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Indication of water in the coordination sphere of rhodium by conversions of 2,5-dimethoxy-2,5-dihydrofuran with syngas

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Abstract

2,5-Dimethoxy-2,5-dihydrofuran did not form the expected aldehydes when water-soluble rhodium-catalysts were used for the conversion with syngas. Instead of hydroformylation, hydrogenation was the main reaction path in water, where 2,5-dimethoxytetrahydrofuran and its hydrolysis product, succinic dialdehyde, were obtained. The formation of hydrogenation products indicates water in the coordination sphere of rhodium. This may provide us with information on the environment of an active metal in aggregated structures like micelles and vesicles which are gaining in importance in biphasic catalysis. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The effective separation or recycling of complex catalysts can be achieved by applying biphasic aqueous catalysis [1]. The catalysts are dissolved in water and have only negligible solubility in the organic phase containing the educts and products. The solubilization of the catalysts in water can be accomplished by substitution of the ligands with hydrophilic groups [1,2]. Biphasic catalysis has been used in industrial processes [3] where sulfonated triphenylphosphines such as $P(3\text{-}C_6H_4\text{–}SO_3Na)_3$ (TPPTS) have been employed. Although aqueous two-phase catalysis offers major advantages, it has not been industrially applied to the hydroformylation of long-chained olefines affording aldehydes for the production of plasticizers. The low solubilities of higher olefins in the aqueous catalyst phase limit their conversion rates because of their linear dependence on the olefin concentrations [4]. To overcome these limitations, the addition of surfactants has been suggested. In contrast to Rh/TPPTS-systems, amphiphilic catalysts as developed by Hanson et al. [5,6] can form aggregate structures like micelles or vesicles. These catalysts are much more active than Rh/TPPTS-systems in the hydroformylations of 1-octene and 1-tetradecene. This has been explained by enhanced phase-transfer of the olefins in the presence of the amphiphilic sulfonated ligands. Catalysts embedded in micelles, vesicles or other aggregated structures are expected to gain in importance in biphasic catalysis, especially when the substrates have low solubilities in water [7,8].

In principle, the catalysis could take place in the aqueous bulk phase, in the hydrophobic regions inside of micelles or related structures or in the interface layers between hydrophilic and hydrophobic microphases. For an optimal design of biphasic aqueous catalysts, it is important to know where the catalyst works. Going on the assumption that the hydroformy-

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lation of propylene occurs in the interphase region between water and the organic phase, Cornils and co-workers [9] used a productivity function of the interfacial area for the refinement of a kinetic model. It described the experimental results more accurately than a model for the reaction in the aqueous bulk phase. Further indicators such as a chemical probe giving different results in aqueous and organic environments would be desirable to shed light on the problem of ‘where the reaction takes place’ [9]. We found the conversion of 2,5-dimethoxy-2,5-dihydrofuran (**1**) with syngas to be a probe reaction of this kind.

2. Experimental

2.1. Materials

2,5-Dimethoxy-2,5-dihydrofuran (**1**), 2,5-dimethoxytetrahydrofuran-3-carbaldehyde (**2**), 2,5-dimethoxytetrahydrofuran (**3**) (mixtures of *cis–trans*-isomers), tris-(3-sulfophenyl)-phosphin trisodium salt (TPPTS), triphenyl phosphine (PPh_3), 1,2-bis-(diphenylphosphino)ethane (DPPE), sodium dodecyl sulfate (SDS) and $(acac)Rh(CO)_2$ were used as purchased. $Ph_2P–(CH_2)_2–P(O)(OEt)_2$ and $Ph_2P–(CH_2)_3–PO_3Na_2$ were made according to Ref. [10]. The procedures described therein were modified to sythesize the ligands $Ph_2P–(CH_2)_{10}–PO_3Na_2$ and $Ph_2P–(CH_2)_{12}–PO_3Na_2$, which have not been reported before. **1**, water, hexane, and 1-dodecene were desoxygenated prior to their use. The catalyst precursors were formed in situ by adding $(acac)Rh(CO)_2$ to the ligand solutions.

