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The role of promoter metals in the hydrocarbonylation of methanol over active carbon supported cobalt catalysts

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Abstract

The role of the promoter metals palladium and ruthenium in the mechanism of the hydrocarbonylation (reductive carbonylation) of methanol over cobalt/active carbon catalysts has been investigated. It has been found that the reduction steps on active Co sites are strongly affected by activated hydrogen transferred from promoter metal particles. Several indications for the existence and importance of hetero-bimetallic centers have been obtained by comparing activities and selectivities of mechanical mixtures of monometallic catalysts, of catalysts prepared by co-impregnation using different precursors and of mixed-metal cluster-derived catalysts. The close neighborhood of promoter metal and cobalt centers seems to be a precondition for the cooperative carbonylation and hydrogen activation, and spillover does not play an important role in the transfer of activated hydrogen. The role of the promoter metals may change with the loading. For example, ruthenium supported on active carbon showed a considerable hydrocarbonylation activity at low loadings.

Keywords: Cobalt; Hydrocarbonylation; Methanol; Ruthenium; Supported catalysts

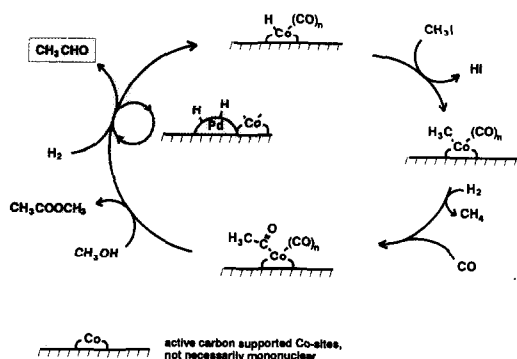
1. Introduction

Cobalt-catalyzed reactions with synthesis gas like hydroformylation, hydrocarbonylation (reductive carbonylation) and Fischer–Tropsch synthesis [1–4] can be significantly promoted by electron-rich transition metals, which are known for their high activity in hydrogenations. Synergistic effects between Co and Pd, Pt or Ru have been observed in both homogeneous and heterogeneous catalysis [5–11]. It is generally accepted that the promoter metals enhance hydrogen activation steps, but a clear distinction between the alternatives of an intramolecular hydrogen trans-

fer at hetero-bimetallic centers or of an intermolecular hydrogen transfer between different mobile catalytic centers is difficult to make, even if heteronuclear cluster precursors and mixtures of salt precursors are compared in liquid phase reactions. Bimetallic synergies found for the hydroesterification [7], in which hydrogen is not consumed, suggest that the role of the hydrogenation active metals may be more complex.

The mobility of the metals on supported catalysts is much lower than in the liquid phase and intermolecular hydrogen transfer by mobile metal hydrides as discussed in homogeneous catalysis can be neglected. We tried to gain a better understanding of the bimetallic effects by investigating the hydrocarbonylation of methanol to acetalde-

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Scheme 1. Catalytic cycle of the methanol hydrocarbonylation.

hyde on heterogeneous catalysts in the vapor phase. Unlike carbonaceous materials, oxidic supports like silica or alumina suppressed the carbonylation activity of cobalt [10,11] and thus active carbon (A.C.) was employed as the support material for the Co–Pd and Co–Ru catalysts presented in this work. Some aspects of the reaction network on Co/A.C. catalysts, considering the established reaction mechanism in the liquid phase [3,8], are illustrated in Scheme 1. Co–methyl intermediates are formed with the promoter methyl iodide (MeI), and subsequent methyl group migration gives cobalt–acetyl species. Both the hydrogenolysis and nucleophilic attack of methanol induce the reductive elimination of acetyl groups to form acetaldehyde and methyl acetate respectively. Transition metals, which are more active for hydrogen activation than Co, enhance the hydrogenolysis of Co–acetyl species and accelerate the hydrocarbonylation route. Hydrogenolysis of Co–methyl intermediates results in the formation of methane and should be affected by the promoter metals. Furthermore, increasing the partial pressure of the MeI promoter has been found to enhance the carbonylation route but to decrease the acetaldehyde selectivity [10,11]. The reductive removal of iodide ligands from supported Co species appears essential for the hydrocarbonylation and should also be promoted by metals like Pd or Ru.

