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Liquid phase methanol hydrocarbonylation with homogeneous and heterogeneous Rh and Ru catalysts

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Abstract

Heterogeneous rhodium and ruthenium catalysts supported on activated carbon were studied in the liquid phase hydrocarbonylation of methanol. The activity and selectivity of the catalysts were determined and compared with the respective homogeneous metal precursors. The stability of the catalysts were determined by analysing the metal contents of the catalysts before and after the hydrocarbonylation reaction. The supported metal catalysts showed comparable activity to the respective homogeneous metal precursors, evidently because the activity originated from the metal leached from the support and was therefore based on the homogeneous catalysis of the dissolved metals. The stability of the metal on the support decreased with higher metal dispersion and was most closely related to the oxygen content of the carbon support.

Keywords: Methanol; Hydrocarbonylation; Rhodium; Ruthenium; Activated carbon support; Supported catalysts

1. Introduction

Methanol (hydro)carbonylation, the reaction of methanol with synthesis gas, provides a promising route to the synthesis of valuable chemicals such as ethanol, acetaldehyde and acetic acid [1]. The primary products are C_2 compounds formed through insertion of $-CO-$ or $-CH_2-$ groups into the C–O bond of methanol. All reactions of methanol with synthesis gas have misleadingly been termed 'methanol homologation'. Strictly speaking, however, methanol can only be homologated to higher n-alcohols. The use of the term hydrocarbonylation is preferable since it more precisely describes the wide range of products. In this work, the term hydrocarbonylation covers both methanol homologation and methanol carbonylation. The reactions of methanol homologation produce acetaldehyde and ethanol, whereas methanol carbonylation produces acetic acid or methyl acetate. In addition to the homologation and carbonylation reactions, several other reactions may occur under hydrocarbonylation conditions. Hydrogenation of methanol produces methane, dehydration of methanol produces dimethyl ether and the water–gas shift reaction gives carbon dioxide. Since none of these reactions are thermodynamically excluded, kinetic

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control directs over the number of possible reactions [2].

A variety of transition metals have been investigated as potential methanol hydrocarbonylation catalysts [3,4]. Cobalt complexes have shown the best activity and selectivity to acetaldehyde [3–6]. However, the requirement for a corrosive iodide promoter [7] and high syngas pressure of 200–400 bar [1] have hindered the commercial use of cobalt catalyzed methanol hydrocarbonylation. Ruthenium catalysts have high hydrogenation activity yielding ethanol with considerable amounts of methane, ethane and dimethyl ether as side products [2,8]. Rhodium catalysts are more active and require considerably lower pressures (1–100 bar) than the cobalt catalysts, but their selectivity is towards carbonylation [2]. Methanol carbonylation with homogeneous rhodium catalysts promoted with iodide produces acetic acid with nearly 100% conversion and selectivity, and has an industrial application in the Monsanto process [9].

In methanol hydrocarbonylation, the main research emphasis has been on homogeneous catalysis and the reaction has traditionally been carried out in high-pressure autoclaves in the liquid phase. Although homogeneous catalysts are highly active and selective, their use on a large scale is complicated by the difficulties in catalyst recovery. The problems of the separation could be solved by heterogenizing the catalyst. Only a few studies have been reported on the liquid and gas phase hydrocarbonylation of methanol with heterogeneous catalysts [10–12]. In the liquid phase, Tempesti et al. [10] have investigated the hydrocarbonylation of methanol with several oxide supported rhodium catalysts and Hardee et al. [11] with polymer supported cobalt and ruthenium catalysts. Hardee et al. [11] showed that the polymer supports were not sufficiently stable for the hydrocarbonylation reaction. Several investigations deal with methanol carbonylation with heterogeneous catalysts in the gas phase [13–18]. Fujimoto et al. [16,17] reported, for example, that catalysts supported on activated carbon were active in methanol (hydro)carbonylation, whereas the same metals supported on oxide carriers were inactive, producing only dimethyl ether. Evidently, the activated carbon support plays an essential role in the catalysis. In general, little attention has been paid to the stability of the metal on the support.