2.2. Conversion of 2,5-dimethoxy-2,5-dihydrofuran with syngas

The syngas conversions of **1** were carried out in a 100 ml autoclave (Parr Instrument Inc.). The reactor was flushed with argon before the catalyst solution was added using a stainless steel burette. After three purging cycles with syngas, the solution was pressurized to about 20 bar and heated up to 70°C. The stirring speed was 600 rpm. When the reaction temperature of 70°C was reached, the substrate **1** was introduced into the reactor using the steel burette. The pressure was kept constant at 30 bar. The reactions were stopped after 3 h by cooling the reactor with water. The analyses were done with a GC (HP 5890, Hewlett-Packard) using a 50 m×0.32 mm HP5 column. Reaction products **2** and **3** were identified by comparing them with the GC–MS data (HP 5890+MSD HP5972, Hewlett-Packard, EI, 70 eV) on the commercially available compounds. Product **4** was identified as 1,4-butandial (succinic dialdehyde) by GC–MS and by reduction with $NaBH_4$ which afforded 1,4-butandiol.

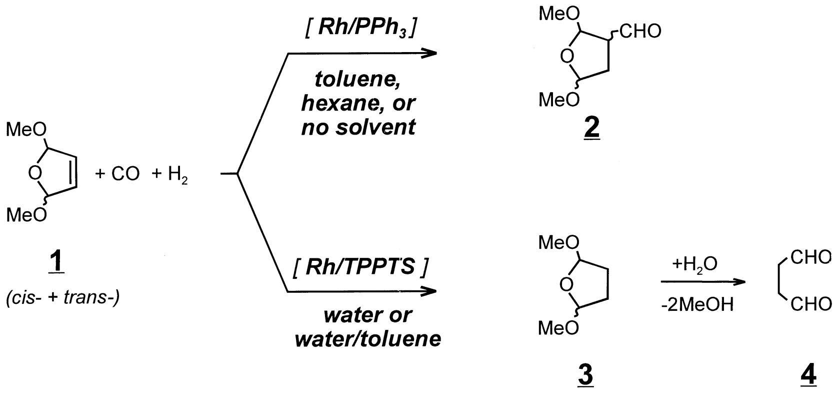
2.3. Hydroformylation of 1-dodecene

The hydroformylation experiments were carried out in the autoclave as mentioned above. The reactor was flushed with Argon and 20 ml of an aqueous catalyst solution, containing 10 mg $(acac)Rh(CO)_2$ and the water-soluble ligands $Ph_2P–(CH_2)_{10}–PO_3Na_2$ or $Ph_2P–(CH_2)_{12}–PO_3Na_2$ at ligand/Rh molar ratios of 5 (pH 8), were added using a steel burette. After three purging cycles, the catalyst solution was treated with syngas at 30 bar and 120°C for 2 h. The reactor was cooled down to 70°C and depressurized to a pressure of 20 bar. A mixture of 5 ml 1-dodecene (22.5 mmol) and 1 ml **1** (8.2 mmol) was transferred into the autoclave. The pressure was adjusted to 30 bar and the reactions were conducted at 70°C for 4 h. Samples of 0.5 ml size were taken hourly over a period of 4 h. After adding of 1 ml acetone, the samples were analyzed by gas chromatography as described above.

3. Results and discussion

3.1. Conversion of 2,5-dimethoxy-2,5-dihydrofuran with syngas

Hydroformylation of 2,5-dimethoxy-2,5-dihydrofuranes (**1**) yields 2,5-dimethoxy-tetrahydrofuran-3-carbaldehydes (**2**) [11–13] which are interesting for the production of fine chemicals (Scheme 1). The formation of **2** from **1** and syngas can be catalyzed effectively with homogeneous Rh/PPh_3-catalysts in benzene, in toluene, and in other organic solvents. We tried to improve the catalyst recycling by applying aqueous biphasic systems. Substrate **1** was dissolved in toluene, and a Rh/TPPTS-catalyst was dissolved in the aqueous phase. Surprisingly, the syngas conversion of substrate **1**, which is also soluble in water, produced



Scheme 1. Conversions of 2.5-dimethoxy-2.5-dihydrofuran (**1**) with syngas.

no aldehydes **2**. Instead, the hydrogenation product, 2,5-dimethoxy-tetrahydrofuran (**3**), was formed.