Compared to co-impregnated bimetallic catalysts, mixed-metal cluster-derived (MMCD) catalysts [12–14] should hold more bimetallic

ensembles. If the direct neighborhood of hydrogenation-active and carbonylation-active sites is a necessary condition for synergisms, MMCD catalysts can be expected to be more active than co-impregnation catalysts. Catalysts prepared with hetero-bimetallic clusters of varying metal composition should furthermore differ from their co-impregnated counterparts with respect to activity and selectivity. The investigation of a row of co-impregnated Co–Pd, Co–Ru catalysts and active carbon supported Co–Pd and Co–Ru clusters like $\text{HRu}_3\text{Co}(\text{CO})_{12}$, $\text{Ru}_2\text{Co}_2(\text{CO})_{13}$, and $\text{HRuCo}_3(\text{CO})_{12}$ was aimed at the clarification of this problem and at a better understanding of the bimetallic catalysis of the hydrocarbonylation of methanol on supported catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

$\text{Ru}(\text{acac})_3$, $\text{Ru}_3(\text{CO})_{12}$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 , $[\text{Pd}(\text{OAc})_2]_3$ (Alfa Products), [1-2-bis(diphenylphosphino)ethane (DPPE)] PdCl_2 , $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich Chem. Co.), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka), silica gel (Kalichemie), alumina, active carbon, methanol (Merck) were used as delivered. All the hetero-bimetallic clusters investigated were prepared via established literature procedures: $\text{HCoRu}_3(\text{CO})_{13}$ was prepared with $\text{Ru}_3(\text{CO})_{12}$ according to [15], but $\text{Na}[\text{Co}(\text{CO})_4]$ [16] was employed instead of the K salt. Red–brown crystals were isolated in 53% yield after chromatography. $\text{Na}[\text{Co}(\text{CO})_4]$ and $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ were used as starting materials for the synthesis of $\text{Co}_2\text{Ru}_2(\text{CO})_{13}$ [17]. The intermediate $\text{RuCo}_2(\text{CO})_{11}$ was not isolated, but its hexane solution was heated up to 65°C for 3 hours and after the separation of $\text{Co}_2(\text{CO})_8$, concentration and cooling, black crystals were obtained in 40% yield. $\text{H}[\text{RuCo}_3(\text{CO})_{12}]$ was prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}[\text{Co}(\text{CO})_4]$ [18]. The intermediate $\text{Na}[\text{RuCo}_3(\text{CO})_{12}]$ was converted with H_3PO_4 in aqueous solution without further isolation to form $\text{H}[\text{RuCo}_3(\text{CO})_{12}]$ in

38% isolated yield. $[\text{DPPE}]\text{PdCl}_2$ and $\text{Na}[\text{Co}(\text{CO})_4]$ were converted to $[\text{DPPE}][\text{PdCo}_2(\text{CO})_7]$ according to [6].

MMCD catalysts were prepared by impregnation of active carbon with CH_2Cl_2 solutions of the according cluster compounds. THF was employed as solvent for catalysts derived from $[\text{Pd}(\text{OAc})_2]_3$. The chlorides and also $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in water before impregnation. Several halogenide-free Co–Pd/A.C. catalysts were prepared by impregnation of active carbon with $\text{Pd}(\text{OAc})_2/\text{THF}$, drying, and subsequent impregnation with aqueous $\text{Co}(\text{OAc})_2$ solutions. One catalyst was prepared by reaction of active carbon supported $\text{Pd}(\text{OAc})_2$ with an aqueous solution of $\text{Na}[\text{Co}(\text{CO})_4]$ and subsequent drying. Catalysts derived from the air-sensitive clusters were dried by evaporation at 120°C ; the other catalysts were dried at 120°C in an air oven. Metal compositions of the clusters have been confirmed by XRF measurements (SEA 2010 Seiko Instruments). Total metal loading varied between 0.1 and 4 wt.%. Metal loadings measured by XRF, and for monometallic Co and Pd catalysts determined by complexometric titration, were found to be in good agreement with the theoretical values. For the XRD measurements (Cu-K α , Ni-filtered and Co-K α , Fe filtered) the fresh and spent catalysts were pretreated with H_2 or Ar and treated with paraffin oil to avoid extensive air contact. A conventional glass apparatus connected with on-line GC and a Shimadzu QP 1500 (70 eV) was used for temperature programmed reaction of metal–methyl species (TPR–GC) and temperature programmed reduction (TPR–MS) respectively. The heating rate of both temperature-programmed methods was 6 K/min. N_2 physisorption was carried out with a Sorptomatic 1900 (Fisons).