The main goal of our study was to determine the stability of rhodium and ruthenium catalysts supported on activated carbon in the liquid phase hydrocarbonylation of methanol. The activity and selectivity of the heterogeneous catalysts were compared with the respective homoge-

Table 1
Metal contents of catalysts before and after the reactions

Catalyst	Metal content of catalyst	Metal content			
		after 1st cycle		after 3rd cycle	
	wt-%	Catalyst wt-%	Product % [a]	Catalyst wt-%	Product % [a]
Rh/A.C. (N)	4.2	3.1	30	–	–
Rh/A.C. (C)	4.5	2.1	60	2.1	b.d.l.
Rh/A.C. (J&M)	3.9	3.6	20	–	–
Rh/A.C. (COMM)	5.0	1.8	70	1.2	–
Ru/A.C. (N)	2.5	0.2	85	0	b.d.l.
Ru/A.C. (STREM)	5.0	0	100	–	–

[a] The relative metal amount (wt-% of total metal content of catalyst) leached from the support in the liquid product. b.d.l. = below detection limit.

Table 2
Physical properties of supports and catalysts

Catalyst	Surface area m^2/g [a]	Pore volume cm^3/g	Volume of pores > 1 nm cm^3/g
Norit Rox (N)	1150	1.0 [b]	0.228
Coconut (C)	1030	0.6 [b]	0.024
Rh/A.C. (N)	1075	0.583	0.174
Rh/A.C. (C)	1140	0.506	0.047
Rh/A.C. (J&M)	1090	0.477	0.039
Rh/A.C. (COMM)	1140	0.525	0.066

[a] BET isotherm (0.001–1).
[b] Data from the manufacturer.

neous metal salts, to elucidate the role of the support in the reaction.

2. Experimental

2.1. Catalyst preparation

Commercially available peat based Norit Rox 0.8 (N) and coconut based activated carbon (A.C.) from Johnson Matthey (C) were used as catalyst supports. The catalysts were prepared by incipient wetness impregnation using aqueous solutions of $Ru(NO_3)_3$ or $Rh(NO_3)_3$. The support was dried in vacuum at 1–4 mbar at 200°C for 2 h and prewetted with ethanol before impregnation. The catalysts were dried for 12 h in air at 120°C, calcined at 400°C (1°C/min) under nitrogen flow and reduced under hydrogen at 400°C (5°C/min) for 1 h. Ru/A.C.(STREM) and Rh/A.C.(J&M) from Johnson Matthey and another commercially available catalyst Rh/A.C.(COMM) were tested as reference catalysts. The commercial reference catalysts were reduced under hydrogen at 400°C (5°C/min) for 1 h before use. The metal contents of the catalysts are shown in Table 1.

2.2. Support and catalyst characterization

Metal contents of the supports, catalysts and liquid products were analysed by atomic absorption spectroscopy (AAS). The inorganic elements of supports and catalysts were dissolved in a mixture of hydrochloric and nitric acid. The supports contained minor amounts (500 ppm) of impurities such as iron and sodium. The metal contents of the rhodium and ruthenium catalysts were determined before and after the reaction. The metal contents of the liquid products were also determined. Before analysis the liquid product was evaporated to dryness, the solid residue was dissolved in nitric acid and the metal content was determined by AAS.

The surface areas and pore volumes of the supports and catalysts were determined by static volumetric physisorption measurement with nitrogen at 77 K (Table 2). Samples were outgassed at 300°C and below 0.001 Pa for 8 h before the measurement.

The dispersions of the supported rhodium catalysts reduced at 400°C for 2 h were deter-

Table 3
Chemisorption and XPS measurements of catalysts

Catalyst	Chemisorption measurements			XPS	
	H_2 uptake dispersion cm^3/g_{kat}	Rh particle size nm	%	Rh/C [c]	C/O [c]
Rh/A.C. (N)	0.3	15 [a]/(X-ray amorphous) [b]	7.1	0.006	8.5
Rh/A.C. (C)	1.1	4.8 [a]/(X-ray amorphous) [b]	22.7	0.018	10.3
Rh/A.C. (J&M)	0.08	57 [a]/(20) [b]	1.9	0.007	19.3
Rh/A.C. (COMM)	1.4	4.0 [a]/(X-ray amorphous) [b]	27.3	0.019	4.0

[a] Determined by hydrogen chemisorption.
[b] Determined by XRD.
[c] The atomic ratios were calculated from the intensities of the photoelectron peaks at binding energies of 284.6, 286.3(0.3, 289.1(0.5 and 290.2(0.5 eV (C 1s line), 532.7 (0.7 and 534.5 (0.5 eV (O 1s line), 307.5 (0.2 and 311.9 (0.4 eV (Rh $3d_{5/2}$ line).

