Some aspects on the losses of metal from the support in the hydrocarbonylation of methanol

M.E. Halttunen [a, *], M.K. Niemelä [a], A.O.I. Krause [a], A.I. Vuori [b]

[a] *Helsinki University of Technology, Department of Chemical Technology, Laboratory of Industrial Chemistry, P.O. Box 6100, 02015 Hut, Finland*
[b] *Kemira Agro Oy, Luoteisrinne 2, FIN-02270, Espoo, Finland*

Abstract

The stability of the Rh/C catalysts during hydrocarbonylation of methanol was studied by subjecting the catalysts to the individual reactants as well as their combinations in vapour phase (250°C and 1 bar) and in liquid phase (220°C, 120 bar). Neither methanol and methyl iodide, nor hydrogen or carbon monoxide alone effectuated metal leaching, but hydrogen did induce agglomeration of metallic species. In the vapour phase reaction, 20–30% of the metal was lost at 1 bar, and 50% at 15 bar, and in liquid phase the losses were 20–70% at 120 bar, i.e., the losses increased with increasing reaction pressure. Nevertheless, the activated carbon support affected product selectivity in the vapour phase conditions at 1 bar. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst stability; Methanol hydrocarbonylation; Rhodium/activated carbon

1. Introduction

Cobalt catalysed homogeneous hydrocarbonylation and carbonylation date back to the 1940s [1,2] and 1960s [3], but nevertheless, the homogeneous rhodium catalyst, developed in the late 1960s, dominates in commercial carbonylation known as the Monsanto process [4]. Since 1970s, extended research efforts have been directed to heterogenising the homogeneous catalysts [5–14].

Catalysts have been supported on alumina [6,8], silica [6,7], zeolites [10,11] and carbon [5,12–14]. Out of these, the activated carbon support has been by far the best support for homologation and carbonylation catalysts [6,9]. Omata et al. [15] suggested that the role of carbon was to suppress hydrogen adsorption, promote multiple adsorption of carbon monoxide, and inhibit the dissociation of adsorbed carbon monoxide. In accordance, we have found Rh/C highly active in the liquid [16] and vapour phase [17] hydrocarbonylation of methanol.

Although the heterogeneous catalysts have often been active, their stability has been poor

---

* Corresponding author. Present address: Helsinki University of Technology, Department of Forest Technology, Laboratory of Forest Products Chemistry, P.O. Box 6300, 02015 Hut, Finland. Tel.: +358-9-451-4235; Fax: +358-9-451-4259; E-mail: mari.halttunen@hut.fi

[16,18] or remained uncommented [7,8]. In the liquid phase, the losses of metals from the support have apparently, at least in part, been due to the formation of soluble metal carbonyls [19–21]; homogeneous catalysts can be prepared in situ from various starting materials. The insufficient stability may, however, also be due to weak metal–support interaction or due to the acidic character of the liquid reaction medium [22].

In this work, the effects of the reactants and reaction conditions on the stability of the Rh/C catalysts were determined in an attempt to provide tools for minimizing the losses and thus, to facilitate the development of a truly heterogeneous hydrocarbonylation catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

Rh/C catalysts were prepared [23] by incipient wetness impregnation, using an aqueous solution of $Rh(NO_3)_3$ (Fluka). Peat-based Norit Rox 0.8 (N), coconut-based carbon (C) from Johnson Matthey, and wood-based Takeda Shirasaki (T) were used as catalyst supports, as described in more detail in our previous publications [16,17,23]. The catalysts were calcined at 400°C under nitrogen flow for 3 h, and reduced under $H_2:N_2$ (1:2) flow for 1 h. A commercially available, activated carbon supported rhodium catalyst, Rh/C(COMM) was tested as a reference catalyst.

