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OLEFIN HYDROFORMYLATION AND SELECTIVE HYDROGENATION OF ACETALDEHYDE ON Mo-PROMOTED Rh/SiO_2 CATALYSTS DERIVED FROM METAL SALT AND HETERONUCLEAR CLUSTER PRECURSORS

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Molybdenum promoted Rh/SiO_2 catalysts have been prepared by using the heteronuclear cluster $(C_5H_5)_3RhMo_2(CO)_5$ as well as metal salt precursors. The promoting effect of molybdenum has been studied for the hydroformylation of ethene and propene and the hydrogenation of acetaldehyde. It has been found that molybdenum, especially on the cluster-derived catalyst, increases both the hydrogenation and the hydroformylation rate of the olefins. No specific influence on the CO insertion reaction could be obtained. As an explanation, the promotion of the initial step to form intermediate surface alkyl groups has been proposed as the rate determining step for ethene hydroformylation. The promotion of the alcohol formation by bimetallic centers having Rh and Mo in close vicinity has been supported by the results of the hydrogenation of acetaldehyde.

Keywords: Supported Mo-promoted Rh-catalysts, heteronuclear clusters, olefin hydroformylation, acetaldehyde hydrogenation

1. Introduction

Recently, it has been demonstrated, that the catalytic properties of supported rhodium in CO hydrogenation are significantly altered in the presence of molybdenum as a promoter [1–8]. In dependence on the catalyst preparation, the promoted catalysts exhibit an increased activity and/or additionally an improved selectivity toward oxygenated products such as alcohols and aldehydes. It is still a challenging subject of research to clarify the specific role of electropositive transition metal ions like Fe^{3+}, Zr^{4+}, and Mn^{2+} [9] in promoting especially the formation of oxygen containing compounds on supported rhodium catalysts. The promoter can affect different elementary steps in the overall reaction scheme for hydrogenation of carbon monoxide [10], such as CO dissociation, CO insertion into a surface metal-alkyl bond or hydrogenation of surface intermediates. The hydroformylation of olefins, which passes through a CO-insertion step, has been used as a catalytic probe reaction to test the insertion ability of metal catalysts [11–21]. A high C_3-oxygenate selectivity in case of ethene is assumed to be related with favoured C_2-oxygenate formation in CO hydrogenation reaction. On Ni/SiO_2, however, the situation seems to be reverse [20]. An increasing number of active sites for ethene conversion to propanal has been found not to be accompanied with an improved C_2-oxygenate selectivity in CO hydrogenation.

We report here about results in vapour-phase ethene and propene hydroformylation as well as acetaldehyde hydrogenation experiments on Rh/SiO_2 and $RhMo/SiO_2$ catalysts, prepared by carbonyl cluster deposition and conventional methods.

2. Experimental

$Rh_4(CO)_{12}$ and the heteronuclear carbonyl cluster $(C_5H_5)_3RhMo_2(CO)_5$ [22] were used as precursors for cluster derived catalysts. The clusters were deposited on the support (silica-gel GR-10301, Fuji-Davison, mesh 20 to 12) from CH_2Cl_2-solution. After removing the solvent in vacuum at room temperature, the supported clusters were oxidized (O_2, flow rate 60 ml min^{-1}) for two hours at 373 K. The bimetallic salt derived catalysts were prepared by impregnation of SiO_2 with an ethanolic solution of $RhCl_3$ and $MoCl_5$ or an aqueous solution of $RhCl_3$ and $(NH_4)_6Mo_7O_{24}$, respectively. The solvents were removed in vacuum at 313 K. Then, the catalyst, derived from aqueous solution was supplementary dried in air at 393 K for eight hours.

