

Catalytic activity of ruthenium 2,2'-bipyridine derived catalysts in 1-hexene hydroformylation and 1-heptanal hydrogenation

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Abstract

Method and conditions of preparation strongly affect the hydroformylation activity of the ruthenium cluster derived $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst. The highest activities have been achieved with a dichloromethane impregnated catalyst. A major problem with this catalyst is poor reproducibility of the hydroformylation activity, probably due to uncontrolled formation of several supported surface species. Reproducibility can be improved by using a non-chlorinated impregnation solvent such as tetrahydrofuran. In hydroformylation, $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 has a strong tendency to convert alkenes directly to alcohols. The limiting step in this process is the initial hydrocarbonylation of alkenes to aldehydes. $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyzes the second step, hydrogenation of aldehydes to alcohols, in good yield. Use of an effective, aldehyde-producing cocatalyst such as Rh together with $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 allows very high alcohol yields to be achieved. The detailed surface structure of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 is not known, but one probable active species is oligomeric or polymeric $[\{\text{Ru}(\text{bpy})(\text{CO})_2\}_n]$. Monomeric and dimeric ruthenium monobipyridines showed at most only moderate activity in hydroformylation. By contrast, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ are highly active in hydrogenation of C_7 aldehydes to C_7 alcohols.

Keywords: Bipyridine; Carbonyl complexes; Heptanol; Hexene; Hydroformylation; Hydrogenation; Ruthenium; Supported catalysts

1. Introduction

$\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 is active in the hydroformylation of alkenes [1,2] and in the water gas shift reaction [3–5]. In hydroformylation it favors the direct formation of alcohols and isomerization of linear alkenes, demonstrating its good hydrogen transfer properties. The catalytic behavior of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 varies markedly with the method of preparation. The highest activities have been obtained by impregnating $\text{Ru}_3(\text{CO})_{12}$ and 2,2'-bipyridine

onto SiO_2 from dichloromethane, but reproducibility of the catalyst is then relatively poor [1,2]. Reproducibility can be improved by using a more easily controllable method of preparation, such as an ALE (atomic layer epitaxy)-related gas phase method [6] or pulse impregnation from THF [7], which suggest the significant solvent effect in the catalyst preparation. In this work we studied the effect of impregnation solvent on the activity of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 in hydroformylation and in 1-heptanal hydrogenation to 1-heptanol. Monomeric and dimeric ruthenium bipyridine compounds were investigated as pos-

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sible model compounds for $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 .

2. Experimental

$\text{Ru}_3(\text{CO})_{12}$ was obtained from Johnson Matthey or prepared by a literature method [8]. 2,2'-Bipyridine was purchased from Aldrich Chemicals, while $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ and $\text{Rh}/\text{Al}_2\text{O}_3$ (5 wt% Rh) were from Johnson Matthey. The synthesis of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$, $[\text{Ru}_2(\text{bpy})_2\text{Cl}_3\text{N}(\text{H}_2\text{O})]$ (Fig. 1)

and $[\text{Ru}_3(\text{bpy})(\text{CO})_{10}]$ has been described elsewhere [9–11].

Catalysts supported on silica (silica gel 60; Merck, surface area $500 \text{ m}^2/\text{g}$, specific pore volume 0.8 ml/g , $\text{Ø} 0.063\text{--}0.200 \text{ mm}$ or silica F-22; Akzo Chemie, surface area $400 \text{ m}^2/\text{g}$, $\text{Ø} 0.074\text{--}0.179 \text{ mm}$, calcinated at 600°C for 24 h) were prepared by impregnation from an organic solvent (dichloromethane, tetrahydrofuran (THF), or methanol) with subsequent thermal treatment for 14–24 h at 100°C . In the case of poorly soluble compounds such as $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$, the precursor was mixed with the silica support in an organic solvent for 14–24 h. Metal loading of the supported catalysts varied between 1.2 and 1.9

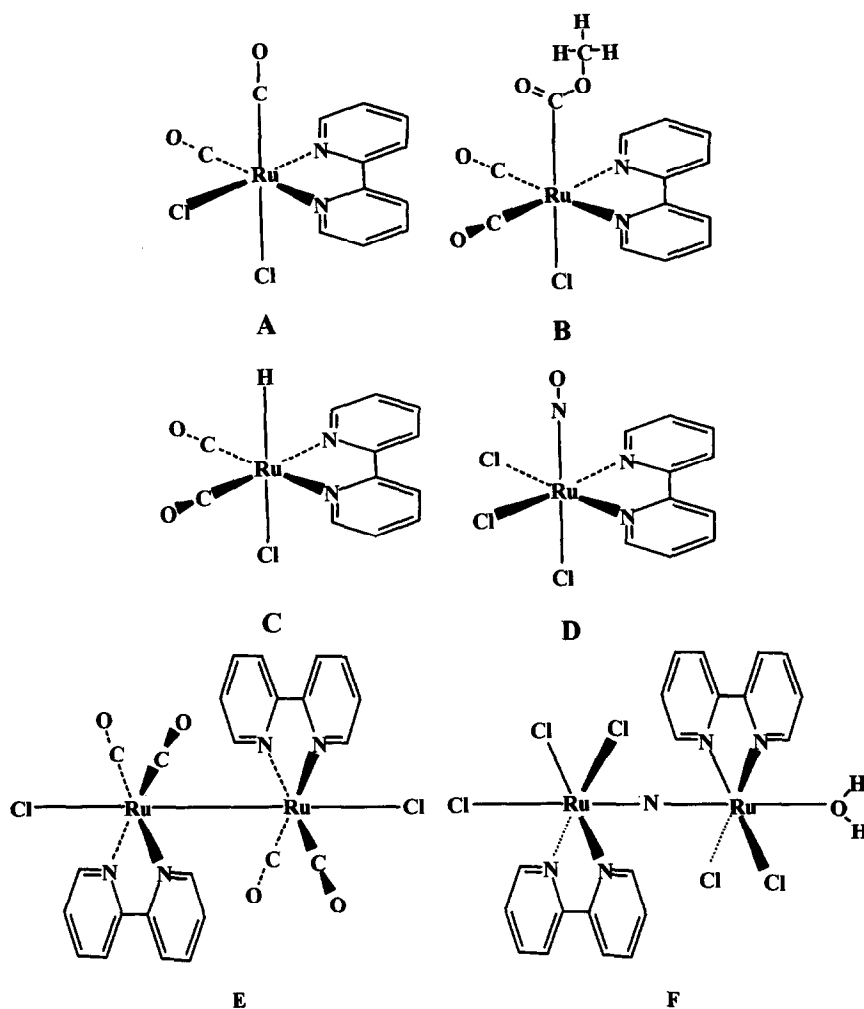


Fig. 1. Schematic structures of (A) *cis*-carbonyl-*cis*-chloro- $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, (B) $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, (C) $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, (D) *fac*-chloro- $[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$, (E) $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$, and (F) $[\text{Ru}_2(\text{bpy})_2\text{Cl}_3\text{N}(\text{H}_2\text{O})]$.

wt%. All impregnations were done under nitrogen atmosphere. NaOH treatments of the supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$ were likewise done under inert atmosphere. Samples were allowed to stand in 0.1 mol/l NaOH solution overnight, after which they were washed with water and dried under vacuum.