The hydrogenation of the C=C bond of **1** did not require the presence of molecular hydrogen. This reaction also took place with aqueous catalysts when syngas was replaced by pure CO (Table 1, entry 3). Obviously, the tetrahydrofuran-derivative **3** was formed by a transfer hydrogenation with CO and water. Such reactions have recently been reviewed by Nomura [14]. It is known that unsaturated aldehydes

Table 1
Hydroformylation and hydrogenation products of **1** in aqueous and non-aqueous systems[a]

Entry	Ligand	$n_{\text{lig}}/n_{\text{Rh}}$	Hexane: *V* (ml)	Water: *V* (ml)	Surfactant[b] (g)	Yields (%)		
						Aldehydes **2**	Hydrogenation products	
							3	**4**
1	TPPTS[c]	5	–	20	–	0	7.4	92.6
2[d]	TPPTS[c]	5	5	10	–	0	75.0	3.6
3[d,e]	TPPTS[c]	5	5	10	–	0	61.3	3.9
4	PPh_3	5	20	–	–	89.8	0	0
5	PPh_3	5	–	20	0.5	3.6	5.4	81.7
6	PPh_3	5	5	10	–	69.2	17.3	5.3
7	PPh_3	5	5	10	1.0	0	41.0	29.7
8	PPh_3	5	20	0.18	0.2	90.9	5.2	1.7
9	DPPE[f]	3	20	–	–	28.8	0	0
10	DPPE[f]	3	5	10	–	22.9	21.1	0
11	DPPE[f]	3	5	10	1.0	0	45.6	11.4
12	$Ph_2P–(CH_2)_2–PO(OEt)_2$	2.5	20	–	–	94.9	5.1	0
13	$Ph_2P–(CH_2)_3–PO_3Na_2$	2.5	–	20	–	0	24.2	26.8
14[g]	$Ph_2P–(CH_2)_{12}–PO_3Na_2$	10	–	20	[h]	7.5	0	15.0
15[g]	$Ph_2P–(CH_2)_{12}–PO_3Na_2$	10	5	10	[h]	13.9	0	6.4

[a] Reaction conditions: 8.2 mmol **1**, 30 bar syngas, 70°C, 3 h, 1.9×10^{-2} mmol $(acac)Rh(CO)_2$ (5 mg).
[b] Sodium dodecyl sulfate.
[c] TPPTS=$P(m\text{-}C_6H_4–SO_3Na)_3$.
[d] 42 mmol **1**.
[e] CO instead of syngas.
[f] DPPE: $Ph_2P–(CH_2)_2–PPh_2$.
[g] 1 h.
[h] Ligand has surfactant character.

can be selectively converted to saturated aldehydes by Rh-catalyzed transfer hydrogenation of the C=C bond [15]. In this reaction, water serves as a reagent and enters the coordination sphere of the metal. Educt **1** is a cyclic half-acetal of an unsaturated aldehyde (*cis*-butenedial) and produced different products depending on the environment. The very different reaction paths in water and in organic solvents prompted us to check whether the phenomenon could be used as a chemical criterion of water in the coordination sphere of the metal. For this purpose, we conducted the conversion of **1** with syngas using several catalysts in different environments. The results are presented in Table 1.

The syngas conversion of **1** (*cis*/*trans*-mixture) with the homogeneous aqueous Rh/TPPTS-catalyst (Table 1, entry 1) yielded no aldehydes **2**, but rather hydrogenation products **3** (*cis*/*trans*) and their hydrolysis product, succinic dialdehyde (**4**) [16,17]. In the following text, **3** and **4** will be summarized as hydrogenation products. The hydrolysis of **3** can be prevented by its extraction in an organic phase with low water content. This was achieved with biphasic systems using hexane (entry 2 and others). As already mentioned, the hydrogenation of **1**–**3** does not require the dihydrogen of the syngas. It also occurs when the syngas is replaced by CO (entry 3). Only the transfer hydrogenation of **1** with CO and water can explain the formation of the hydrogenation products. This means that water is a reagent and must interact with the Rh-centers as has already been proven for other hydrogenation catalysts [18,19]. Further reductions with CO in aqueous media, such as the selective conversion of hydroxymethyl to methyl groups, have recently been reported by Sheldon and co-workers [20].