All samples contain 2 wt% rhodium and were reduced in hydrogen (flow rate 60 ml min^{-1}), raising the temperature stepwise to 673 K and keeping this temperature for two hours. According to TEM measurements the metal particle size is not influenced significantly by the addition of molybdenum. The vapour-phase hydroformylation reaction was carried out in a flow-mode Pyrex glass reactor with a mixture of C_2H_4 (C_3H_6), CO and H_2, each at 20 ml min^{-1}, at the total pressure of 0.1 MPa and 393–473 K. For actetaldehyde hydrogenation at 415–493 K and 0.1 M Pa the same reactor was used. Hydrogen or synthesis gas ($n_{CO} : n_{H_2} = 1:1$) were saturated with CH_3CHO at 241 K (15 mol% CH_3CHO, flow rate 30 ml min^{-1}). The oxygenated products were collected by bubbling the effluent gas through a water trap (50 ml). The analyses of the solutions were conducted by FID gas chromatography with a Chromosorb 101 column (4 m) at 423 K for ethene hydroformylation and acetaldehyde hydrogenation products and 428 K for propene hydroformylation products, respectively. The gas analyses were performed by TCD gas chromatography with a Porapak Q column (4 m) at 343 K for C_2H_4/C_2H_6, an Al_2O_3/DMF column (4 m) at 298 K for C_3H_6/C_3H_8 and an active carbon column (2 m) at 298 K for CH_4.

Activities and selectivities were measured one hour or more after exposure to the gas mixture, when the catalyst reached a stationary state. The hydroformylation activity was maintained over 20 hours, the duration of a standard experiment.

3. Results and discussion

The specific rates of formation in ethene hydroformylation at 419 K are summarized in fig. 1. Rhodium on silica is moderately active and produces ethane and propanal in a molar ratio of 3 : 1. A sample, which contains exclusively molybdenum on silica, is completely inactive for C_2H_4-conversion under comparable reaction conditions. In contrast to that, the bimetallic cluster-derived catalyst $(C_5H_5)_3RhMo_2(CO)_5/SiO_2$ shows an unusual high overall activity. The apparent activation energies for hydrogenation as well as for hydroformylation are lowered in the presence of the promoter by 16 kJ mol^{-1} to 52 kJ mol^{-1} and 30 kJ mol^{-1}, respectively. In table 1 the selectivities, evaluated at an ethene conversion of 3 mol%, are compared. Since the hydrogenation rate as well as the hydroformylation rates are enhanced by molybdenum to the same extent, the total selectivity for oxygenates is not affected. On the other hand, molybdenum