mined by static volumetric chemisorption measurements with hydrogen. The results are based on irreversible hydrogen uptake at 25°C. The irreversible hydrogen adsorption was applied because of the possible hydrogen spillover on the carbon support [19]. The dispersions and particle size estimates assuming spherical geometry of uniform size were corrected with the extent of reduction. Particle sizes were also determined by XRD measurements (Table 3). The extent of reduction and the Rh/C and C/O atom ratios of the carbon surface were determined by X-ray photoelectron spectroscopy (XPS) (Table 3). Samples were reduced at 400°C for 1 h before the XPS measurement.

2.3. Catalyst activity testing

All the experiments were carried out in a 250 ml AISI316 magnetically stirred autoclave equipped with a separate zirconium vessel. The activated carbon supported catalysts were prereduced under the hydrogen flow. The reduced catalyst, methanol and methyl iodide were packed in the zirconium vessel in a glove box under nitrogen atmosphere and transferred to the autoclave. The autoclave was flushed with synthesis gas ($CO/H_2 = 1/2$), pressurized and heated to the reaction temperature of 220°C. The total pressure used was 120 bar. The reaction time was 7 h for ruthenium catalysts and 5 h for rhodium catalysts. At the end of the experiment the autoclave was cooled to room temperature and depressurized. The liquid fraction was analysed with a gas chromatograph with flame ionization and thermal conductivity detector. The quantitative off-line analysis of ethers was uncertain because of the high volatility of these compounds. Thus, the catalyst activity and selectivity were determined from the hydrocarbonylation products. The reproducibility of the hydrocarbonylation product analysis was ca. 5%.

The heterogeneous catalysts were also tested in several consecutive batches. After one batch the catalyst was washed with methanol and packed in the autoclave with fresh methanol and methyl iodide. The amount of metal leached from the support during one reaction cycle was found by determining the metal content of the product by AAS. The catalytic activity of the metal leached from the support was also tested

Table 4
Catalyst activities and selectivities

Catalyst	Methanol conversion to hydrocarbonylation products/ (total conversion), %	Selectivities, %		
		EtOH [b]	MeOAc [c]	AcOH [d]
Rh–N homogeneous	58/(78)	1	75	24
Rh/A.C. (N)	22/(43)	1	70	29
Rh/A.C. (C)	36/(63)	2	70	28
Rh/A.C. (J&M)	15/(31)	2	70	28
Rh/A.C. (COMM)	46/(71)	2	61	37
Ru–N homogeneous	2.0/(20)	30	70	0
Ru/A.C.(N)	1.2/(15)	25	75	0
Ru/A.C.(STREM) [a]	3.2/(24)	38	62	0

[a] Twice the amount of catalyst.
[b] Ethanol.
[c] Methyl acetate.
[d] Acetic acid.

in the reaction brought about by adding pure methanol and methyl iodide to the product solution.

3. Results

3.1. Blank tests

The reactivity of methanol over the support and the methyl iodide promoter was quantified. The conversion of methanol to dimethyl ether was 3% in the presence of carbon support, 10% in the presence of methyl iodide and in the presence of both, 15–20%. The products detected were methyl acetate and dimethyl ether with selectivities of 1% and 99%, respectively. Hence, the activated carbon support and methyl iodide promoter did not alone appreciably affect the activity or selectivity of the methanol hydrocarbonylation.

3.2. Activity of homogeneous and heterogeneous catalysts

As can be seen from Table 4, the activities of the supported rhodium and ruthenium catalysts were lower but comparable to those of the homogeneous metal precursors. The formation of dimethyl ether was the main reaction on both the homogeneous and the heterogeneous catalysts. The homogeneous rhodium nitrate catalysts also produced traces of branched ethers like dimethoxy methane and 1,1-dimethoxy ethane. The hydrocarbonylation product distribution of the different catalysts is shown in Table 4. The rhodium catalysts produced acetic acid and methyl acetate as the main hydrocarbonylation products. The selectivity to ethanol was 1 mol-% and traces of acetaldehyde and ethyl acetate were found as well. With both the homogeneous and the heterogeneous ruthenium catalysts the yield of hydrocarbonylation products was below 2%, whereas the yield of ethers was about 15% (Table 4). Unlike the rhodium catalysts, the hydrocarbonylation product selectivity of the ruthenium catalysts was mainly towards homologation products. The main hydrocarbonylation products were methyl acetate and ethanol, but traces of acetaldehyde were detected as well. Since ruthenium is a good hydrogenation catalyst [20], most of the product, acetaldehyde, was probably hydrogenated to ethanol. The reaction network of the products is shown in Fig. 1.