A typical hydroformylation catalysis experiment was carried out as a batch reaction in a Berghof's 100 ml autoclave with Teflon liner. 1-Hexene (1 ml, 8 mmol) was transferred to the autoclave in toluene solvent (5 ml) with 0.2 ml benzene or cyclohexane as internal standard. All solvents were dried and deoxygenated before use. The total amount of supported catalyst per reaction varied between 500 and 800 mg and the total amount of metals was 0.05–0.16 mmol. With unsupported metallic catalysts, also much larger amounts of metal were tested. In all experiments the catalysts were packed into the autoclave under nitrogen atmosphere. H_2/CO (1:1) reaction gas was introduced into the autoclave to 50 bar total pressure and the reaction was carried out at 150°C for 17 h.

Hydrogenation of 1-heptanal to 1-heptanol was performed by using 50 bar of pure H_2 or a H_2/CO mixture. Otherwise the reaction conditions were similar to those for 1-hexene hydroformylation (5 ml toluene, 1–1.3 ml 1-heptanal, 0.2 ml benzene or cyclohexane).

Most of the hydrogenation and almost all hydroformylation products were colored. With ruthenium 2,2'-bipyridine based catalysts, the product solution was typically yellowish and it darkened with the oxygenate yield; this may indicate to leaching of the catalyst [2]. The ruthenium content of the products was not determined.

3. Results and discussion

3.1. Solvent effects of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst

In previous studies on the impregnated $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst we

found its activity in hydroformylation to be rather poorly reproducible [1,2]. Reproducibility can be improved by using a more easily controllable preparation method, such as pulse impregnation [6] or an atomic layer epitaxy (ALE) related gas phase method [7]. The highest activities have nevertheless been achieved with a catalyst impregnated from CH_2Cl_2 [1,2], which indicates that the solvent may play an important role in the formation of the active catalyst. A characteristic feature of both the unsupported or silica supported $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine catalyst is its tendency to favor direct formation of C_7 alcohols in hydroformylation of 1-hexene. This is due to the presence of 2,2'-bipyridine [1,2]. The alcohol selectivity of an ruthenium catalysts can also be improved by using tertiary amine such as Et_3N as cocatalysts [12]. A similar 'amine effect' has been found for rhodium catalysts [13,14].

The hydroformylation activities of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts impregnated from different solvents are shown in Table 1. In all impregnations a highly air-sensitive, dark blue catalyst was obtained after thermal activation. The lowest alcohol yields (3 wt%) were obtained with CH_2Cl_2 impregnated catalysts with a ruthenium content of 0.072 mmol (Table 1). However, also the highest alcohol yields (76 wt%) were obtained with a CH_2Cl_2 impregnated catalysts (Ru content of 0.092 mmol). Still higher activities have been reported for catalysts supported on silica F-22 (maximum yield 97 wt%) [1,2].

IR studies have shown that more than one surface species may be formed during the impregnation, especially when chlorinated solvents such as CH_2Cl_2 are used [15]. It has been proposed that the presence of a chlorine source in impregnation may cause chlorination/oxidation of the catalyst and subsequent lowering of the activity. In a typical impregnation the catalyst is dried under vacuum before thermal activation to remove the solvent, but if drying is insufficient, residues of CH_2Cl_2 will remain on the silica surface and chlorination of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 may occur during activation.

Table 1
1-Hexene hydroformylation activity of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts impregnated from different solvents

Impregnation solvent	Treatment	Support	Ru (mmol)	2,2'-bpy (mmol)	1-Hexene (%)	<i>t</i> -2-, <i>c</i> -2-, <i>t</i> -3-, hexenes, hexane (%)	C ₇ aldehydes		C ₇ alcohols	
							(%)	<i>n</i> / <i>i</i>	(%)	<i>n</i> / <i>i</i>
CH_2Cl_2	–	SG60	0.072	0.075	2–36	62–84	0–2	≤ 1	3–33	≥ 2.4
CH_2Cl_2	–	SG60	0.093	0.096	2	10–77	4	≥ 0.7	21–77	1.4–5.0
CH_2Cl_2	–	F-22	0.071	0.074	3	76	0	–	21	3.6
CH_2Cl_2	CH_2Cl_2	F-22	0.072	0.075	11	79	0	–	11	3.2
CH_2Cl_2	CH_2Cl_2	SG60	0.090	0.093	9	80	0	–	10	<i>n</i>
CH_2Cl_2	air	SG60	0.074	0.077	3	68–78	0	–	19–30	2.0–3.1
CH_2Cl_2	–	Al_2O_3	0.074	0.077	26	73	0	0	0	–
THF	–	SG60	0.072	0.074	3	56–81	1	0.8	16–37	2.0–4.9
THF	–	SG60	0.093	0.096	3	60–81	1	1.1	16–34	2.0–6.0
THF	–	F-22	0.072	0.074	3	67–80	1	<i>n</i>	17–29	3.0–4.0
THF	CH_2Cl_2	SG60	0.092	0.096	4	77	1	<i>n</i>	18	4.6
THF	CH_2Cl_2	F-22	0.072	0.074	2–11	73	2	0.8	9–25	2.0–4.4
THF	air	SG60	0.093	0.096	3	79	0	–	18	4.9
$\text{CH}_2\text{Cl}_2/\text{THF}$	–	SG60	0.072	0.075	3–18	5–82	0–14	0.8	14–63	1.5–5.5
$\text{CH}_2\text{Cl}_2/\text{THF}$	–	SG60	0.092	0.096	2	71	0	–	27	3.1
methanol	–	SG60	0.075	0.077	2	67	0	–	30	3.0

Reaction conditions: 150°C, 50 bar H_2/CO (1:1), reaction time 17 h, 1-hexene 8 mmol, toluene 5 ml. The product distribution is given as wt%.

Chlorination is not possible in THF impregnations. According to IR studies, the formation of surface species is also more reproducible in THF impregnations, even though more than one surface species can still be formed [15]. Only moderately active catalysts with 16–37 wt% alcohol yields were obtained with THF impregnations (Table 1). Maximum activities of these catalysts are similar to those of catalysts prepared by pulse impregnation (THF as a solvent) [7] and gas phase methods [6]. A typical feature of THF impregnations was that the solvent adsorbed strongly onto silica. In all experiments small amounts of THF were removed from the support into the hydroformylation solution even though the catalysts were dried under vacuum for several hours.

Methanol was used as another non-chlorinated impregnation solvent. Activities of these catalysts were comparable to THF-impregnated catalysts (Table 1).