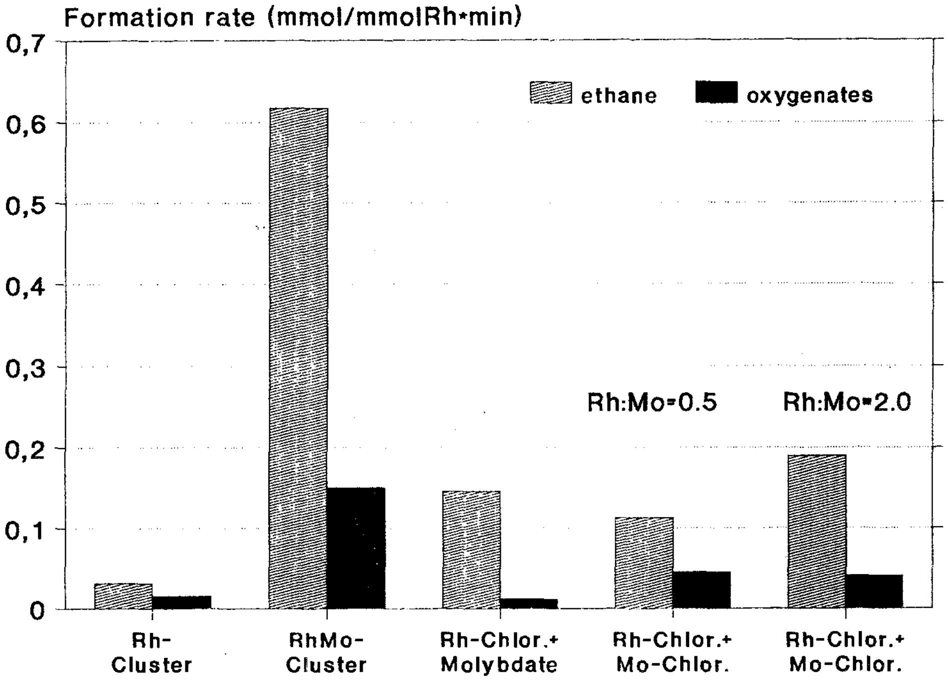


Fig. 1. C_2H_4 hydroformylation on $Rh_4(CO)_{12}/SiO_2$, $(C_5H_5)_3RhMo_2(CO)_5/SiO_2$, $RhCl_3 + (NH_4)_6Mo_7O_{24}/SiO_2$ and $RhCl_3 + MoCl_5/SiO_2$ ($n_{Rh} : n_{Mo} = 0.5$; 2.0) at $T = 419$ K, $p = 0.1$ MPa, flow rate = 60 ml min^{-1} and $C_2H_4 : CO : H_2 = 1 : 1 : 1$.

Table 1
Selectivities (mol%) in olefin hydroformylation

Precursor/SiO_2	$\frac{n_{Rh}}{n_{Mo}}$	C_2H_4 hydroformylation[a]		C_3H_6 hydroformylation[b]	
		oxygenates	C_3H_7OH	oxygenates	n-isomers
$Rh_4(CO)_{12}$	–	27	0	11	82
$Cp_3RhMo_2(CO)_5$	0.5	24	54	11	80
$RhCl_3$ + $(NH_4)_6Mo_7O_{24}$	0.5	7	74	2	(100)
$RhCl_3$ + $MoCl_5$	0.5	25	69	10	70
$RhCl_3$ + $MoCl_5$	2.0	17	58	–	–

[a] C_2H_4-conversion = 3 mol%.
[b] C_3H_6-conversion = 1 mol%.

has an influence on the composition of the oxygenated products. Whereas the aldehyde is formed on Rh/SiO_2, in the presence of the second metal, the corresponding alcohol is the dominating oxygen containing compound in the product mixture.

It is remarkable that the catalytic performance of the promoted catalysts strongly depends on the catalyst precursors: $RhCl_3/MoCl_5/SiO_2$ is less active than $(C_5H_5)_3RhMo_2(CO)_5/SiO_2$, but the oxygenate selectivity remains constant. This suggests that both cluster and salt derived catalysts have the same active sites for hydrogenation and hydroformylation of olefins.

Ammoniumparamolybdate is less suitable as Mo-precursor for the preparation of promoted hydroformylation catalysts. In comparision to $RhCl_3/MoCl_5/SiO_2$ the sample shows a similar ethene conversion. This is, however, due to an increased ethane, but decreased oxygenate formation. As a consequence, the oxygenate selectivity is significantly reduced. The molybdenum content has only a minor influence on activity and selectivity. With increasing molar ratio n_{Rh}/n_{Mo} the hydrogenation rate slightly increases and the selectivity to oxygenates decreases.

In summary, no specific promotion of molybdenum towards oxygenates based on the carbon monoxide insertion reaction could be observed on the RhMo-catalysts. On the contrary, this element may favour the hydrogenation of CH_x– as well as oxygen containing intermediates, adsorbed on the catalyst surface.

These results are also supported by activity and selectivity data, obtained in propene hydroformylation. This reaction requires higher temperatures. In fig. 2 specific rates of formation of propane and the oxygenates butanal, 2-methylpropanal, 1-butanol and 2-methylpropanol at a reaction temperature of 455 K are compared. The enhanced hydrogenation capacity of promoted catalysts is reflected in increased specific formation rates of hydrogenation and hydroformylation products. But neither oxo-selectivities nor regio-selectivities are shifted by adding molybdenum to Rh/SiO_2 (table 1). The n-isomer selectivity reaches about