The metal contents of the catalysts were determined by flame atomic absoption (FAAS) using a Varian SpectrAA-600 with N_2O/C_2H_2-flame. Prior to analysis, the samples were dissolved in aqua regia in closed vessels. The surface topography of the catalysts was determined by scanning electron microscopy, using a Cambridge S360 equipped with EDS-detector. The samples were characterized at tension voltages of 15 and 20 kV, and the results were expressed as secondary electron images (SEI).

2.2. Reaction experiments

The effect of individual reactants on the characteristics of the catalysts was evaluated. The pre-reduced catalysts were treated with methanol and methyl iodide under nitrogen pressure in the vapour phase at atmospheric pressure and 250°C, and in the liquid phase in an autoclave at 120 bar and 220°C. The catalysts were also treated with hydrogen or carbon monoxide in a tubular reactor at 250°C and atmospheric pressure for 12 h in order to determine the influence of the gaseous reactant on the catalyst structure. The SEM images were taken before and after the treatments.

In our previous paper [17], the vapour phase carbonylation reaction (methanol, methyl iodide and carbon monoxide) and hydrocarbonylation reaction (methanol, methyl iodide, carbon monoxide and hydrogen) were studied at 250°C and atmospheric pressure in a continuous flow reactor. We now provide the SEM images taken after these reactions. In the present work, the hydrocarbonylation reaction was investigated at 15 bar, the partial pressures of methanol, methyl iodide, carbon monoxide and hydrogen being 0.48, 0.048, 9.7 and 4.8 bar, respectively. The product stream was cooled (-1°C) and the liquid products collected were analysed using a gas chromatograph with flame ionisation and thermal conductivity detector. The metal contents of the catalysts were determined, and the SEM images recorded. To provide an in-depth analysis of the effect of reaction conditions, we also characterized the catalysts reacted in the liquid phase using SEM, in an autoclave at 220°C and 120 bar [16].