Although a highly active catalyst was not obtained by impregnation from THF, the use of a THF/ CH_2Cl_2 mixture (20/80% v/v) gave a catalyst with good maximum alcohol yield of 63 wt%. Unfortunately, the reproducibility was as

poor as with the CH_2Cl_2 -impregnated catalysts. It is thus possible that CH_2Cl_2 facilitates the formation of highly active surface species in addition to poorly active chlorinated/oxidized species. High activities may arise from a single active surface species or a mixture of species. Competition in the formation of different species may be the primary reason for the variation in the hydroformylation activity, even more important than leaching [2].

When the activated catalysts (impregnated form THF or CH_2Cl_2) were allowed to stand in dichloromethane overnight, dried and tested in hydroformylation, the activity was in most cases reduced. IR studies have shown that such CH_2Cl_2 treatment leads to an increase in the amount of chlorinated/oxidized surface species [15]. However, the reactivity suppressing effect of CH_2Cl_2 was not systematic and not observed in all experiments. With some THF-impregnated catalysts, the activity was even slightly improved after the CH_2Cl_2 treatment.

The $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst has a clear tendency to isomerize olefins [1,2]. Thus the dominating side reaction with all $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts was

Table 2
Activity of reference compounds in hydroformylation of 1-hexene

Catalyst	Support	Impreg- nation solvent	Ru	Rh	Co	bpy	1-Hexene	<i>t</i> -2-, <i>c</i> -2-, <i>t</i> -3-, hexenes, hexane	C ₇ aldehydes		C ₇ alcohols	
			(mmol)	(mmol)	(mmol)	(mmol)	(%)	(%)	(%)	n/i	(%)	n/i
Co	–	–	–	–	2.726	–	0	2	87	2.1	8	1.8
Co/bpy	–	CH ₂ Cl ₂	–	–	2.730	0.026	0	2	75	1.8	17	1.7
Co/bpy	–	THF	–	–	2.560	0.089	37–64	10–23	26–40	1.6–1.9	0	–
Co ₂ (CO) ₈	SG60	CH ₂ Cl ₂	–	–	0.085	–	1	0	74–85	1.0–1.8	7	1.3
Rh	Al ₂ O ₃	–	–	0.074	–	–	0	0	46–56	0.3–0.4	21–29	0.5–0.6
Rh/bpy	Al ₂ O ₃	THF	–	0.066	–	0.087	0	0	39	0.4	55	0.7
Rh/bpy	Al ₂ O ₃	CH ₂ Cl ₂	–	0.074	–	0.029	0–9	0	35–65	0.4–0.7	34–42	0.7–0.9
Ru	–	–	0.106	–	–	–	98	2	0	–	0	–
Ru/bpy	–	CH ₂ Cl ₂	0.055	–	–	0.052	99	1	0	–	0	–
[Ru(CO) ₃ Cl ₂] ₂	SG60	CH ₂ Cl ₂	0.074	–	–	–	0	77	0	–	19	1.0
[Ru(CO) ₃ Cl ₂] ₂ /bpy	SG60	CH ₂ Cl ₂	0.072	–	–	0.072	100	0	0	–	0	–
[Ru(CO) ₃ Cl ₂] ₂ /bpy	–	CH ₂ Cl ₂	0.200	–	–	0.801	82	0	0	–	0	–
[Ru ₃ (bpy)(CO) ₁₀]	–	–	0.082	–	–	–	2	61	34	3.0	4	n
[Ru ₃ (bpy)(CO) ₁₀]	SG60	THF	0.078	–	–	–	3	77	2	1.1	18	3.0
[Ru(bpy)(CO) ₂ Cl] ₂	–	–	0.089	–	–	–	34	59	4	n	0	–
[Ru(bpy)Cl ₃ (NO)]	–	–	0.082	–	–	–	94	3	0	–	1	n
[Ru ₂ (bpy) ₂ Cl ₃ N(H ₂ O)]	–	–	0.094	–	–	–	16–94	3–58	0–12	1.9	0–5	n

Reaction conditions: 150°C, 50 bar H₂/CO (1:1), reaction time 17 h, 1-hexene 8 mmol, toluene 5 ml. The product distribution is given as wt%.

an isomerization of 1-hexene, mostly to *trans*-2-hexene. Another common feature for all tested Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalysts was the change in stereospecificity with increasing activity. The n/i ratio of the alcohols was typically high with poorly active catalysts and decreased with increasing alcohol yield. In the mixture of isomerized hexenes this is due to the higher reactivity of 1-hexene than of internal or branched hexenes. Poorly active catalysts are only able to hydroformylate 1-hexene and leave the other isomers intact [16].

The Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst is highly air sensitive, losing its dark blue color rapidly when exposed to air. Oxidation can also be detected by IR [15]. Despite the drastic color change from dark blue to brown, moderately active CH₂Cl₂- and THF-impregnated catalysts (original alcohol yields < 30 wt%) did not, however, lose their catalytic activity completely even after 1–5 days exposure to air. The moderate activity of an air-treated, oxidized catalyst supports the assumption that a complex mixture of surface species is formed on the silica during impregnation. Although impregnations were carried out under

nitrogen atmosphere, the formation of oxidized surface species is possible through reaction with oxygen residues or the silica surface.

3.2. Activity of Ru, Co, and Rh reference catalysts in hydroformylation

Metallic Co, Rh and Ru catalyst were used as reference catalysts in hydroformylation (Table 2). Unsupported metallic Co and silica supported Co₂(CO)₈ behaved very similarly, yielding mainly aldehydes. This is in good agreement with the activities reported for unsupported Co₂(CO)₈ and CoCl₂·6H₂O [12]. No amine effect has been observed with these unsupported cobalt catalysts. Similarly, addition of 2,2'-bipyridine as a cocatalyst with metallic Co did not change the product distribution. Alumina supported metallic Rh gave somewhat higher yields of C₇ alcohols than Co catalysts, but again the main products were C₇ aldehydes, as is expected for rhodium catalysts without amine-based cocatalyst [16]. Presence of amine cocatalyst with rhodium tends to favor a direct formation of alcohols [13,14]. However, addition of 2,2'-bipyri-

Table 3

Activity of silica supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ in hydroformylation of 1-hexene