2.2. Catalytic measurements

The catalysts were investigated without a further activation procedure. A continuous flow type reaction apparatus with a fixed bed was used for the hydrocarbonylation reactions. The reactor

(made of a stainless steel tube, inner diameter 6 mm) was heated up to reaction temperature in an Ar stream under atmospheric pressure. Syn gas was fed to build up the reaction pressure of 5 MPa. The mixture of methanol and the promoter Methyl iodide was introduced with a Shimadzu LC 10AD HPLC pump. Product gas analysis was conducted with an on-line GC (Hewlett Packard 5890 II) using $3\text{ m} \times 0.32\text{ mm}$ DB wax connected with a $50\text{ m} \times 0.32\text{ mm}$ HP-5 capillary column and running with a temperature program (5 min 32°C , 10 min 19 deg/min). Yields and selectivities of the products were calculated based on the consumed methanol [19]. To avoid excessive condensation and side reactions, conversions were generally kept below 15%.

3. Results and discussion

Hydrocarbonylation, affording acetaldehyde (AcH) and its dimethyl acetal (DMA), carbonylation, leading to methyl acetate (AcOMe), and methane formation were observed as the primary reactions at the applied reaction conditions. Ethanol was generally obtained in traces, displaying that the promoting effects of Pd or Ru are not limited to the reduction of acetaldehyde to ethanol. Hydrogenation of CO and AcOMe did not occur under the applied conditions. As expected, synergistic effects due to the promoter metals Pd and Ru have been observed (Fig. 1, 7) and the preparation method did influence the product composition. One key step of the reaction is the reductive elimination of Co–acetyl species leaving low-valent Co- or Co-hydrido species. This reduction step and the reduction of methyl species are probably facilitated in the presence of Pd or Ru. Accordingly, halogenide-free systems showed generally higher activities than impregnation catalysts prepared from chlorides, demonstrating that the anions in the precursor salts influence number and structure of active sites formed under the reducing reaction conditions. The Co–Pd–MMCD catalyst derived from $[\text{DPPE}][\text{PdCo}_2(\text{CO})_7]$ and the catalyst prepared by surface reaction of

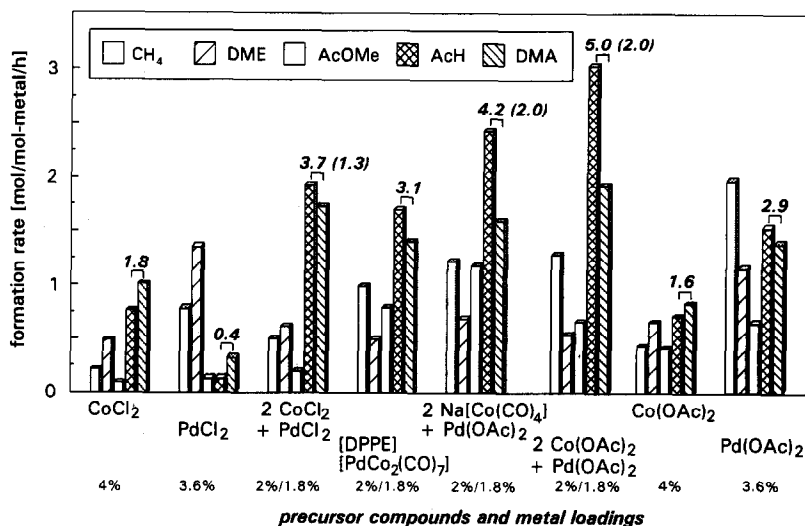


Fig. 1. Activities of active carbon supported mono- and bimetallic Co and Pd catalysts derived from different precursor compounds. The (bold, italic) numbers over the bars denote the total hydrocarbonylation activity, expected activities without synergisms are given in brackets. Reaction conditions: 180°C, 5 MPa, 400 mg catalyst, metal loading 2 wt.% Co, 1.8 wt.% Pd on bimetallic and 4 wt.% Co or 3.6 wt.% Pd on monometallic catalysts, $W/F = 1 \text{ g}_{\text{cat}} \cdot \text{h/mol}$, $\text{H}_2/\text{CO}/\text{CH}_3\text{OH}/\text{CH}_3\text{I} = 4/4/1/0.005$.

$\text{Na}[\text{Co}(\text{CO})_4]$ and $\text{Pd}(\text{OAc})_2$ have no superior features with respect to activity and acetaldehyde selectivity. This behavior could be caused by loading effects as discussed below. Interestingly, Pd also promoted the carbonylation to methyl acetate in the last mentioned catalysts.