3. Results and discussion

First of all, the effects of all reactants were determined separately in the vapour phase. Under atmospheric pressure of hydrogen alone at 250°C, metal was not lost from the support, although it was mobilized, as evidenced by agglomeration, see Fig. 1c. In regard to agglom-
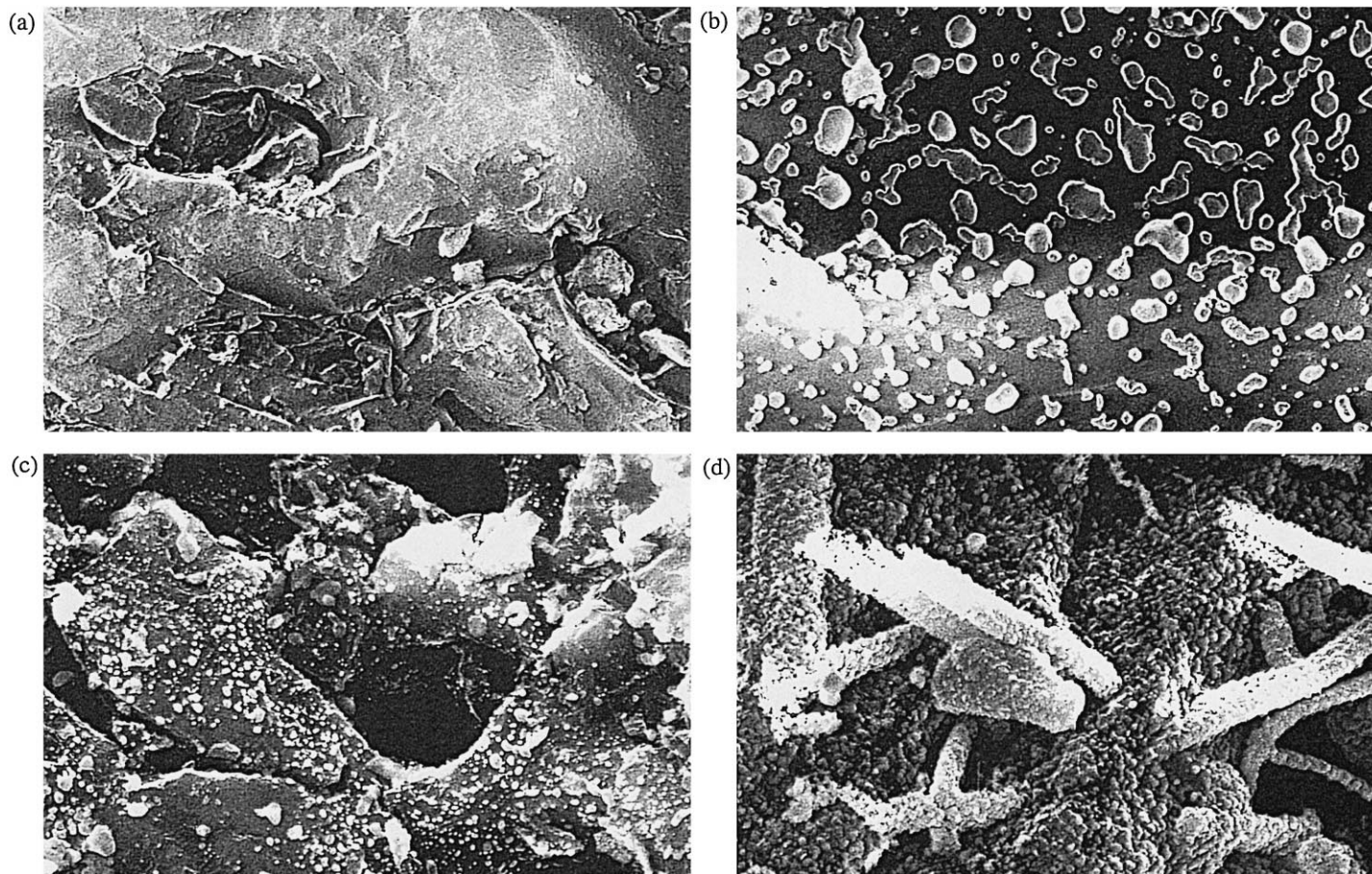
Fig. 1. SEM/SEI images of catalysts. (a) Fresh Rh/C(COMM) after reduction, (b) Rh/C(COMM) after