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CATALYST EFFECT ON THE SYNTHESIS OF ETHYL ACETATE VIA REDUCTIVE CARBONYLATION OF METHYL ACETATE

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The effect of several catalysts and binary catalyst mixtures is examined in the formation of ethyl acetate from methyl acetate in presence of CO-H_2. The most effective catalytic system is a combination of ruthenium-cobalt compounds. The optimum conversion and selectivity to ethyl acetate is achieved with an atomic ratio Co/Ru = 0.4.

The homologation of methanol has been thoroughly investigated[1] and is continuing to gain high interest[2] due to its evident basic source for a wide range of chemicals. Carbonylation-homologation reactions of other simple oxygenated substrates are also highly worthy to study. Braca and al.[3] were interested in the homologation of methyl acetate (MeAc) in presence of ruthenium catalysts, but observed rather low turnover rates. Recent articles[4] described the homologation of MeAc into ethyl acetate (EtAc) or methanol[5] with Ru-Co catalysts. The present note reports shortly the results of preliminary experiments on the catalyst effect on the reductive carbonylation of MeAc :

$$CH_3COOCH_3 + 2H_2 + CO \longrightarrow CH_3COOC_2H_5 + H_2O$$

The reaction is supposed to proceed via formation of intermediate ethanol with subsequent esterification with acetic acid produced in the reaction.[3]

The given table summarizes the results of the catalyst influence.

- Ruthenium catalysts show low activity, among them the bests seem to be Ru(acac)$_3$ and RuO_2. It is rather surprising that $Ru_3(CO)_{12}$ is only weakly active, since it was shown[6] that Ru(acac)$_3$ in presence of CO and H_2 is a precursor of $Ru_3(CO)_{12}$. The non soluble catalyst RuO_2 has nearly the same activity as Ru(acac)$_3$ producing comparable turnovers (AcEt and AcOH), the only difference is that large amounts of water are formed in the heterogeneous catalysis. This behavior is suggestive of a common active species despite the different nature of catalysis.

- As ruthenium catalysts do not seem very appropriate, we examined carbonylation catalysts (cobalt and rhodium). As expected, cobalt acetate promotes the

Reductive carbonylation of methyl acetate (a)
Turnover rates (b)

Catalyst	P(c)	Liquid Phase (d) (f)					Gaseous Phase	
		AcH	MeOH	EtOH	EtAc	AcOH	CH_4	CO_2
$Ru(acac)_3$ (d)	32	0	6.5	1.8	8.4	15.3	5.0	0.7
$RuCl_3$, $3H_2O$	21	0	5.8	1.7	4.2	8.5	0	0
RuO_2	30	0	4.7	1.7	7.4	15.5	2.5	0.8
$Ru_3(CO)_{12}$	25	0	1.7	0.5	1.9	4.5	4.0	0.4
$Coac_2$, 4 H_2O	75	23.8	3.7	1.1	10.1	90.4	5.5	0
$RhCl_3$, $3H_2O$	35	1.5	0.9	0	0.9	0	1.5	0
$Rhac_2$	33	4.4	0	0	14.1	40.4	2.8	0
(e) $Coac_2$, $4H_2O/Ru(acac)_3$	127	0.5 (1.0)	8.7 (17.3)	11.8 (23.5)	37.6 (75.2)	41.0 (81.8)	7.7	1.2
$/Ni(acac)_2$	23	(g)	1.4 (2.7)	0	1.2 (2.3)	23.7 (47.4)	2.8	0
$/Fe(acac)_3$	21	(g)	2.0 (4.0)	0	0.4 (0.9)	8.2 (16.4)	1.5	0
$/Pd(acac)_2$	30	(g)	1.3 (2.6)	0	1.0 (2.0)	28.1 (56)	2.3	0
$/H_2PtCl_6$, $6H_2O$	28	(g)	0.8 (1.6)	0	1.4 (2.7)	54.5 (109)	5.0	0
(e) $Rhac_2/Ru(acac)_3$	35	0	4.7	1.4	8.8	17.2	11.3	1.4
$/Coac_2$, $4H_2O$	68	6.1	8.3	1.7	17.7	48.8	13.0	0
(e) $Coac_2$, $4H_2O/Ru(acac)_3$	127	0.5 (1.0)	8.7 (17.3)	11.8 (23.5)	37.6 (75.2)	41.0 (82.0)	7.7	1.2
$/RuO_2$	86	0	8.6 (17.1)	6.5 (13)	32.6 (65.3)	46.4 (92.7)	12.0	0.4
$/Ru_3(CO)_{12}$	91	0	7.0 (14)	6.9 (14)	32.3 (64.6)	44.4 (88.7)	21.0	1.5
$Co_2(CO)_8/Ru_3(CO)_{12}$	93	(g)	7.0 (14)	5.8 (11.9)	35.0 (70.0)	43.2 (86.4)	23.0	1.3

(a) General conditions : catalyst (7.5×10^{-5} at-g of metal), promotor (LiI : 7.5×10^{-2} m/l) MeAc (5 ml), CO/H_2 (1/2), P (280 bar), T (200°C), reaction time (5 h) (ref. 7 for details of GC analysis).

(b) Number of moles of product formed per hour per 1 at-g of metal of catalyst.

(c) P : pressure drop in 5 hours (at 25°C).

