	7.8	80.5	5.0
9	PC4P	3	5	27.3	83.1	3.3	0.4	1.4	6.2	86.3	3.4
10	PC5P	2	5	45.0	74.8	5.3	0.6	2.3	7.5	80.1	5.6
11	PC5P	3	5	30.8	80.1	4.3	0.3	1.6	5.5	84.0	4.5
12	PC6P	2	5	38.6	77.7	4.8	0.5	2.0	8.3	83.7	5.0
13	PC6P	3	5	27.8	84.9	4.7	0.3	1.4	4.7	88.9	5.6
14	Ph_3P	2	5	48.4	69.7	7.1	1.6	0.6	8.4	76.7	7.6

a)Atomic ratio. b) Consumed methanol(mol)/charged methanol(mol)x100. c) One mole of 1,1-dimethoxyethane was regarded as 1 mole of acetaldehyde and 2 moles of methanol. The latter was calculated as the unreacted methanol in the homologation. Similar calculation was done for 1-ethoxy-1-methoxyethane and methyl acetate.



methylation species, which in turn readily reacts with the cobalt complex [Co] to give a methyl cobalt Me[Co]I. The insertion of carbon monoxide leads to an acetyl cobalt MeCO[Co]I, followed by hydrogenolysis to acetaldehyde.[5] Acetaldehyde is hydrogenated by a cobalt hydride to give ethanol as the ultimate product. The high yields of ethanol, acetaldehyde, and their precursors, compared with those of the carbonylation products, may be ascribed to the high reactivity of hydrogen of the acetyl cobalt, in contrast with the low reactivity of an acetyl rhodium.[2,6] The selectivities of ethanol and acetaldehyde on the chain length of the diphosphine ligand would be related with the hydrogenation capability of the cobalt hydride.

Further aspects of this catalysis are now under investigation.

References and Notes

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