methyl iodide, methanol and nitrogen treatment at 250°C for 24 h and (c) Rh/C(COMM) after hydrogen treatment at 250°C for 24 h, (d) Rh/C(COMM) after carbon monoxide treatment at 250°C for 24 h.
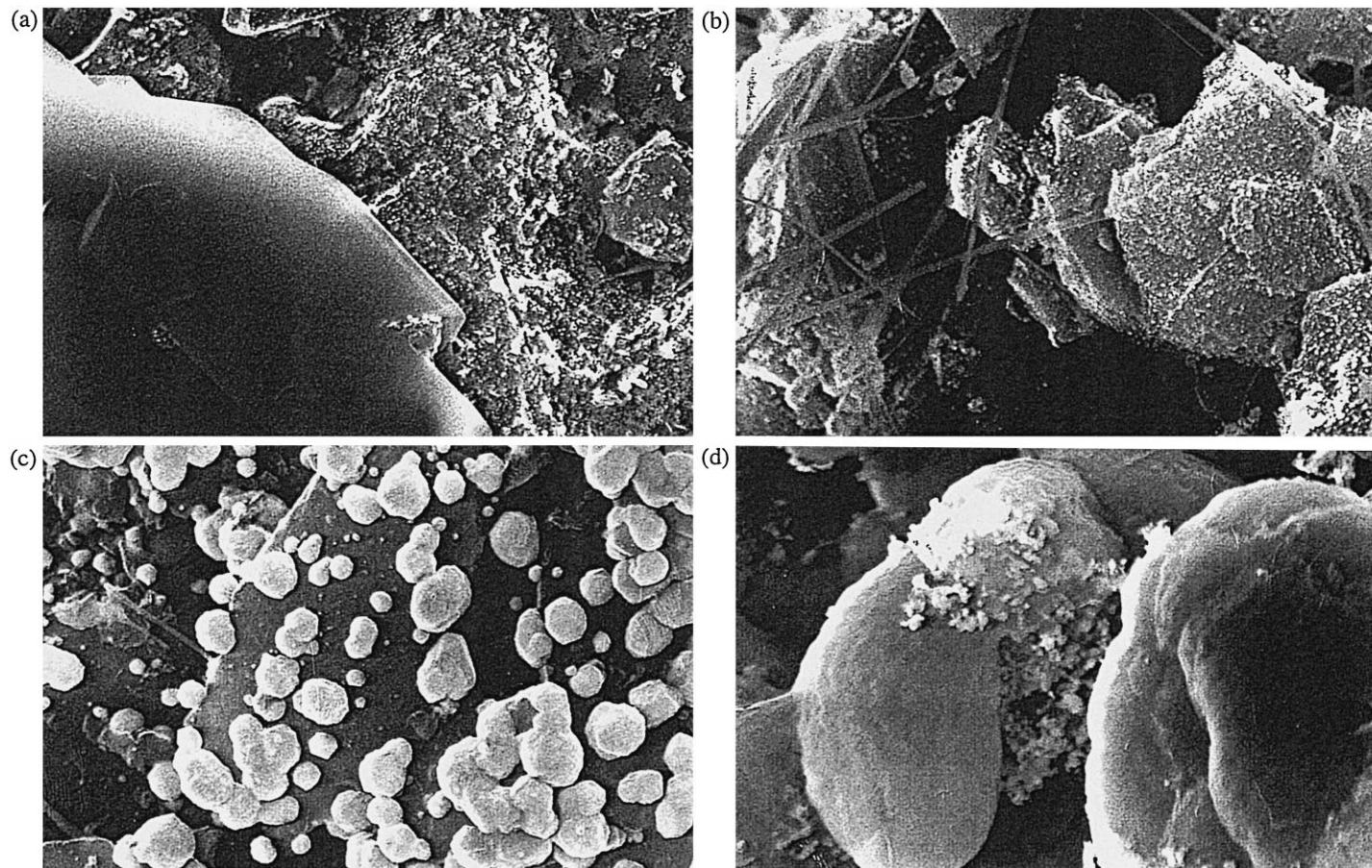
Fig. 2. SEM/SEI images of catalysts. (a) After hydrocarbonylation at 1 bar, (b) after carbonylation at 1 bar, (c) after hydrocarbonylation at 15 bar, (d) after carbonylation at 15 bar.