Catalyst	Impregnation solvent	Ru (mmol)	1-Hexene (%)	<i>t</i> -2-, <i>c</i> -2-, <i>t</i> -3-, hexenes, hexane (%)	C ₇ aldehydes		C ₇ alcohols	
					(%)	n/i	(%)	n/i
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$	CH_2Cl_2	0.064	21–85	15–71	0–7	≥1.9	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$	CH_2Cl_2	0.076	2	52	39	0.7	7	1.4
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]^a$	CH_2Cl_2	0.075	4	74	21	1.4	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$	THF	0.064	1	28	45	0.6	25	1.2
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]^a$	THF	0.064	5	76	8	1.0	12	1.9
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$	THF	0.077	5	75	10	0.7	11	1.8
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]^a$	THF	0.076	3	69	17	0.6	12	1.6
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$	CH_2Cl_2	0.077	18–96	4–72	0–10	2.3	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]^a$	CH_2Cl_2	0.071	92	8	0	–	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$	CH_2Cl_2	0.093	92	8	0	–	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$	THF	0.071	92	8	0	–	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]^a$	THF	0.071	71	26	3	n	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$	THF	0.093	90	10	0	–	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]^b$	–	0.071	97	3	0	–	0	–
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$	THF	0.075	17	77	0	–	4	n
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]^a$	THF	0.075	8	82	0	–	7	n
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]^b$	–	0.082	30–59	34–59	7–12	2.7	0	–

Reaction conditions: 150°C, 50 bar H₂/CO (1:1), reaction time 17 h, 1-hexene 8 mmol, toluene 5 ml.^a Thermally treated at 100°C for 17–20 h. The product distribution is given as wt%.^b Unsupported.

dine to alumina supported Rh effected no considerable change in catalyst selectivity. As seen in Table 2, unsupported metallic ruthenium and Ru/bpy behaved very similarly to $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ [12], showing no activity in the hydroformylation of 1-hexene. $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]/\text{SiO}_2$ was only slightly active and had a strong tendency to effect isomerization. Addition of 2,2'-bipyridine inactivated the catalyst completely. A cluster derived unsupported $[\text{Ru}_3(\text{bpy})(\text{CO})_{10}]$ showed moderate activity, but unlike $\text{Ru}_3(\text{CO})_{12}/\text{bpy}$, the main hydroformylation products were aldehydes. Silica supported $[\text{Ru}_3(\text{CO})_{10}(\text{bpy})]$ yielded mainly alcohols as a hydroformylation product, indicating a clear support effect. However, the activity remained moderate.

3.3. Activity of silica supported mononuclear ruthenium monobipyridines in hydroformylation

Schematic structures of the ruthenium monobipyridines tested are shown in Fig. 1.

$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ is found to be relatively stable [9]; it is dechlorinated only slightly under H₂/CO pressure at 150°C, yielding dimeric $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$. It is also rather stable against chlorination even in concentrated HCl [10]. As expected, the yellow or orange-yellow $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ showed no activity in hydroformylation (Table 3). Even isomerization was negligible with this compound. Impregnation from THF instead of CH_2Cl_2 made no difference. Similarly, a thermal treatment had no effect on the activity.

$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ is more reactive than $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$; it is converted rather easily to dimeric $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$, and also reacts with CH_2Cl_2 converting in part to $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ [9]. Because of the reactivity of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ with chlorine sources, we carried out impregnations only from THF. Impregnation yielded a gray product and no change in color occurred during thermal treatment at 100°C. $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ showed no appreciable activity in hydroformylation, but as

compared to $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ it was effective in the isomerization of 1-hexene (most favorable isomer, *trans*-2-hexene). This behavior is not a surprising since a hydride intermediate has been proposed to be included in the isomerization reaction pathway catalyzed by metal carbonyls [17].

Yellow $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ was clearly the best catalyst among the mononuclear compounds, giving moderate aldehyde yields (Table 3). The same moderate activity has been obtained for unsupported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ [18]. IR studies on supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ suggested that the methoxycarbonyl group is lost during impregnation, which should lead to a similar surface structure than supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ [15]. However, in adsorptions of both $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ onto SiO_2 alternative routes are possible. The adsorption may be merely physisorption, or the chlorine ligand may also be replaced by a surface bond. According to IR studies physisorption is dominating for all monomers $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$, and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ [15]. Such behavior explains the difference in activities between monomers. Unlike $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ favored the formation of aldehydes, especially when it was impregnated from CH_2Cl_2 . Impregnation from THF improved the alcohol yield. In the case of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, a slight support effect was also found. While unsupported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ produces aldehydes with low yield, supported complex favors alcohols (Table 3). Behavior of both $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ is due to co-existence of several supported surface complexes, which is affected by the impregnation solvent [15].

$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$, and $[\text{Ru}_2(\text{bpy})_2\text{Cl}_5\text{N}(\text{H}_2\text{O})]$ were practically insoluble in CH_2Cl_2 or THF and therefore were

not supported onto SiO_2 . Because all three complexes are quite stable, they were expected to be only poorly active in hydroformylation.

$[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$ proved to be almost totally inactive; only a slight isomerization of 1-hexene occurred (Table 2). $[\text{Ru}_2(\text{bpy})_2\text{Cl}_5\text{N}(\text{H}_2\text{O})]$ showed some activity in isomerization, although the variations between experiments were considerable. Aldehyde and alcohol yields were typically very low. $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$ was clearly able to isomerize 1-hexene, but it was virtually inactive in hydroformylation. Only aldehydes were produced, and in very low yield.

3.4. Activity of NaOH-treated supported ruthenium monobipyridines in hydroformylation

The dark blue color of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 was not achieved by supporting mononuclear ruthenium monobipyridines. Through electrochemical reduction [19,20] however, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ can be dechlorinated to polymeric $[\{\text{Ru}(\text{bpy})(\text{CO})_2\}_n]$, a dark blue polymer that is highly air sensitive and active in the electrochemical reduction of CO_2 . The physical properties of the polymer are thus similar to those of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 . Furthermore, $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst is highly active in the water gas shift reaction [3–5], which is closely related to CO_2 reduction. Since electrochemical methods are not suitable for supported complexes, we tested the NaOH treatment [15] for the dechlorination of silica supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$. The blue or bluish black color was obtained in all experiments and the preliminary activity tests in WGSR showed considerable activity. The IR spectra of NaOH treated products closely resembled those of the activated $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 [15].

Although the hydroformylation activities of NaOH-treated ruthenium monobipyridines remained at most moderate, both $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ and dimeric $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$ were clearly activated by the NaOH

Table 4

Activity of supported and NaOH-treated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$

Catalyst	Support	Impregnation solvent	Ru (mmol)	1-Hexene (%)	<i>t</i> -2-, <i>c</i> -2-, <i>t</i> -3-, hexenes, hexane (%)	C ₇ aldehydes		C ₇ alcohols	
						(%)	n/i	(%)	n/i
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$	SG60	THF	0.075	3	82	0	–	15	4.4
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$	SG60	THF	0.075	3	77	0	–	20	3.8
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$	SG60	CH_2Cl_2	0.076	5	84	0	–	11	3.0
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$	SG60	THF	0.075	3	81	0	–	15	5.4
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2^a$	SG60	THF	0.076	2	62	4	1.8	32	3.5

Reaction conditions: 150°C, 50 bar H_2/CO (1:1), reaction time 17 h, 1-hexene 8 mmol, toluene 5 ml. The product distribution is given as wt%.
^a $T = 165^\circ\text{C}$.

treatment (Table 4). Even more important is that all catalysts showed very high alcohol selectivity, similarly to the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 .