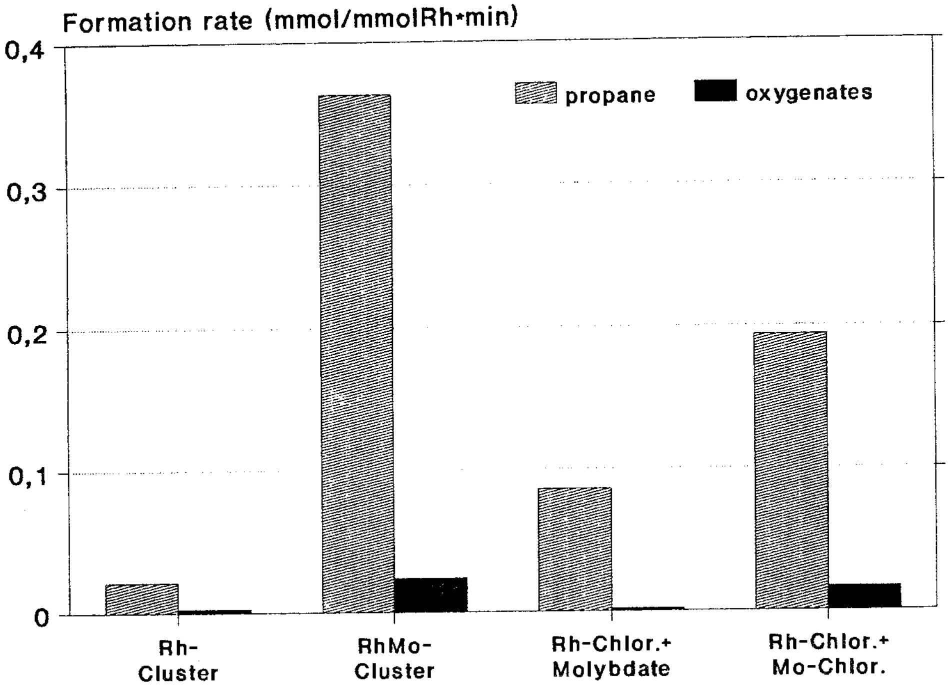
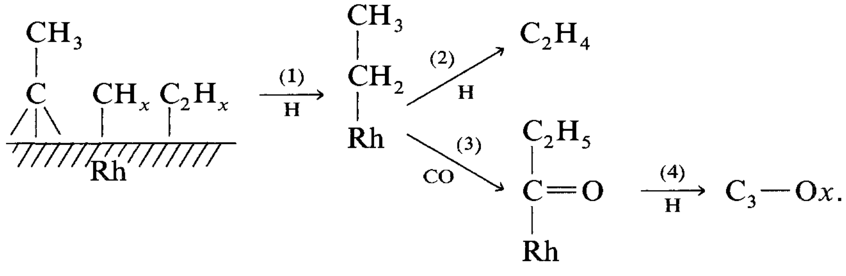


Fig. 2. C_3H_6 hydroformylation on $Rh_4(CO)_{12}/SiO_2$ $(C_5H_5)_3RhMo_2(CO)_5/SiO_2$, $RhCl_3 + (NH_4)_6Mo_7O_{24}/SiO_2$ and $RhCl_3 + MoCl_5/SiO_2$ ($n_{Rh} : n_{Mo} = 0.5$) at $T = 455$ K, $p = 0.1$ MPa, flow rate = 60 ml min^{-1} and $C_3H_6 : CO : H_2 = 1 : 1 : 1$.

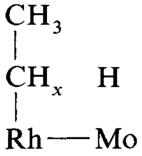
80%. While butanal and 2-methylpropanal are the most important oxygenated compounds on $Rh_4(CO)_{12}/SiO_2$, on $(C_5H_5)_3RhMo_2(CO)_5/SiO_2$ mainly alcohols are formed. The precursor dependence is similar to that obtained in ethene hydroformylation.