eration, Moreno-Castilla et al. [24] have reported that as a result of cobalt catalysed hydrogasification of the support, cobalt particles agglomerate on a carbon support at 500°C during reduction. Since the hydrogasification activity of the transition metals is reported to decrease in the order Rh ≥ Ru ≥ Ir > Pt > Ni ≫ Pd ≥ Co ≥ Fe, and it occurs below 200°C in case of the most active metals [25], we presume that the agglomeration was due to rhodium catalysed hydrogasifigation of the support.

Under atmospheric pressure of CO alone, no losses of metal were observed, and the catalyst appeared very different from its hydrogen treated counterpart, see Fig. 1c and d. Evidently, rhodium agglomerated after hydrogen treatment, whereas after CO treatment, rhodium was present in the form of small particles that formed large needle-like crystals. The crystals were identified as rhodium by SEM/EDS.

Under the action of methanol and methyl iodide (in a nitrogen atmosphere), metal was not lost from the support, but slight agglomeration was observed (Fig. 1b). Thus, none of the reactants alone induced loss of Rh from the support, but the species were mobilized in the presence of hydrogen and reactants (agglomeration). The simulations by Aspen also confirmed that the reactants (at 1 and 15 bar) were in gaseous form.

In the carbonylation reaction, the losses of metal from the support were approx. 30%. The surface contained long and thin thread-like rhodium species, similar to the species after CO treatment, see Figs. 1d and 2a. In carbonylation, the activity of the catalysts remained quite stable, see Fig. 3. Thus, the results indicate that the decrease in activity of the Rh/C catalysts is not substantial in the case of CO induced needle-like species. Fujimoto et al. [12] have assumed that the Ni/C reacts with CO to form nickel carbonyls, which decompose to redisperse the metal over the catalyst surface, thus preventing catalyst deactivation by metal agglomeration.

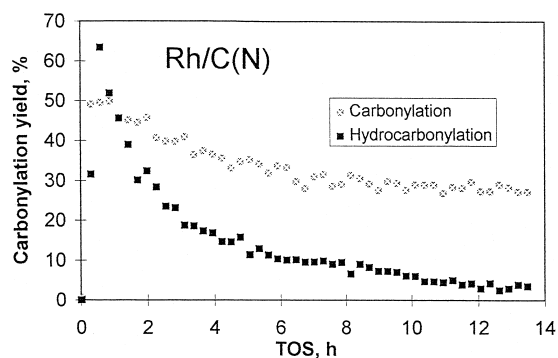Under the action of all reactants at atmospheric pressure, i.e., in the hydrocarbonylation

Fig. 3. Catalyst yield in (a) hydrocarbonylation and (b) carbonylation as a function of reaction time.

reaction, the losses of rhodium were 20–30% [17]. Thus, the losses clearly originated from the combined action of reactants, reactive intermediates or products. In accordance, the activity of the catalysts in the vapour phase reaction decreased 50–90% during the reaction [17]. However, the decrease in activity was not directly proportional to the amount of metal lost from the support, but was rather related to hydrogen induced metal agglomeration [17,23]. This assumption is confirmed by the SEM micrographs (see Fig. 2). Evidently, the rhodium particles are agglomerated in the presence of hydrogen and, as a result of agglomeration, the activity decreases dramatically, as discussed in more detail in our previous paper [17]. In agreement with this, Fujimoto et al. [12] have also reported that metal agglomerates and the activity declines in the presence of hydrogen on Ni/C catalysts.

An increase in reaction pressure from 1 bar to 15 bar increased the activity and metal agglomeration (Fig. 2c and d), as well as the metal losses from the support (Table 1). Thus, the higher losses of rhodium on the surface can be related to the higher partial pressure of carbon monoxide, i.e., the enhancement of the formation of rhodiumiodocarbonyls and other organometallic rhodium species. The volatility of the active rhodium species or rhodium containing intermediates is not, however, a standard text book issue. We may estimate the volatility

Table 1

Metal contents of catalysts before and after the treatments and reactions at 250°C and atmospheric pressure unless otherwise stated

Catalysts	Metal contents (wt.%)		
	Fresh catalysts	Catalysts after treatment/reaction	Decrease in Rh content (%)
Rh / C(N)			
H_2/CO treatment	5.3	5.3	< 10
MeOH + MeI + N_2	5.3	5.2	< 10
Hydrocarbylation[c] [17]	5.3	4.0	25
Carbonylation[c]	5.3	4.1/1.5[a]	25/70
Carbonylation at 15 bar	5.3	1.0	80
Hydrocarbonylation at 120 bar[d] [16]	4.2	3.1	30
Rh / C(C)			
MeOH + MeI + N_2	7.8	7.8	< 10
Hydrocarbonylation [17]	7.8	5.6	30
Carbonylation at 15 bar	7.8	3.6[b]	50
Hydrocarbonylation at 120 bar[d] [16]	4.5	2.1	50
Rh / C(T)			
MeOH + MeI + N_2	6.7	6.7	< 10
Hydrocarbonylation [17]	6.7	4.5	30
Rh / C(COMM)			
H_2/CO treatment	5.0	5.0	< 10
MeOH + MeI + N_2	5.0	5.0	< 10
Hydrocarbonylation	5.0	3.2	35
Carbonylation	5.0	3.0	40
Hydrocarbon at 15 bar	5.0	2.4	50
Carbonylation at 15 bar	5.0	1.0	80
Hydrocarbonylation at 120 bar[d] [16]	5.0	1.8	65