3.1. Enhancement of the reducibility of Co

As shown in Fig. 2, the reducibility of the active carbon supported cobalt can be improved by metals such as Pd. $\text{PdCl}_2/\text{A.C.}$ is already reduced at about 120°C (curve a), the reduction of $\text{CoCl}_2/\text{A.C.}$ occurs at temperatures above 300°C; because the larger peak coincided with a water peak, the smaller first peak in plot b is assigned to (partly) dehydrated CoCl_2 . In the bimetallic CoCl_2 - $\text{PdCl}_2/\text{A.C.}$ catalyst (curve c), the reduction peak of the more noble metal shifted slightly to 140°C and a remarkable increase in the reducibility was observed for the supported CoCl_2 . The plateau between the two peaks could be explained by migration of reduced Pd particles to Co particles or by hydrogen spillover, but a distinction between these alternatives cannot be made on the base of the available data. As it will be shown

below, Co–Pd alloys can be formed from highly dispersed systems during reduction at elevated temperatures, proving the possibility of active metal migration.

Temperature-programmed reaction (TPR–GC) of spent catalysts with H_2 converts metal–methyl-, -methoxy and -acetyl species into methane (Fig. 3). Based on the assumption that only one of these groups is bonded per metal atom, high metal dispersions of 45, 75 and 60% were estimated for the Co/A.C., Pd/A.C. and Co–Pd/A.C. catalysts, respectively. This is in accord with

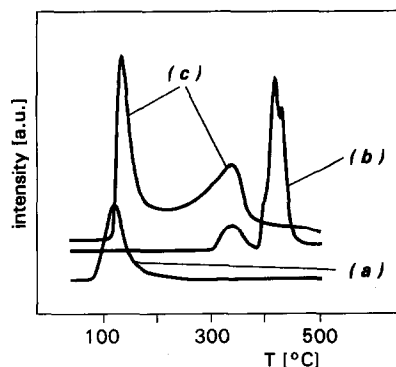


Fig. 2. Temperature programmed reduction of catalyst precursors: (a) $\text{PdCl}_2/\text{A.C.}$, (b) $\text{CoCl}_2/\text{A.C.}$, (c) $\text{PdCl}_2 + \text{CoCl}_2/\text{A.C.}$; 60 ml H_2/h , 6 K/min, plots for HCl released.

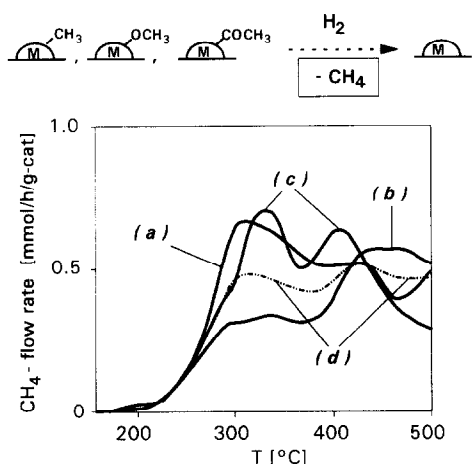


Fig. 3. Temperature programmed reactions with spent catalysts: (a) Pd/A.C., (b) CoCl₂/A.C., (c) PdCl₂ + CoCl₂/A.C., (d) 1:1-linear combination of the plots (a) and (b), 60 ml H₂/h, 6 K/min.

the results of XRD analysis, where no crystallites were detectable on spent catalysts. The shape of the TPR–GC plot for the bimetallic catalyst is different from any linear combination of those for the monometallic catalysts and might hint at the formation of hetero-bimetallic sites, which are more active than monometallic cobalt sites.

3.2. Methane formation as a probe reaction for the nature of the bimetallic effects

The fact that reducibility of supported metals can be enhanced by metals known for their high capability of hydrogen activation is already established [20–22], but does not explain how the hydrogenation-active and the carbonylation-active metal interact under the conditions of such a complex reaction like the hydrocarbonylation of methanol. Although methane formation is an undesired side reaction, it may provide useful information on the reaction mechanism. Generally, methane can be formed by proteolysis or hydrogenolysis of metal–methyl species; both alternatives are depicted in the left part of Fig. 4. To find out which process predominates, methanol-d₁, CH₃OD, was employed as the substrate of the reductive carbonylation. Interestingly, on the monometallic Co catalyst, prepared from CoCl₂, both processes hydrogenolysis and proteolysis

occurred in a ratio of 2:1. On the other hand, hydrogenolysis strongly dominated over the monometallic Pd/A.C. catalyst. The ratio of hydrogenolysis and proteolysis rates expresses the capability of active carbon-supported transition metals for hydrogen activation under carbonylation conditions. For example, the methane formation on Ni/A.C. catalysts proceeds mainly via proteolysis of Ni–methyl species [23] and hydrogen cannot be incorporated into the products even using synthesis gas (CO:H₂ = 1:1). The CH₄/CH₃D ratio of the bimetallic Co–Pd/A.C. catalyst was found to be similar to that of the monometallic Pd/A.C. catalyst, strongly suggesting that the hydrogen activation occurs mainly on palladium sites and activated hydrogen migrates to cobalt-carbonylation sites. Both steps must proceed much faster than hydrogenolysis on cobalt centers, if one considers that proteolysis, proceeding at about half the rate of hydrogenolysis on monometallic cobalt catalysts, is widely suppressed by Pd.