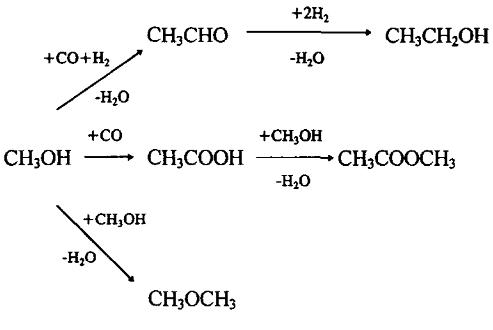

Fig. 1. Reaction network [2,27].

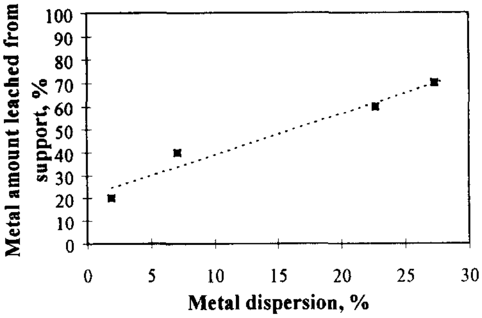

Fig. 2. The effect of metal dispersion on the metal stability on the support during the first reaction cycle.

3.3. Stability of the heterogeneous catalysts

The metal contents of the catalysts were determined before and after the hydrocarbonylation reaction (Table 1). The stability of the rhodium catalysts varied considerably. Only 20% of the metal was leached from the support in the case of Rh/A.C.(J & M), but approx. 60% in the case of Rh/A.C.(COMM). The stability

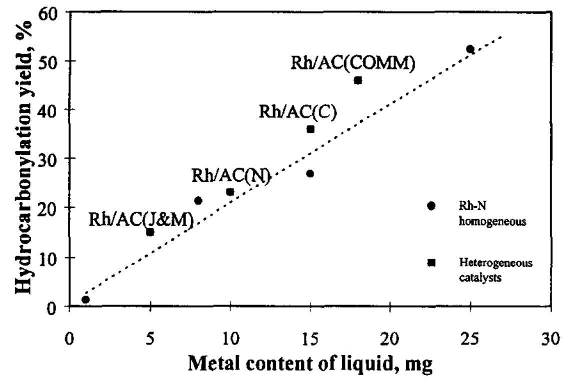

Fig. 3. The hydrocarbonylation yield vs. the metal content of product solution.

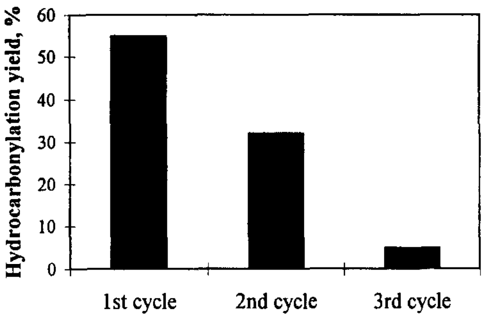

Fig. 5. The hydrocarbonylation yield of Rh/A.C.(COMM) durind the consecutive reaction cycles.

of the rhodium on the support was related to the metal dispersion: the higher the dispersion the lower the stability (see Fig. 2). The results also indicated the rhodium catalysts to be more stable than the ruthenium catalysts. With ruthenium, 85% and 100% of the total metal loading of Ru/A.C.(N) and Ru/A.C.(STREM), respectively, were leached from the support during the reaction.

The activity of the supported rhodium catalysts correlated with the amount of metal leached from the support, and the liquid product that contained the leached metal was catalytically active. The hydrocarbonylation activity of the homogeneous rhodium catalysts was also linearly related to the rhodium metal concentration. Thus the activity of all the rhodium catalysts was related to the amount of metal dissolved in the reaction media (see Fig. 3).