To summarize the results of olefin hydroformylation, molybdenum appears to have no influence on migratory insertion, but increases the hydrogenation ability of supported rhodium. The function of molybdenum can be understood in terms of accelerating the hydrogenation steps in the hydroformylation as well as in the hydrogenation pathways of ethene (step 1, 2 or 4 in scheme 1). Under reaction conditions, the rhodium surface is covered with partially dehydrogenated carbon



Scheme 1

containing intermediates, formed by irreversible ethene chemisorption. At temperatures between 393 K and 453 K, as used in the present experiments, ethylidyne species are supposed to be present together with further dehydrogenated CH_x- and C_2H_x-fragments [23]. These species represent the starting point for the formation of rhodium ethyl groups by hydrogenation (step 1), which are the initial intermediates for both alkane formation and hydroformylation. The subsequent hydrogenation of $Rh\text{–}C_2H_5$ leads to ethane formation (step 2). Acyl-species, alternatively formed by carbon monoxide insertion into a rhodium alkyl bond (step 3), are converted to C_3-oxygenates likewise by hydrogenation (step 4). From our results an effect of Mo on step 3 can be excluded. It seems unlikely that the hydrogenation of oxygen-free and oxygen-containing intermediates, like $-C_2H_5$ and $-COC_2H_5$, are promoted by molybdenum in the same manner. The similar decrease in apparent activation energies of ethane as well as of oxygenate formation, caused by molybdenum promotion, is a striking argument, which support the idea that the hydrogenation of carbonaceous surface intermediates (step 1) might be rate determining and specifically influenced by the promoter. As already suggested by Bhore et al. [5], activated hydrogen is probably provided by molybdenum sites, forming a surface species like



$$\begin{array}{ll} CH_3 & \\ | & \\ CH_x & H \\ | & \\ Rh & \!\!\!\text{——}\, Mo \end{array}$$

In case of bimetallic cluster deposition a close contact between the metallic components is ensured and, consequently, an unusual high catalytic activity has been obtained.

To prove the idea of an enhanced hydrogenation ability by surface centers having Rh and Mo in a close vicinity, the hydrogenation of acetaldehyde has

Table 2
Specific formation rates r ($mmol\,mmol_{Rh}^{-1}s^{-1} \times 10^{-3}$) and selectivities S (mol%) in acetaldehyde hydrogenation[a]

Precursor/SiO_2	CH_3CHO+H_2			CH_3CHO+H_2+CO		
	r		S	r		S
	CH_4	C_2H_5OH	C_2H_5OH	CH_4	C_2H_5OH	C_2H_5OH
$Rh_4(CO)_{12}$	23	7	20	1.5	0.2	13
$Cp_3RhMo_2(CO)_5$	11	378	95	1	210	98
$RhCl_3+MoCl_5$	26	530	90	0	392	99

[a] Reaction conditions:
$T = 436K$ (CH_3CHO+H_2),
$T = 473K$ (CH_3CHO+H_2+CO),
$p = 0.1$ MPa, flow rate 30 ml min^{-1},
15 mol% CH_3CHO,
by-products: CH_3COCH_3, $CH_3COCOCH_3$.

been performed on the same catalysts. Acetaldehyde can be selectively converted to ethanol or decarbonylated by C–C– bond splitting. The latter reaction requires an ensemble of rhodium atoms, whereas the ensemble is not expected to be necessary in the acetaldehyde hydrogenation. The results are shown in table 2. The C–C– bond splitting is significantly suppressed by the addition of the promoter, whereas the hydrogenation is promoted by more than one order of magnitude. A similar effect of the promoter was obtained for Rh/SiO_2 by adding CO to the feed mixture. Strongly adsorbed carbon monoxide molecules are responsible for the effective suppression of the decarbonylation of acetaldehyde at 436 K by blocking rhodium ensembles active for C–C– bond splitting. Small amounts of methane are formed by increasing the temperature to 473 K. On $RhMo/SiO_2$ the influence of carbon monoxide is less dramatical, which also points to hydrogenation sites located on molybdenum oxide, resulting in the substantial promotion of alcohol formation (98–99% selectivity).

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