3.3. The role of the arrangement of Co and promoter metals

Filling layers of monometallic catalysts into the reactor is a useful technique to detect spillover phenomena [24] under reaction conditions, and in the present work, Co/A.C. and Pd/A.C. catalysts were applied for this purpose. Fig. 5 displays results of the experiments. As in all the other catalytic runs, the feed gas stream was led from the upper to the lower part of the tube reactor. Placing a Pd/A.C. layer over A.C. and Co/A.C. led to a slight increase in the methanation and hydrocarbonylation activity, which is probably caused by the specific activity of Pd (Fig. 1). It will be shown below that the role of the promoter metals is not merely the H₂ activation and depends on the loading.

Chemical analysis of fresh and spent catalysts showed no Pd loss over the vapor phase and the formation of bimetallic sites can be excluded in this layer arrangement. When the order of the monometallic catalyst layers was reversed (Co

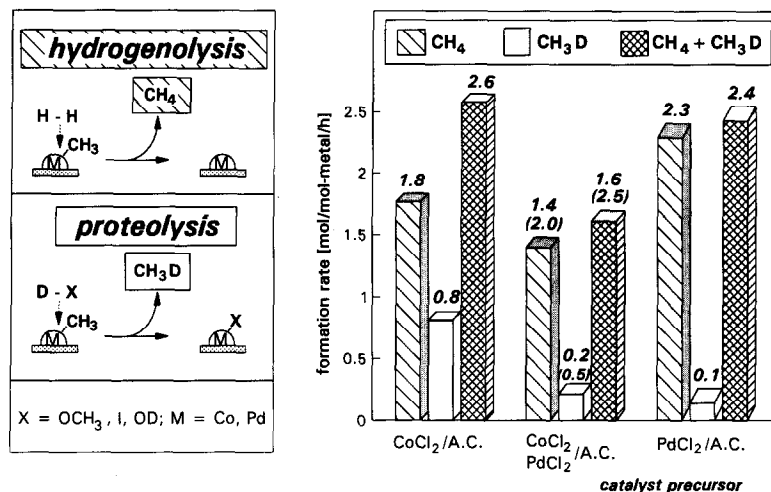


Fig. 4. Methane formation in the hydrocarbonylation of CH₃OD as a probe reaction. The (bold, italic) numbers over the bars denote the methane formation rates, expected rates without synergisms obtained from linear combinations are given in brackets. Reaction conditions: 195°C, 5 MPa, 400 mg catalyst, total metal loading 4 wt.%, $W/F = 1 \text{ g}_{\text{cat}} \cdot \text{h/mol}$, $\text{H}_2/\text{CO}/\text{CH}_3\text{OD}/\text{CH}_3\text{I} = 4.5/4.5/1/0.005$.

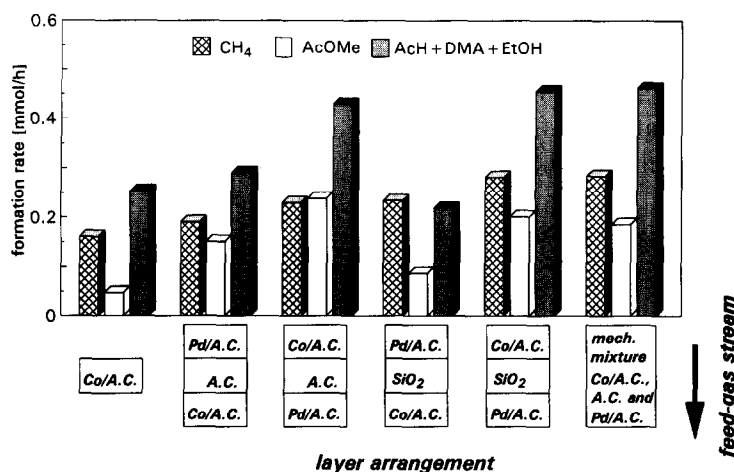


Fig. 5. Influence of the layer arrangement on the activity of catalysts derived from Co(OAc)₂ and Pd(OAc)₂. reaction conditions: 195°C, other conditions as stated in Fig. 1.