[a] With 0.3 and 1 bar CO partial pressures, respectively.
[b] TOS = 8 h.
[c] At atmospheric pressure.
[d] In the liquid phase.

of the iodine containing species from a knowledge of the respective chlorinated species. The sublimation temperature of $Rh(CO)_2Cl_2$ is 125°C, and therefore, it has been used as a metal carbonyl precursor in the preparation of catalysts by sublimation [26]. Also, $Rh(CO)_2$-(acac) and related complexes are excellent precursors for their plasma enhanced deposition due to high volatility [27,28], i.e., volatile substituted rhodium carbonyls are known in the literature. For further comparative purposes, we note that the b.p. of MeCl is −24.2°C, and that of MeI is 42.4°C. Thus, we presume that the sublimation temperature of $Rh(CO)_2I_2$ is higher than that of $Rh(CO)_2Cl_2$ by at least 60°C, being

approx. 200°C. Consequently, $Rh(CO)_2I_2$ may be volatile at the reaction temperatures used during the gaseous phase reaction.

Under less moderate conditions, in the presence of higher partial pressures of carbon monoxide and hydrogen in the liquid phase, the losses of metal from the support were high 20–70%. The results thus provided more evidence for the formation of soluble rhodium species under the action of synthesis gas through in situ formation of catalytic species [29,30], since the liquid media alone did not leach the metal from the support. However, the formation of the soluble active component may not be the only source of soluble compounds. It is also

possible that some reaction intermediates, or the products formed, may dissolve rhodium from the support and thereby enhance leaching. In case of 1-hexene hydroformylation, for example, the dissolution of active species has been related to the presence of product aldehydes [31,32]. We have also observed [19] losses of cobalt from Co/SiO_2 under typical hydroformylation conditions (150°C, 100 bar), in the presence of product aldehyde and nitrogen only. Thus, it is highly likely that, in particular, some acidic products may also contribute to the dissolution.

4. Summary and conclusions

The paper describes the changes occurring on the Rh/C catalysts during contact with individual reagents, as well as during vapour or liquid phase hydrocarbonylation of methanol.

In the vapour phase (1 bar, 250°C), rhodium formed large plate-like agglomerates under hydrogen flow, whereas needle-like crystals were formed under CO flow. During vapour phase reaction (1 bar, 250°C), the activity decrease was considerably higher during hydrocarbonylation than during carbonylation although 30% of the metal was lost in both cases. Thus, the hydrogen induced agglomeration affected the catalyst activity more than did the losses of metal. On the other hand, the losses of metal increased (max. 70%) with increasing pressure (max. 120 bar) being therefore due to the soluble rhodium species formed through the combined action of the reactants, reactive intermediates and/or reaction products.

To summarise, hydrogen induced agglomeration as well as losses of rhodium under the combined action of methanol, methyl iodide and synthesis gas seemed inevitable. Nevertheless, under mild conditions the activated carbon support clearly affected the product selectivity, and thus, it might be interesting to investigate whether modification of the support could improve the stability.