The homogeneous non-aqueous Rh/PPh_3-system hydroformylated **1** selectively to aldehyde **2** as expected (entry 4). The chemoselectivity was reversed when this catalyst was dissolved in water using a surfactant. Solubilized in water by a surfactant, the Rh/PPh_3-catalyst showed a product distribution similar to that of the Rh/TPPTS-system (entry 5). Hydrogenated products were formed when water was added to the organic phase containing the Rh/PPh_3-catalyst (entry 6). The selectivity shifted completely to hydrogenated products when a surfactant was added to the above aqueous two-phase system (entry 7). It is assumed that the surfactant facilitates the phase-transfer of the Rh/PPh_3-catalyst in the water, where hydrogenation is the preferred reaction path (also see entry 5). Also, smaller amounts of water affect the Rh-catalyzed conversion of **1** with syngas. Hydrogenation products were even formed with a low water content of about 1% (entry 8), reflecting the sensitivity of the probe reaction to water.

To examine whether water can change the reaction paths of catalysts other than triphenylphosphine complexes, the chelating ligand 1,2-bis-(diphenylphosphino)-ethane (DPPE), the hemilabile ligand $Ph_2P–(CH_2)_2–P(O)(OEt)_2$, and amphiphilic ligands were used to form soluble Rh catalysts. As expected, the Rh chelate complex-catalyst DPPE was less active than Rh/PPh_3. However, the responses to the changes in the catalyst environment from homogeneous to biphasic and biphasic with surfactant were qualitatively the same as observed with Rh/PPh_3 (entries 9–11). In hexane, the homogeneous Rh/$Ph_2P–(CH_2)_2–P(O)(OEt)_2$-catalyst produced the aldehyde **2** with a high yield (entry 12). In accordance with the other results, an analogous water-soluble Rh/$Ph_2P–(CH_2)_3–PO_3Na_2$ catalyst only afforded hydrogenated products in the aqueous medium (entry 13).

Having surfactant character, sodium phosphonate–phosphines with long carbon chains are assumed to form aggregated structures in which the hydrophilic phosphonate groups are oriented to the aqueous phase and the alkylene and phosphine groups form hydrophobic microphases. So, the metal should be coordinated within the hydrophobic regions where water has limited access. Assuming the catalysis takes place in organic microphases, such aggregated systems should even produce aldehydes **2** in water. The results obtained for the amphiphilic phosphonate–phosphine $Ph_2P–(CH_2)_{12}–PO_3Na_2$ confirm this (entry 14). The selectivity of hydroformylation products **2** was increased when a biphasic system was formed by adding hexane (entry 15). This could be explained by the formation of cooperative surfactant complexes [21] from the surface-active ligand and hexane that impart greater strength to the oil/water interface. Because the Rh/$Ph_2P–(CH_2)_{12}–PO_3Na_2$-catalyst is insoluble in hexane, the formation of **2** in the hexane phase can be excluded. The hydrophobic shielding of the rhodium centers does not seem to work with the Rh/$Ph_2P–(CH_2)_3–PO_3Na_2$-catalyst, which, due to

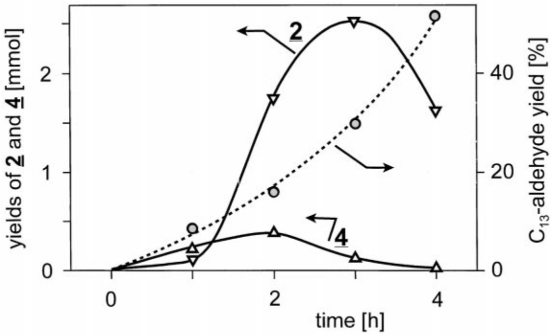


Fig. 1. Hydroformylation of 1-dodecene in the presence of **1**: yields of tridecanal and 2-methyldodecanal (C_{13}-aldehydes) and of **2** and **4** as function of time. Reaction conditions: 3.9×10^{-2} mmol (acac)Rh$(CO)_2$, 0.19 mmol Ph_2P–$(CH_2)_{10}$–PO_3Na_2 in 20 ml aqueous catalyst solution, 22.5 mmol 1-dodecene, 8.2 mmol **1**, 70°C, 30 bar syngas, stirring speed 600 rpm.

the shorter carbon chain of the ligand, cannot form hydrophobic microphases.