over Pd), the methane formation (CH₄), the carbonylation (AcOMe) and the hydrocarbonylation route (AcH + DMA + EtOH) were enhanced independent on the nature of the metal-free layer A.C., SiO₂ or Al₂O₃ (the last not presented in this picture) between the active phases. Cobalt losses of 2 wt.% metal from initial loadings of 4 wt.% within 24 h were observed at monometallic Co/A.C.. The vapor-phase migration of Co (probably via volatile carbonyls) to the Pd/A.C. layer seems to lead to the formation of bimetallic Co–Pd sites,

which are more active for the reductive carbonylation. The same activities and selectivities found for the arrangement Co over Pd, the mechanical mixture and the co-impregnated catalyst and the observation that the induction periods for mechanical mixtures are several times longer than those of the co-impregnated bimetallic systems support the assumption of heterobimetallic site formation, leading to a more effective transfer of activated hydrogen under carbonylation conditions. Moreover, hydrogen spillover over distances of several

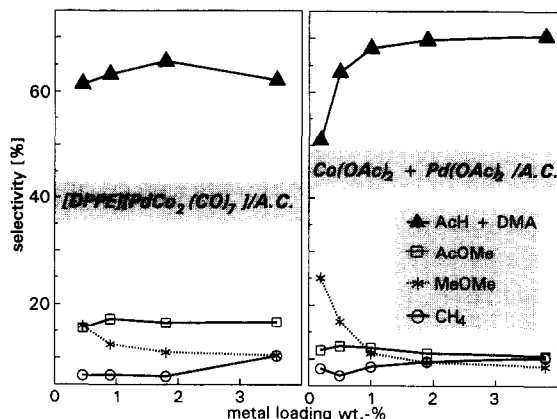


Fig. 6. Influence of the loading on the selectivities of active carbon supported catalysts derived from $[\text{DPPE}][\text{PdCo}_2(\text{CO})_7]/\text{A.C.}$ and from $\text{Co}(\text{OAc})_2$ and $\text{Pd}(\text{OAc})_2$; reaction conditions as in Fig. 1.

millimeters can be neglected because the positions of the layers containing Co or Pd in the gas stream did influence the activities.

If the close neighborhood between Ru, Pd and Co sites in the range of several Ångström is a necessary condition for the smooth transfer of the activated hydrogen from Ru or Pd to Co sites, MMCD catalysts should be superior to co-impregnated catalysts. Mixed metal-carbonyl clusters of Pd, Ru and Co appeared as suitable precursor com-

pounds and were impregnated on the carbonaceous support. As already mentioned, the supported $[\text{DPPE}][\text{PdCo}_2(\text{CO})_7]$ cluster did neither exhibit superior activity nor extraordinary aldehyde selectivity. While the selectivities on the MMCD catalyst did not alter significantly over a wider range of loadings (Fig. 6), the co-impregnated $\text{Co}(\text{OAc})_2\text{-Pd}(\text{OAc})_2/\text{A.C.}$ catalyst afforded lower acetaldehyde but constant methyl acetate selectivities at low loadings. The diminished synergistic effect is interpreted by smaller likelihood of bimetallic center formation with decreasing loading of the co-impregnated catalyst.

At total metal loadings above 3 wt.%, the MMCD catalyst from $\text{HRuCo}_3(\text{CO})_{12}$ showed only a slightly higher total activity than the Ru-Co-co-impregnation catalyst and afforded an even worse hydrocarbonylation selectivity (Fig. 7). If the synergies in the hydrocarbonylation are caused by hydrogen transfer within Ru-Co-bimetallic centers and not by hydrogen spillover over greater distances between different centers, they should be better visible at lower loadings, where the average distances between the different active ensembles can be assumed to be higher. At the applied lower metal loadings, the activities related to the