3.5. Hydrogenation of 1-heptanal to 1-heptanol

The ability of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 and related monobipyridines to convert aldehydes to alcohols was tested in hydrogenation of 1-heptanal under hydrogen pressure (Table 5). With the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst the hydrogenation was practically complete. Conversion was also very high with an air treated catalyst. With use of a gas mixture (H_2/CO , 1:1) the activity was slightly lower but still very high. The impregnation solvent seemed to have little or no effect on hydrogenation activity.

As in hydroformylation, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ exhibited no activity in the hydrogenation of 1-heptanal to alcohols. Conversely, although supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ was poorly active in hydroformylation, it showed considerable hydrogenation ability. However, unsupported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ showed only moderate activity, indicating a clear support effect. Supported $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ was also highly active in hydrogenation even though in hydroformylation it favored the formation of aldehydes. The hydrogenation activity under pure hydrogen pressure may be due to lack of carbon monoxide, the presence of which in hydroformylation may prevent the hydrogenation reaction.

The hydrogenation activity of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ was strongly reduced under H_2/CO -mixture (Table 5), which supported the inhibiting role of carbon monoxide.

Hydrogenation properties of supported $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ differ considerably from those of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst and ruthenium(mono)bipyridines. With $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ the conversion of 1-heptanal was complete, but selectivity for 1-heptanol was low, the main product being *n*-diheptyl ether (75 wt%). With other ruthenium, cobalt and rhodium catalysts the side products were more likely long chain C_{14} aldol condensation products, but hardly any *n*-diheptyl ether was observed. Occasionally some heptanoic acid was produced as well. Addition of 2,2'-bipyridine to the $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ catalyst reduced the conversion of 1-heptanal considerably and prevented the formation of *n*-diheptyl ether completely, directing the reaction towards other long chain products. Another side reaction with supported $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ was the hydrogenation of the toluene solvent to methylcyclohexane (and benzene mainly to cyclohexane). In most cases the conversion of toluene was low, but in some experiments conversions up to 40% were obtained. Variations in toluene hydrogenation indicate that the silica supported $[\{\text{Ru}(\text{CO})_3\text{Cl}_2\}_2]$ has some ability to hydrogenate aromatic compounds.

Cobalt metal and alumina supported Rh (5 wt%) were tested as reference compounds in 1-heptanal hydrogenation. Metallic cobalt proved to

Table 5
Hydrogenation of 1-heptanal to 1-heptanol

Catalyst	Support	Impregnation solvent	Ru (mmol)	Rh (mmol)	Co (mmol)	bpy (mmol)	1-Heptanal (%)	1-Heptanol (%)
Ru ₃ (CO) ₁₂ /bpy	SG60	CH ₂ Cl ₂	0.075	–	–	0.077	0	97
Ru ₃ (CO) ₁₂ /bpy	SG60	CH ₂ Cl ₂	0.092	–	–	0.096	0	95
Ru ₃ (CO) ₁₂ /bpy ^a	SG60	CH ₂ Cl ₂	0.075	–	–	0.077	7	91
Ru ₃ (CO) ₁₂ /bpy	SG60	CH ₂ Cl ₂ /THF	0.092	–	–	0.096	0	98
Ru ₃ (CO) ₁₂ /bpy	SG60	THF	0.092	–	–	0.096	0	98
Ru ₃ (CO) ₁₂ /bpy ^b	SG60	THF	0.092	–	–	0.096	1	81
Ru ₃ (CO) ₁₂ /bpy	SG60	MeOH	0.075	–	–	0.077	0	96
[Ru(CO) ₃ Cl ₂] ₂	SG60	CH ₂ Cl ₂	0.075	–	–	–	0	20
[Ru(CO) ₃ Cl ₂] ₂ /bpy	SG60	CH ₂ Cl ₂	0.073	–	–	0.072	62	3
[Ru(bpy)(CO) ₂ Cl ₂]	SG60	CH ₂ Cl ₂	0.075	–	–	–	70	3
[Ru(bpy)(CO) ₂ Cl ₂]	SG60	THF	0.092	–	–	–	83	2
[Ru(bpy)(CO) ₂ Cl(C(O)OCH ₃)]	SG60	THF	0.071	–	–	–	1	95
[Ru(bpy)(CO) ₂ Cl(C(O)OCH ₃)] ^b	SG60	THF	0.077	–	–	–	55	20
[Ru(bpy)(CO) ₂ ClH]	SG60	THF	0.075	–	–	–	0	94
[Ru(bpy)(CO) ₂ ClH]	–	–	0.082	–	–	–	47	45
[Ru(bpy)(CO) ₂ Cl] ₂	–	–	0.090	–	–	–	31–71	29–66
[Ru(bpy)Cl ₃ (NO)]	–	–	0.090	–	–	–	68–90	1
[Ru ₂ (bpy) ₂ Cl ₂ N(H ₂ O)]	–	–	0.091	–	–	–	55–82	2
Co	–	–	–	–	2.720	–	59–70	9–18
Co ^a	–	–	–	–	2.820	–	68	14
Co/bpy ^c	–	CH ₂ Cl ₂	–	–	2.730	0.026	0	91
Co/bpy ^c	–	CH ₂ Cl ₂	–	–	2.580	0.089	0–22	21–76
Co/bpy ^{a,c}	–	CH ₂ Cl ₂	–	–	2.585	0.089	74	0
Rh	Al ₂ O ₃	–	–	0.078	–	–	0	77
Rh ^a	Al ₂ O ₃	–	–	0.077	–	–	61–75	6–16
Rh/bpy	Al ₂ O ₃	CH ₂ Cl ₂	–	0.078	–	0.033	45	29
Rh/bpy	Al ₂ O ₃	CH ₂ Cl ₂	–	0.067	–	0.088	63	19
Rh/bpy ^a	Al ₂ O ₃	CH ₂ Cl ₂	–	0.067	–	0.089	29–57	37–64

Reaction conditions: 150°C, 50 bar H₂, reaction time 17 h, 1-heptanol 9.6 mmol, toluene 5 ml.

^a *p*(H₂/CO) = 50 bar, 1:1.

^b Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst treated under air.

^c bpy supported on metallic Co. The product distribution is given as wt%.

be only poorly active, and addition of 2,2'-bipyridine had a very little effect on the hydrogenation activity. Again, aldol condensation side products, mainly 2-pentyl-5-nonenal, were observed. The low hydrogenation activity is in agreement with the hydroformylation results, where alcohol yields were not improved by adding amines as cocatalyst (Table 2).

