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CATALYST AND SOLVENT EFFECTS ON THE SYNTHESIS OF ACETIC ACID FROM METHYL FORMATE

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Summary : Methyl formate can be catalytically converted to acetic acid in the presence of transition metal compounds under carbon monoxide pressure. The nature of the metal catalyst, the promoter and the solvent are determining. Palladium and cobalt compounds associated with lithium iodide are the most efficient catalysts provided that the reaction is carried out in N-methylpyrrolidone under an adequate CO pressure.

In the last years, several papers reported the transition metal catalyzed "isomerization" of methyl formate to acetic acid

$$HCOOCH_3 \longrightarrow CH_3COOH$$

The reaction occurred only under CO pressure and in the presence of a combination of a transition metal compound and an ionic (HgI_2,CoI_2) or a covalent iodide (CH_3I). The most active catalysts were rhodium[3] and iridium[4] , also leading to the highest selectivity into acetic acid. Though, at the present time, the methyl formate route to acetic acid is industrially not competitive with the rhodium-catalyzed carbonylation of methanol, it provides an industrial synthetic alternative in plants producing methyl formate as an undesirable by-product[3] . However, Rh and Ir catalysts are expensive. It is therefore of interest to use more accessible catalysts. The aim of this paper is to report the effect of the catalytic system and of the solvent in the synthesis of acetic acid from methyl formate.

A critical parameter in the isomerization reaction is the nature of the iodide used as promoter. In the rhodium-catalyzed reaction, Schreck and al. showed that the use of lithium iodide instead of methyl iodide greatly improved the selectivity into acetic acid, mainly by lowering or suppressing the formation of formic acid[3]. On the other hand, former studies carried out by Pruett[4] and Isogai[5] outlined the role played by the solvent.

In a first stage, we have used lithium iodide as the promoter and N-methylpyrrolidone (NMP) as a possible solvent. A catalyst screening was then made in order to compare the catalytic performances at two different CO pressures (Table).

The Table clearly indicates that, when the experiments are performed without NMP, the only efficient catalyst is rhodium. All other transition metal catalysts show extremely small activities. This is in accordance with earlier results obtained with CH_3I as promoter[1,6]. The reactivity sequence was found as :

$$Ir \simeq Rh > Ru > Pd > Co$$

Introduction of a solvent such as NMP in the medium modifies completely the reactivity. Palladium, nickel, cobalt and even iron catalysts show considerably enhanced activity for the production of acetic acid, while the catalytic activity of the rhodium compound is dramatically reduced. It should be noted that in the latter case the major product is acetaldehyde[7].

Under the conditions of the Table , the order of reactivity is :

$$Pd \gg Co \simeq Ni > Rh > Fe \quad \text{at 50 bar}$$

$$Pd > Co \gg Ni > Fe > Ru \quad \text{at 150 bar}$$

As can be observed, the effect of the CO pressure is not negligible. The cobalt catalyst is noticeably promoted by an increase in pressure, whereas the activity of the palladium and nickel catalysts is apparently independent of pressure. The same applies to the iron catalyst : however its activity remains low at any pressure. Finally ruthenium and platinum catalysts are not suitable for the isomerization reaction. The ruthenium results are in conflict with those previously reported[8], though the conditions were different (use of $CO+H_2$ mixtures).

The selectivity data show large differences depending on whether the reaction is carried out in NMP or not. A high selectivity for acetic acid is related with a high turnover. Rhodium displays the highest selectivity (98%), however only when no NMP is used. In the presence of NMP, the runs carried out with cobalt at 150 bar and palladium at 50 bar also lead to excellent selectivity results (92-93%).

Isomerization of methyl formate. Effect of the transition metal catalyst on formate conversion C, on selectivity S for acetic acid formation, on turnover frequency TF[a] .

Catalyst	CO (50 bar)						CO (150 bar)					
	no solvent			NMP			no solvent			NMP		
	C	S	TF	C	S	TF	C	S	TF	C	S	TF
$RhCl_3.xH_2O$	99	98	252	17	23	10	no	run		no	run	
$Pd(OAc)_2$	23	6	3	100	92	249	no	run		93	93	233
$Co(OAc)_2.4H_2O$	0	-	0	36	38	20	6	19	1.7	97	91	128
$Ni(acac)_2$	19	11	1.5	65	36	18	no	run		74	33	19
$Fe(acac)_3$	10	26	1.3	25	46	6	no	run		32	23	4
$PtCl_2$	10	13	1	0	-	0	0	-	0	0	-	0
$RuCl_3.xH_2O$	0	-	0	0	-	0	0	-	0	12[b]	9	1.5

[a] Methyl formate (40.5 mmol), catalyst (0.26 mmol), LiI (3 mmol), NMP (2.5 ml), T(175°C), t(0.5-3h depending on catalyst) C and S are given in %, TF is given in mol acetic acid/mol catalyst/h

[b] CO (250 bar)

The main by-product is methyl acetate, the only product together with acetic acid in the aforementioned runs. In the absence of NMP, dimethyl ether, methanol and mostly formic acid are also produced. A selectivity of nearly 100% can be reached at sufficiently long reaction times, either with cobalt or palladium catalysts : in the presence of $Co(OAc)_2.4H_2O$ and NMP at 150 bar, acetic acid is formed in 99% yield after 3 h reaction. This implies that the methyl acetate by-product is also converted to acetic acid during the reaction. A two-hour run carried out in the same conditions but with methyl acetate as substrate shows that 63% of the ester is converted with 100% selectivity to acetic acid. We shall report on mechanistic details in a forthcoming paper.

In conclusion, the catalytic conversion of methyl formate into acetic acid can be efficiently effected in the presence of metal transition catalysts like palladium and cobalt providing that the reaction is carried out in a solvent like N-methylpyrrolidone and with lithium iodide as promoter. For some metal catalysts, there is the need of a higher CO pressure, palladium is active at any pressure whereas cobalt is a good catalyst only under 150 bar. Our data obtained with cobalt and palladium catalysts are among the bests and are approaching those shown for rhodium compounds.

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