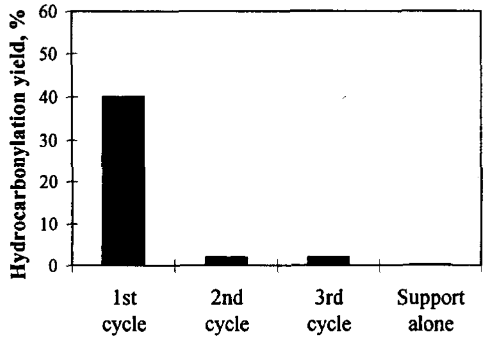

Fig. 4. The hydrocarbonylation yield of Rh/A.C.(C) during the consecutive reaction cycles.

3.4. Activity and stability of heterogeneous catalysts in consecutive reaction cycles

Activity and stability of the metal remaining on the support were determined for the Rh/A.C.(C), Rh/A.C.(COMM) and Ru/A.C.(N) catalysts in three consecutive reaction batches. The hydrocarbonylation activity of the rhodium catalysts decreased considerably in the second and third reaction cycles. The hydrocarbonylation yield of Rh/A.C.(C) was 40% in the first cycle and 2% in the second and third reaction cycle (Fig. 4). The hydrocarbonylation yield of Rh/A.C.(COMM) decreased more gradually, being 55% in the first cycle, 32% in the second cycle and only 5% in the third cycle (Fig. 5). After the three reaction cycles, the metal content of Rh/A.C.(C) was about half that of the original catalyst, and the metal content of Rh/A.C.(COMM) was 25% of the original content.

The hydrocarbonylation activity of Ru/A.C.(N) was about 2% in the first reaction cycle and about half that in the second reaction cycle. In the third cycle the activity was comparable to that of the pure support (hydrocarbonylation yield (0.2%). Ru/A.C.(N) lost 85% of its metal content during the first reaction cycle and the rest of the metal on the support was leached in the second reaction cycle.

4. Discussion

4.1. Activity of rhodium and ruthenium catalysts

The poor activity and selectivity of the catalysts to hydrocarbonylation products and the abundant formation of dimethyl ether were primarily due to the insufficient concentrations of carbon monoxide and hydrogen in the liquid phase. Especially with the ruthenium catalysts, higher total pressures would have been needed for catalyst activity [8]. The hydrocarbonylation product selectivities of the rhodium and ruthenium catalysts were similar to those of their previously reported homogeneous counterparts [21,22]. The activity and stability of the heterogeneous ruthenium catalysts in the hydrocarbonylation were considerably lower than those of the heterogeneous rhodium catalysts. We therefore discuss in detail only the results for the rhodium catalysts.

4.2. Homogeneous or heterogeneous catalysis?

As can be seen in Fig. 3, the activity of the heterogeneous catalysts was a function of the metal leached from the support. Furthermore, the liquid product containing the metal leached from the support was catalytically active. Thus, in the first reaction cycle the activities of the heterogeneous catalysts must be due to the leached metal functioning as homogeneous catalysts. In the experiments involving consecutive reaction cycles the metal content of Rh/A.C.(C) in the second and third reaction cycles remained constant at 2% (half of the original metal content) and the hydrocarbonylation yield was 2% (see Fig. 4). The yield was about 5% of that obtained with the homogeneous catalyst with the same metal concentration. The activity detected in the second and third reaction cycles could be attributed to heterogeneous catalysis. In general, the heterogeneous catalysts have exhibited lower activity and poorer selectivity than their respective homogeneous counterparts [23]. In gas phase methanol carbonylation, Scurrell [23] found the turnover numbers (TON) of heterogeneous rhodium catalysts to be 1–3% of the TON of the 'homogeneous' unsupported rhodium metal salts [23]. The activity of our heterogeneous catalysts thus is in agreement with Scurrell. However, the origin of the activity detected during the second and third reaction cycles is unclear. Even though the metal content of the product solution in the second and third reaction cycles with Rh/A.C.(C) was below the detection limit (< 1 mg/l), trace amounts of metal might have been present to produce the observed hydrocarbonylation conversion of 2%. Thus, the precision of the metal analysis of the catalyst and the product solution was not good enough to identify the source of the detected hydrocarbonylation activity.