Rh/Al₂O₃ (5 wt% Rh) was more effective in hydrogenation of 1-heptanal than was metallic cobalt, when pure hydrogen was used. However, if the reaction was carried out using the H₂/CO mixture (1:1), the conversion to 1-heptanol was strongly reduced. Addition of 2,2'-bipyridine suppressed the hydrogenation activity of Rh/Al₂O₃

in pure H₂, but with use of a 1:1 H₂/CO mixture the alcohol selectivity was improved. In addition to 1-heptanal conversion, Rh/Al₂O₃ also catalyzed hydrogenation of toluene (and benzene).

An addition of amines to unsupported rhodium catalysts considerably improves the alcohol selectivity considerably in hydroformylation. By contrast an amine addition to phosphine- or phosphite-containing rhodium compounds such as HRh(CO)(PPh₃)₃ or Rh₄(CO)₈((P(OPh)₃)₄) has no effect on the alcohol selectivity, indicating that presence of phosphine ligands prevents the amine effect [12]. Improvement in the hydrogenation efficiency of Rh/Al₂O₃/bpy under H₂/CO mixture may be due to

formation of Rh–carbonyl–amine complex, which is known to be highly active in such processes [12–14]. The lower activity of cobalt/bpy under H_2/CO gas mixture may also be due to the formation of metal–carbonyl–amine complex, because with cobalt such complexes do not initiate a hydrogenation of alcohols to aldehydes. The diverse behavior of Rh and Co complexes has been attributed to the different nature of M–H interactions in metal–carbonyl–amine complexes [14].

The wide variations in Co/bpy and Rh/bpy activities were partially due to nonuniform bpy deposition onto metallic cobalt or Rh/ Al_2O_3 . Both catalysts were prepared by impregnating bpy from dichloromethane and activating the catalyst at 100°C in a sealed glass ampoule. During activation, bpy was partially adsorbed onto the glass wall instead of the carrier, so lowering the true bpy content of the catalyst.

3.6. Hydroformylation activity of combined catalysts

As seen in Table 5, the $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 catalyst was highly active in the hydrogenation of aldehydes with pure hydrogen or a H_2/CO mixture. In contrast to hydroformylation (see Table 2), reproducibility of the hydrogenation is reasonably good. Thus the major hurdle in hydroformylation with $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 catalyst seems to be hydrocarbonylation, the actual hydroformylation step from alkene to aldehyde. A typical $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 catalyst is nevertheless effective in hydrogen transfer, as indicated by the strong tendency to isomerization and a direct alcohol production (Table 2).

In hydrogenation experiments with $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 (Table 5), only 1-heptanal was used as a substrate. Therefore, a good aldehyde-yielding catalyst, Co or Rh, was added to the $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 in order to ensure the production of a mixture of aldehydes in high yield. In these experiments the function of $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2

was to hydrogenate formed aldehyde mixture to alcohols (Table 6).

$Co_2(CO)_8$ supported onto SiO_2 showed high activity and selectivity towards aldehydes (Table 2). However, as seen in Table 6, when $Ru_3(CO)_{12}$ and 2,2'-bipyridine were co-impregnated with $Co_2(CO)_8$ onto SiO_2 , and when the total amount of metals in the reaction varied between 0.045 and 0.1 mmol, the combined catalyst did exhibit better alcohol selectivity than $Co_2(CO)_8/SiO_2$ alone. In fact, the activity was lower relative to that with pure $Co_2(CO)_8/SiO_2$ with a comparable metal content of 0.085 mmol. When the Ru content was increased to 0.072 mmol and Co content to 0.085 mmol, a slight improvement in the alcohol selectivity was achieved, indicating the activity of $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 . Alcohol selectivity was also better with the $Ru_3(CO)_{12}/bpy/CoCl_2$ catalyst, although again the main products were aldehydes. The activity of $Ru_3(CO)_{12}/Co_2(CO)_8/2,2'$ -bipyridine on Al_2O_3 was clearly lower than the activity of the corresponding silica catalyst. Furthermore, its alcohol selectivity remained very low. The results indicate a negative support effect of Al_2O_3 on the $Ru_3(CO)_{12}/2,2'$ -bipyridine catalyst. Since $Ru_3(CO)_{12}/2,2'$ -bipyridine/ Al_2O_3 was practically inactive in hydroformylation (Table 1), the activity of the alumina supported combined metal carbonyl catalyst just arise from $Co_2(CO)_8$.

A mechanical mixture of separately impregnated $Ru_3(CO)_{12}/bpy/SiO_2$ and $Co_2(CO)_8/SiO_2$ with total metal content of 0.09 mmol showed only a moderate hydroformylation activity yielding alcohols; isomerization was the dominating reaction (Table 6). This behavior is similar to that of an average $Ru_3(CO)_{12}/2,2'$ -bipyridine/ SiO_2 catalyst (Ru content 0.07–0.09 mmol), indicating that $Ru_3(CO)_{12}/2,2'$ -bipyridine can be partially replaced by cobalt carbonyl catalyst without losing its alcohol selectivity. When the composition of H_2/CO gas mixture was changed from 1:1 to 4:1 the alcohol selectivity became even more pronounced. All the combined $Ru_3(CO)_{12}/bpy/SiO_2$ and $Co_2(CO)_8/SiO_2$ cat-