3.2. Hydroformylation of 1-dodecene in the presence of 2,5-dimethoxy-2,5-dihydrofuran

The probe reaction was applied in the hydroformylation of 1-dodecene to 2-methyldodecanal and tridecanal (C_{13}-aldehydes) at 70°C. Ph_2P–$(CH_2)_{10}$–PO_3Na_2 and Ph_2P–$(CH_2)_{12}$–PO_3Na_2 served as ligands to form the water-soluble Rh-catalysts. Both 1-dodecene and **1** were simultaneously converted with syngas. Under these conditions, only **2** and **4** were observed as reaction products of the probe molecule **1**. Fig. 1 shows the yields of the hydroformylation products of 1-dodecene and the amounts of **2** and **4** as functions of time. The plots of the C_{13}-aldehyde yield versus time for both amphiphilic ligands showed similar shapes during the first 50% of dodecene conversion. The shape of the plot does not correspond to first-order behavior of the olefin [4] and differs from those known from the literature [5] at 120°C. It differed also from the plots we obtained with the above surface-active ligands at 120°C. Aggregated catalyst structures at the lower temperature and the disruption of such structures above 100°C could be a reason for the different kinetics. The predominant formation of carbaldehydes **2** from **1** during the first hour of the reaction ($n_2/n_4=2$) clearly proves there is hydrophobic shielding of the Rh-centers and is indicative of aggregated catalyst structures at 70°C. The catalyst environment changes with progressive conversion, as can be seen from the increasing formation of **4** caused by the catalyst complexes being more accessible to water. It cannot be excluded that the formed C_{13}-aldehydes contribute to significant structural changes in the aggregated catalyst.

However, the selectivities of the dodecene hydroformylation remained constant over the reaction time. The weakly basic catalyst medium (pH 8) is beneficial for the hydroformylation activity [4]. On the other hand, it causes hydrolysis and polymerization of **2** and **4** [22,23], which explains their decreasing amounts in the GC-analyses with time. The rapid progress of these undesired reactions at temperatures above 80° means that the application of the probe reaction with **1** in basic media is only useful at lower temperatures. 2,5-Dihydrofuran has been examined as an alternative probe reagant to overcome the constraints caused by the instability of the products **2**, **3**, and **4**. But in contrast to its dimethoxyderivative **1**, the syngas reaction with 2,5-dihydrofuran was not affected by water and the double bond of this cyclic ether was selectively hydroformylated to the corresponding carbaldehyde, when aqueous catalysts were employed. Thus, 2,5-dihydrofuran cannot replace **1** as probe molecule. Whether unsaturated reagents are suitable for the presented probe reaction seems to depend strongly on their structure.

The fact that the probe reaction is also a syngas conversion is considered an advantage. The conversion of **1** with syngas reflects the accessibility of catalytic Rh-centers for water, which is different in aggregated and non-aggregated catalysts. The probe reaction with **1** complements other methods, such as concentration measurements of dyes with low water-solubility in aqueous systems [5] or pyrene fluorescence [24]. These methods indicate the existence of aggregated structures and also of water penetration, but do not necessarily give us information on the nearer environment of the active metal center. Monitoring of aggregated structures and their changes under pressure seems to be much more difficult with these methods than with the syngas conversion of **1**, which can be analyzed together with the hydroformylation products. It appears to be possible that this probe reaction can provide information on aggregated transition metal catalysts for other reactions such as hydrogenation.

4. Conclusions

The results show that the probe reaction of **1** with syngas works with different Rh-catalysts. The occurrence of **3** or **4** is a sensitive indicator of water in the coordination sphere of these catalysts. On the other hand, the formation of aldehydes **2** in aqueous systems is a good indication of the shielding of Rh-centers by a hydrophobic neighborhood. The probe reaction can indicate structural changes in aggregated catalysts in the course of hydroformylations. It provides information on where the reaction takes place in aqueous two-phase systems and complements kinetic and spectroscopical methods to study the catalysts environment. Substrates other than **1** will be tested to find a probe reaction for temperatures higher than 70°C.

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