Liquid phase hydrocarbonylation of methanol with heterogeneous catalysts has only infrequently been studied. One comparable investigation is that of Tempesti et al. [10]. The authors observed moderate catalyst activity with SiO_2, Al_2O_3, La_2O_3 and ThO_2 supported rhodium catalysts. In their view, the equivalence of the rates for the homogeneous and supported catalysts seems to indicate that similar sites control the reaction pathway. In the light of our results the similar performance of the homogeneous and oxide supported catalysts might also be due to the insufficient stability of the metal on the support. That homogeneous catalysis was involved is also supported by the widely accepted opinion that the oxide supported catalysts are inactive in methanol hydrocarbonylation and carbonylation under gas phase conditions [16–18].

4.3. Stability of heterogeneous catalysts

The stability of the metal on the activated carbon support is influenced both by the nature of the metal and by the origin and characteristics of the activated carbon support.

The stability of metals on the Norit Rox 0.8 activated carbon differed considerably. Namely, 85% of the total metal content was leached from the support from Ru/A.C.(N) whereas only 30% was leached from Rh/A.C.(N). Therefore, the interaction of ruthenium with the support was weaker than that of rhodium, and in fact too weak to merit any further studies on the stability of the Ru/A.C. catalysts. Thus, only the stability of rhodium on different types of activated carbons (N, C, J&M and COMM) is discussed in more detail.

The metal content of Rh/A.C.(COMM) decreased gradually in consecutive reaction cycles, whereas with Rh/A.C.(C) there was no detectable change in the metal content during the second and third reaction cycles. In fact, the metal losses were greatest from the catalysts with the finest metal particles. Therefore the decrease of metal content on Rh/A.C.(COMM) may most plausibly be linked to the extraction of metal from the support in an intense metal–solution interaction.

The metal–solution interaction is influenced by dispersion. The metal dispersion is reported to depend on the pore structure, surface area and nature of the surface groups of the carbon support [24]. In our case the surface area was constant, so that only the pore structure and nature of the surface groups could have influenced the dispersion. The pore structure could also influence the diffusion of the reactants and products and thereby affect the extraction of the metal from the support [24]. The measured pore sizes did not, however, correlate in any way with the dispersion or the stability of the metal on the support. We assume therefore that the pore structure did not appreciably influence the leaching of the metal from the support.

With the Rh/A.C.(C) catalyst there was no detectable change in the metal content during the second and third reaction cycles, i.e. in both cases the metal content of the catalyst was 2 wt-%. This might indicate that some of the metal on the support was more strongly bound and could withstand the severe reaction conditions. That being so, the metal–support interaction must have been a more important factor for the stability than the contact between the metal and the solution.

The metal–support interaction has been related to the amount of oxygen groups on the surface of carbon [24–26]. The relative Rh/C and C/O concentrations of our catalysts were determined by XPS. The extent of the reduction of rhodium metal was virtually 100% and the oxygen signal that was detected presumably belonged to the surface oxygen groups of the support or to the oxygen groups attached during the catalyst preparation. In fact, the XPS results may indicate that the higher the oxygen content of the carbon support the higher the metal dispersion and the lower the stability of the metal. With an increase in the number of oxygen groups on the carbon support Prado-Burguete et al. [24,25] observed an increase in Pt metal dispersion, and Bishoff et al. [26] observed a decrease in the stability and activity of Ni/A.C. in the gas-phase carbonylation of methanol. Similarly, in our study the amount of oxygen containing surface groups appeared to have a greater effect on the stability of the metal on the support than did the physical properties of the support.

5. Conclusions

The activity of activated carbon supported rhodium and ruthenium catalysts was similar to that of the respective homogeneous precursors. The good activity of the supported catalysts evidently originated from the metal leached from the support and was therefore based on homogeneous catalysis. Hence, under the conditions of our experiments the stability of heterogeneous catalysts was insufficient and the activity was very low. The stability of the rhodium catalysts correlated with the metal dispersion and was most closely related to the oxygen content of the carbon support.

The poor selectivity to hydrocarbonylation products and the increased formation of dimethyl ether were primarily due to the insufficient concentrations of carbon monoxide and hydrogen in the liquid phase, especially with the ruthenium catalysts. To obtain higher CO and H_2 concentrations would require higher pressures. Under the more severe reaction conditions, however, the stability of the heterogeneous catalysts would be even lower. Perhaps these heterogeneous catalysts could be used in gas phase systems, where the partial pressures of the reacting components are easy to control and the leaching effect of the reaction medium may be less severe. In conclusion, the heterogeneous catalysts did not perform successfully in liquid phase methanol hydrocarbonylation, but may merit further study in the gaseous phase.

Acknowledgements

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