Table 6
Activity of combined catalysts in 1-hexene hydroformylation

Catalyst	Supports	Impregnation solvents	Ru	Rh	Co	bpy	1-Hexene	<i>t</i> -2-, <i>c</i> -2-, <i>t</i> -3-, hexenes, hexane (%)	C ₇ aldehydes		C ₇ alcohols	
			(mmol)	(mmol)	(mmol)	(mmol)	(%)		(%)	n/i	(%)	n/i
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈	SG60 ^b	CH ₂ Cl ₂ /THF	0.021	–	0.025	0.025	63	2	36	3.1	0	–
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈	SG60 ^b	CH ₂ Cl ₂ /THF	0.072	–	0.085	0.075	0	2	60	1.2	28	2.0
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈ ^c	SG60 ^b	THF	0.090	–	0.085	0.093	4	1	60	1.4	29	2.4
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈ ^c	SG60 ^b	THF/CH ₂ Cl ₂	0.037	–	0.051	0.039	44	45	0	–	12	2.5
Ru ₃ (CO) ₁₂ /CoCl ₂	SG60 ^b	THF/MeOH	0.088	–	0.096	0.091	2	0	55	0.9	27	1.3
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈ ^a	Al ₂ O ₃ ^b	CH ₂ Cl ₂ /THF	0.045	–	0.053	0.046	3	57	28	1.2	4	1.7
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈	Al ₂ O ₃	CH ₂ Cl ₂ /THF	0.073	–	0.086	0.076	1	21–32	44–55	1.0	5	1.5
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈ ^{a,c}	SG60	THF/CH ₂ Cl ₂	0.037	–	0.052	0.039	2–26	68–73	1	1.2	3–26	≥ 1.9
Ru ₃ (CO) ₁₂ /Co ₂ (CO) ₈	SG60	THF/CH ₂ Cl ₂	0.046	–	0.044	0.048	2	60	10	1.1	28	2.2
Ru ₂ (CO) ₁₂ /Co ₂ (CO) ₈ ^a	SG60	THF/CH ₂ Cl ₂	0.046	–	0.043	0.048	3	78	0	–	20	2.2
Ru ₃ (CO) ₁₂ /Co	Co ^d	THF	0.075	–	2.819	0.077	2	26–52	9–33	1.3–1.6	38	2.6
Ru ₃ (CO) ₁₂ /Co	Co ^d	CH ₂ Cl ₂	0.036	–	4.147	0.037	1	0	44–75	1.4	16–37	1.4–1.6
Ru ₃ (CO) ₁₂ /Rh	SG60/Al ₂ O ₃	THF	0.092	0.122	–	0.096	0	0	13–23	0.3	73–80	0.9
Ru ₃ (CO) ₁₂ /Rh	SG60/Al ₂ O ₃	THF	0.093	0.085	–	0.096	0	0	2	n	96	0.8
Ru ₃ (CO) ₁₂ /Rh	SG60/Al ₂ O ₃	THF	0.075	0.077	–	0.081	1	0	1	0	97	1.0
Ru ₃ (CO) ₁₂ /Rh ^c	SG60/Al ₂ O ₃	THF	0.092	0.122	–	0.096	0	0	10–30	0.3	64–83	0.8
Ru ₃ (CO) ₁₂ /Rh	SG60/Al ₂ O ₃	CH ₂ Cl ₂	0.074	0.080	–	0.078	0–9	0	0–10	0.3	86–96	0.9
Ru ₃ (CO) ₁₂ /Rh	SG60/Al ₂ O ₃	CH ₂ Cl ₂	0.093	0.079	–	0.096	0	0	16	0.3	81	1.0

Reaction conditions: 150°C, 50 bar H₂/CO (1:1), reaction time 17 h, 1-hexene 8 mmol, toluene 5 ml.

^a *p*(H₂/CO) = 50 bar, 4:1.

^b Both precursors impregnated onto same support.

^c Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst air treated.

^d Impregnated on metallic Co. The product distribution is given as wt%.

alysts exhibited much lower activities than the pure Co₂(CO)₈/SiO₂, in agreement with our observations above that the average Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ is much less effective in hydrocarbonylation of alkenes than the supported cobalt carbonyl.

Mechanical mixtures of Rh/Al₂O₃ and the moderately active Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ (alcohol yield ≤ 37 wt% with 0.07–0.09 Ru content) with total metal contents of 0.154–0.214 mmol showed very high activities (Table 6). Metal components in Rh/Al₂O₃ and Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ seem to have different functions. Rh/Al₂O₃ is highly active in the first stage of hydroformylation producing mainly aldehydes, while Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ acts as

hydrogenation catalysts and converts the aldehydes to alcohols in good yield. A pure Rh/Al₂O₃ catalyst gave the n/i ratio of 0.3 for C₇ aldehydes and 0.5 for C₇ alcohols (Table 2), whereas moderately active Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ favors an n/i ratio higher than 1.5. A typical n/i ratio for C₇ alcohols obtained by the combined Ru/Rh catalyst was ≤ 1.0, indicating that rhodium is mainly responsible for aldehyde formation and Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ for converting C₇ aldehydes to alcohols.

3.7. Behavior of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ in hydroformylation

As discussed in previous chapters the activity and selectivity of Ru₃(CO)₁₂/2,2'-bipyridine/

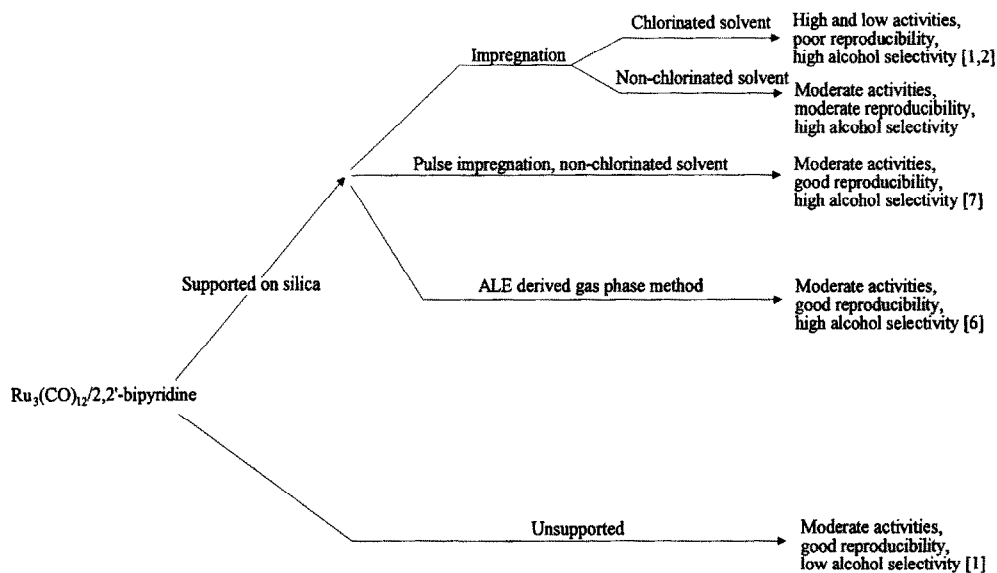


Fig. 2. Effect of the preparation method on hydroformylation activity of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine catalyst.

SiO_2 depend on the method and conditions of preparation. The effect of the preparation method and the behavior of variously active $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts in 1-hexene hydroformylation are summarized in Fig. 2 and 3. An uncontrolled formation of several supported ruthenium species during impregnation reduces reproducibility of the catalyst. In impregnation the optimum Ru/bpy ratio in $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst is found to be 1:1 [1,2]. The same ratio has been found for pulse impregnated catalysts where considerable excess of 2,2'-bipyridine was used during a preparation [15]. This indicates that ruthenium monobipyridines are the most probable surface species. IR studies on the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst have shown some similarities with monomeric ruthenium monobipyridine dicarbonyls and with polymeric $[\{\text{Ru}(\text{bpy})(\text{CO})_2\}_n]$ [15]. A typical oxidation number for a stable monomeric ruthenium bipyridine dicarbonyl compound is +II (Fig. 1) and thus the formation of monomers from $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 requires oxidation of the original ruthenium cluster. If no 'free' oxidizing agents such as oxygen are available, ruthenium may be oxidized by the silica surface. As seen in Table 3, the hydroformylation activity of this type of supported monomers is at

most moderate, the dominating reaction being isomerization. Despite the low hydroformylation activity, supported monomers can be highly active in the hydrogenation of heptanal (Table 5). A similar behavior has been observed with the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst (Fig. 3). If the hydroformylation activity is low, the