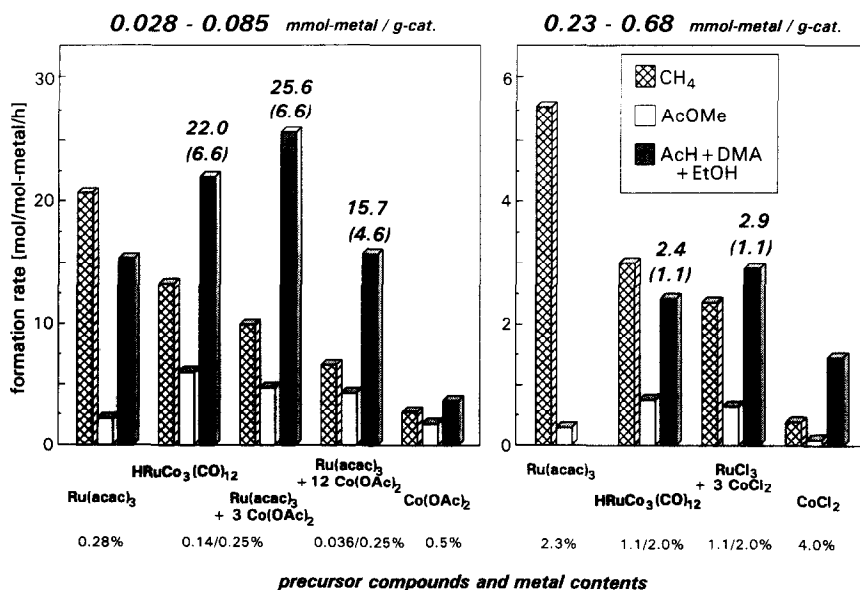


Fig. 7. Loading effects on different Co-Ru/A.C. catalysts. The (bold, italic) numbers over the bars denote the total hydrocarbonylation activity, expected activities resulting from linear combinations of those of separated components are given in brackets. Reaction conditions as in Fig. 5.

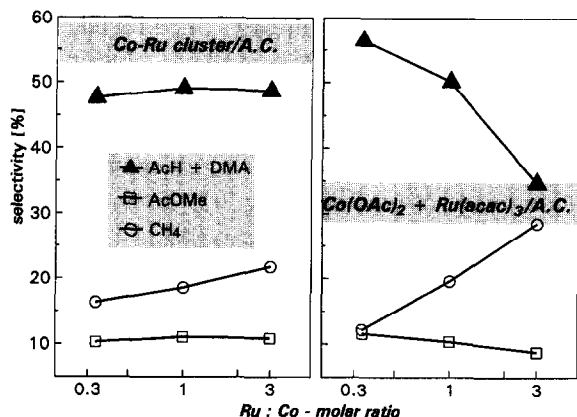


Fig. 8. Effect of the precursor-compound on the selectivity at different Ru:Co molar ratios; Co loading: 0.25 wt.%, reaction conditions as in Fig. 5., Co–Ru cluster precursors: $\text{HRuCo}_3(\text{CO})_{12}$, $\text{Ru}_2\text{Co}_2(\text{CO})_{13}$, $\text{HRu}_3\text{Co}(\text{CO})_{12}$.

metal content were found several times higher than those at loadings above 2 wt.% and generally higher hydrocarbonylation selectivities were observed, hinting at the structure-sensitivity of the reaction, but the synergistic effects on the activity obtained for the MMCD catalyst and the co-impregnation Co–Ru/A.C. catalysts are in the same order. Nevertheless, interesting effects of the Co:Ru molar ratio on the selectivities over MMCD- and Co–Ru-co-impregnation catalysts have been observed (Fig. 8). In both cases, no significant influence of the metal composition on the methyl acetate formation was observed. According to Hidai [18], a maximum in ethanol was obtained in the liquid phase at a Co:Ru ratio of 3:1, but considering that the products were only analyzed after a constant time, conclusions concerning the acetaldehyde selectivity cannot be drawn [8]. We suppressed the acetaldehyde hydrogenation to ethanol by keeping the conversions below 15% and observed a maximum in the hydrocarbonylation selectivity only for the co-impregnated Co–Ru catalysts. Here, we also found a maximum in the AcH/DMA selectivity at the lowest Ru content. The methane selectivity rose with increasing Ru:Co molar ratio on both MMCD and co-impregnated catalysts; this effect is more significant on the co-impregnation cata-