(d) acac (acetylacetonato), ac (acetate), AcH (acetaldehyde), MeOH (methanol), EtOH (ethanol), AcOH (acetic acid).

(e) Atomic ratio metal 1/metal 2 = 1.02. Total concentration : 7.5×10^{-5} at-g of metal.

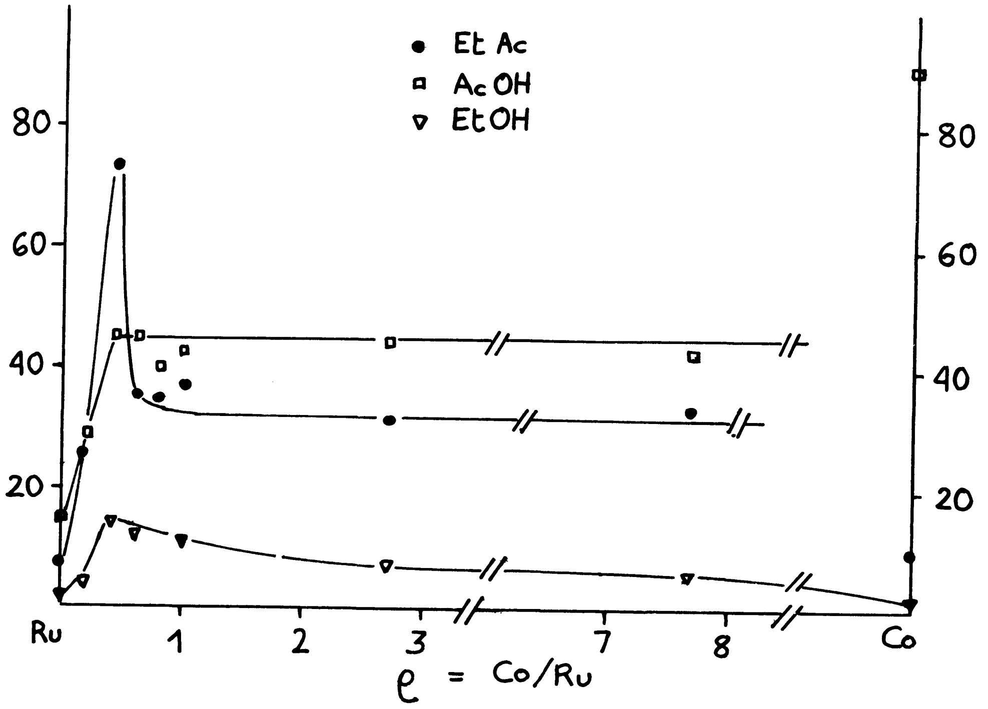
(f) The numbers in parentheses refer to the turnover for 1 at-g of Co.

(g) In GC conditions, AcH and MeOH have very close retention times, so that AcH may be hidden by the MeOH peak if the latter is produced in substantial amount.

production of acetic acid increasing the corresponding turnover by a factor of 6, however the turnover relative to the formation of EtAc is only slightly increased. The most interesting observation is the production of AcH in significant amounts. If Braca's reaction scheme is correct[3)], we should increase the conversion to EtAc by hydrogenation of AcH to EtOH followed by esterification.

- The puzzling behaviour of rhodium catalysts is examplified by the fact that only $Rhac_2$ leads to appreciable formation of EtAc and AcOH.

- To achieve reductive carbonylation, we were therefore prompted to use binary mixtures of catalysts (acting respectively as carbonylation and hydrogenation catalysts). Visibly Ni, Fe, Pd, Pt cocatalysts have weak or no catalytic activity. However combination of $Ru(acac)_3$ with $Coac_2$ hydrated increases noticeably the overall conversion as well as selectivity to EtAc. Ruthenium-rhodium or cobalt-rhodium catalyst mixtures are less active.



Effect of Co-Ru catalyst composition on the homologation of methyl acetate.

- We examined therefore the cobalt-ruthenium system. The importance of catalyst composition is illustrated in the figure. It may be noted that maximum yields of AcEt and EtOH are achieved with an atomic ratio (Co/Ru) ϱ of about 0.4. For the same ratio there is also a maximum in syngas conversion though for higher ρ-values (> 1), the gas conversion is hardly modified. Over a wide range of ρ-values (1 to about 8), there is no variation in selectivities. Visibly acetaldehyde produced with $CoAc_2$ hydr. is more or less reduced to EtOH depending on the Ru charge (from a ρ-value of 8, the reduction of AcH is decreased). The subsequent esterification decreases the amount of AcOH.

Finally it should be pointed out that the water gas shift reaction is relatively unimportant, carbon dioxide is identified only as a minor by-product. Methane is produced in low quantity, this can be taken as proof of the homogeneous nature of the catalysis. Ethane is practically non existent.

The influence of other parameters susceptible to optimize syngas conversion and selectivity to EtAc is currently under investigation. Full experimental details will be given in a forthcoming article.

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7) The GC analyses were performed on Hewlett-Packard 5700 gas chromatograph with catharometer detection. Columns of Porapak R (4 m, inox, 1/8", 80-100 mesh, 60-230°C, 4°C/mn) for liquid products and Chromosorb 102 (2 m, inox, 1/8", 80-100 mesh, 60-230°C, 8°C/mn) for gases were used. Peak areas were converted to millimoles using experimental calibration curves and isoamylalcohol as an internal standard.

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