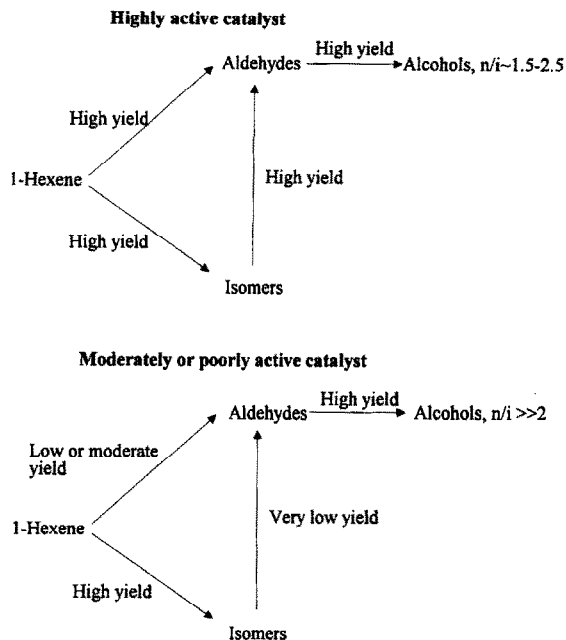


Fig. 3. Catalytic behavior of variously active $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts.

main products are isomers and all hydroformylation products have been converted to alcohols. Furthermore, the high n/i ratio of alcohols indicates that only the energetically more favorable hydroformylation of linear and terminal alkenes occur [16]. With more active catalysts also branched or internal alkenes can be converted and the n/i ratio is closer to one.

The solvent effect in impregnation is clear. Use of chlorinated solvents such as CH_2Cl_2 yields both highly active and almost inactive catalysts, whereas non chlorinated solvents such as THF yields at most moderately active catalysts. The negative effect of chlorinated solvent is most probably due to chlorination of the surfaces species. A similar deactivation with increased number of chlorine ligands is observed with ruthenium monomers. $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ were active at least in hydrogenation (Table 5), while $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ is inactive in both hydroformylation and hydrogenation. Further chlorinated and oxidized $[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$ and $[\text{Ru}_2(\text{bpy})_2\text{Cl}_5\text{N}(\text{H}_2\text{O})]$ are practically inactive (Table 2). Reduced activity is probably due to greater stability of chlorinated complexes. Both $[\text{Ru}(\text{bpy})\text{Cl}_3(\text{NO})]$ and $[\text{Ru}_2(\text{bpy})_2\text{Cl}_5\text{N}(\text{H}_2\text{O})]$ are highly stable. In fact, they can be obtained from $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ under drastic conditions: in concentrated HCl/HNO_3 solution at 240°C [10].

In addition to the possible formation of monomers, another potential deactivation process of $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 is decarbonylation. As seen in Table 2, metallic ruthenium and Ru/bpy are completely inactive in hydroformylation. Formation of supported metallic ruthenium during the activation does not have to be complete to cause a steep drop in the catalyst activity. This is due to the narrow optimum loading of the active Ru species 1.1–1.8 wt% [2,6,7]. In the present work, the theoretical loading usually was set to 1.5 wt%, when relatively small loss of the active component would lead to a sharp drop in activity.

The high hydroformylation activity, found only with CH_2Cl_2 impregnated $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalysts [1,2], is more difficult to explain. Although THF directs the surface reactions more specifically than CH_2Cl_2 , no highly active THF impregnated catalyst were obtained. The activity of THF impregnated and pulse impregnated catalyst [7] is similar to that of the ALE prepared catalyst [6], which indicates that THF itself is not the reason for the lack of highly active catalyst components. However, THF probably direct the reaction to similar surface species at the preparation without solvent. It is thus possible that impregnation from CH_2Cl_2 facilitates the formation of a highly active compound or mixture as well as poorly active species.

The detailed structure of the highly active component in the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst still remains unclear. One possibility is oligomeric or polymeric $\{[\text{Ru}(\text{bpy})(\text{CO})_2]\}_n$. As discussed earlier the blue, air sensitive polymer can be prepared from $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ by electrochemical reduction [19,20]. Similar blue product can be also obtained by NaOH-treatment of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$, or $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$ [15]. Although the relation between an electrochemical $\{[\text{Ru}(\text{bpy})(\text{CO})_2]\}_n$ polymer and NaOH-treated monomers is not yet clear, it seems likely that the NaOH treatment leads, at least partially, to dechlorination and oligo- or polymerization. The preliminary studies with NaOH-treated monomers in WGS showed comparable activities, to those achieved with the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 catalyst. As seen in Table 4, NaOH treatment of supported monomers and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}]_2$ dimer activated the catalyst, even though the activity remained relatively poor. In all cases the main hydroformylation products were C_7 alcohols, which is also typical for $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 . Low activities may be due to a mixture of surface species. Some unreacted monomer or dimer could remain after NaOH treatment or the polymerization of the monomers could have partially stopped at the dimeric (for example

[{Ru(bpy)(CO)₂OH}₂]) or at some poorly active oligomeric stage [15]. Yet another possibility is severe decarbonylation, leading either to metallic ruthenium or to surface oxidized ruthenium species, both of which are expected to be very poorly active. IR studies on NaOH-treated monomers indicate that the amount of unreacted monomer is low and considerable evolution of CO₂ during the treatment is not observed except for [Ru(bpy)(CO)₂Cl(C(O)OCH₃)], where it is probably due to decomposition of the methoxycarbonyl group [15]. The most likely alternative, then, is that the polymerization is incomplete and that unreactive oligomeric or polymeric side products are formed. Such side products could also appear in the preparation of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst with the solvent having an important role in directing their formation.

4. Conclusions

The Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst is highly active in hydrogen transfer processes such as isomerization of alkenes and hydrogenation of aldehydes to alcohols. It is also highly active in the water gas shift reaction, and in the hydroformylation of alkenes where it favors the direct formation of alcohols. Method and conditions of preparation strongly influence properties of the catalyst. A major problem with impregnated Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ in hydroformylation is poor reproducibility. This can be improved, however, by choosing a more easily controlled preparation method such as an ALE-related gas phase method or pulse impregnation. In impregnation, the choice of solvent affects the hydroformylation activity of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂. With use of a chlorinated solvent such as CH₂Cl₂, catalysts vary widely from highly active to very poorly active. The considerable variations in hydroformylation activity of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ are probably due to the co-existence of several surface species. This would explain the effects of the solvent and the preparation method of the catalyst. In the pres-

ence of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalyst, the limiting step in the hydroformylation of alkenes directly to alcohols is alkene hydrocarbonylation. If this initial step is achieved by adding a cocatalyst such as Rh favorable to aldehyde production, alcohols can be obtained directly in good yield. The exact structure of the active surface species of Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ is not known, but one possibility is polymeric or oligomeric [{Ru(bpy)(CO)₂}]_n. Monomeric and dimeric ruthenium monobipyridines are typically only moderately active.

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