References

[1] I. Wender, J. Am. Chem. Soc. 71 (1949) 4160.
[2] W. Keim, Catalysis in C1 chemistry, Reidel, Dordrecht, 1983.
[3] J. Gauthier-Lafaye, R. Perron, Methanol and carbonylation, Rhone-Poulenc Recherhers, Coubervoie, 1987.
[4] J.F. Roth, J.H. Craddock, A. Hersman, F.E. Paulik, Chem. Tech. (1971) 600.
[5] K.K. Robinson, A. Hershman, J.H. Craddock, J.F. Roth, J. Catal. 27 (1972) 389.
[6] K. Fujimoto, T. Shikada, K. Omata, H.-O. Tominga, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 429.
[7] E. Tempesti, A. Kiennemann, S. Rapagna, C. Mazzocchia, L. Giuffre, Chem. Ind. (1991) 548.
[8] A. Krzywicki, G. Pannetier, Bull. Soc. Chim. France, (1977) 64.
[9] K. Fujimoto, T. Setoyama, T. Tominga, Chem. Lett. (1983) 1811.
[10] N. Takashi, Y. Orisaka, T. Yashima, J. Catal. 59 (1979) 61.
[11] B. Christensen, M.S. Scurrell, J. Chem. Soc., Faraday Trans. I 73 (1977) 2036.
[12] K. Fujimoto, S. Bishoff, K. Omata, H. Yagita, J. Catal. 133 (1992) 370.
[13] S. Bischoff, H.-E. Maneck, H. Preiss, K. Fujimoto, Appl. Catal. 75 (1991) 45.
[14] T.-C. Liu, S.-J. Chiu, Ind. Eng. Chem. Res. 33 (1994) 1674.
[15] K. Omata, H. Mazaki, H. Yakita, K. Fujimoto, Catal. Lett. 4 (1990) 123.
[16] M.E. Halttunen, M.K. Niemelä, A.O.I. Krause, A.I. Vuori, J. Mol. Catal. A: Chemical 109 (1996) 209.
[17] M.E. Halttunen, M.K. Niemelä, A.O.I. Krause, A.I. Vuori, The influence of the activated carbon support on Rh/C catalysts: II. Catalytic behaviour, Appl. Catal., accepted.
[18] J.K. Stille, React. Polym. 10 (1989) 165.
[19] T.A. Kainulainen, M.K. Niemelä, A.O.I. Krause, J. Mol. Catal. A: Chemical 122 (1997) 39.
[20] J. Falbe, Synthesen mit Kohlenmonoxyd, Springer, Berlin, 1967, p. 212.
[21] M. Orchin, L. Kirch, I. Goldfarb, J. Am. Chem. Soc. 78 (1956) 5450.
[22] R.S. Drago, E.D. Nyberg, A. El Amma, A. Zombek, Inorg. Chem. 20 (1981) 641.
[23] M.E. Halttunen, M.K. Niemelä, T. Vaara, A.O.I. Krause, A.I. Vuori, The influence of the activated carbon support on Rh/C catalysts: I. Catalyst characterization, Appl. Catal., accepted.

[24] C. Moreno-Castilla, M.A. Ferro-Garcia, J. Rivera-Utrilla, J.P. Joly, Energy and Fuels 8 (1994) 1233.

[25] A. Tomita, Y. Tamai, J. Catal. 27 (1972) 292.

[26] M.P. Keyes, K.L. Watters, J. Catal. 110 (1988) 96.

[27] E.B. Flint, J. Messelhäuser, H. Suhr, Appl. Phys. A 53 (1991) 430.

[28] A.C. Jesse, J.M. Ernsting, D.J. Stufkens, K. Vrieze, Thermochim. Acta 25 (1978) 69.

[29] R.S. Dickson, Homogeneous Catalysis with Compounds of Rhodium and Iridium, Reidel, The Netherlands, 1985, p. 278.

[30] T.W. Dekleva, D. Forster, Advances in Catalysis, Vol. 34, 1986, Academic Press, Orlando, pp. 81–130.

[31] D.L. Hunter, S.E. Moore, P.E. Garrou, R.A. Dubois, Appl. Catal. 19 (1985) 259.

[32] L. Alvila, J. Pursiainen, J. Kiviaho, T.A. Pakkanen, O. Krause, J. Mol. Catal. 91 (1994) 335.