lysts. The most striking difference in the behavior of both catalyst types is, that on MMCD catalysts the selectivity of AcH/DMA was nearly unaffected by the stoichiometry of the Co–Ru precursor clusters, while increasing Ru:Co ratios caused declining AcH/DMA selectivities on co-impregnated systems. This proves clearly that atomic ensemble effects play an important role in the cooperative interaction between the centers of hydrogen activation and carbonylation. However, the estimation of the optimal distances between hydrogen-activating and carbonylation-active sites is complicated by the phenomenon of active metal migration. Fig. 9 illustrates the changes in metal particle size, micropore volume and activity during different reaction conditions. In the first minutes under reaction conditions (see experimental section), only Pd crystallites ($d = 2\text{--}3\text{ nm}$) were detected. After an induction period and a slow deactivation at 210°C , the micropore volume was reduced and no metal crystallites were detected. Subsequent treatment of the catalyst with hydrogen at 400°C led to the formation of Pd–Co mixed metal crystallites ($d = 10\text{ nm}$) showing no hydro(carbonylation) activity. At this point, the micropore volume of the fresh catalyst was restored. The reactivation under reaction conditions was accompanied by the disappearance of the crystallites and in a repeated loss of micropore volume caused by metal redispersion. The experiments clearly show that the active carbon supported transition metals are no static systems and metal migration cannot be neglected.

The promoter metals can also possess an own carbonylation activity depending on the preparation (see Fig. 1: $\text{PdCl}_2/\text{A.C.} < \text{Pd}(\text{OAc})_2/\text{A.C.}$) and pretreatment. Fig. 10 illustrates the influence of the loading on the selectivity of Ru/A.C. catalysts. At very low loadings below 0.3 wt.%, the Ru/A.C. system afforded significant AcH/DMA selectivities and became a (hydro)carbonylation catalyst itself, while at higher loadings above 0.5 wt.%, the methane formation widely predominated. This hints at the structure sensitivity of the hydrocarbonylation over Ru and is consistent with the fact that Ru can also catalyze the hydrocar-

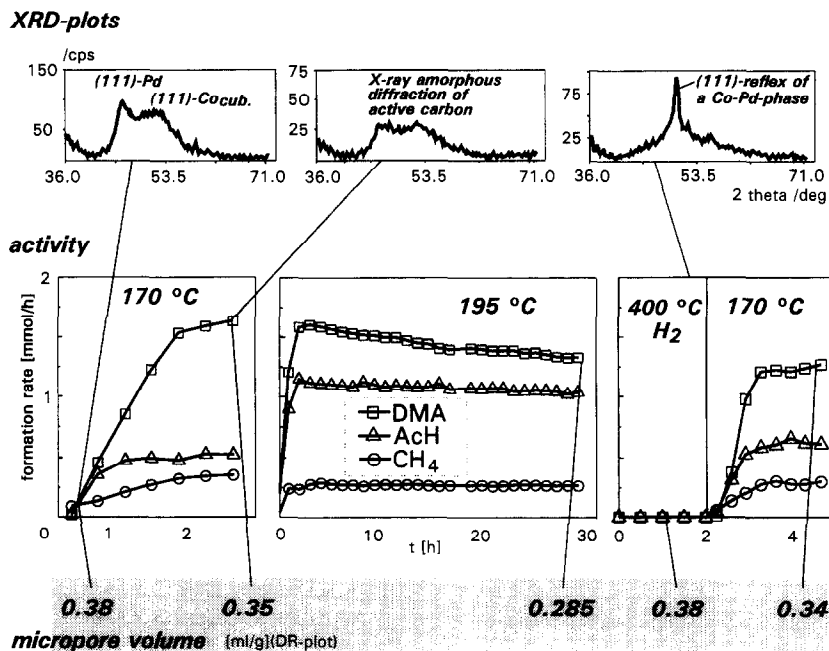


Fig. 9. Structure changes on a Co-Pd/A.C. co-impregnation catalyst during different treatments: induction period at 170°C, isothermic period at 195°C, treatment at 400°C with H₂ in the absence of CO, switching back to syn gas at 170°C, other reaction conditions as in Fig. 1.

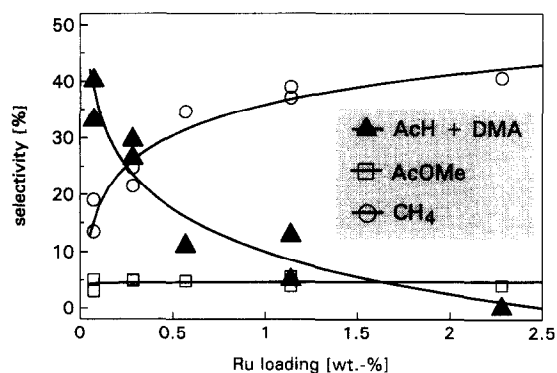


Fig. 10. Loading effects on the selectivity of active carbon supported Ru catalysts; 195°C, other reaction conditions as stated in Fig. 5.

bonylation in the liquid phase [25], where a maximum of dispersion of the soluble catalyst can be assumed.

4. Conclusions

Transition metals like Pd and Ru dramatically influence the mechanism of the methanol hydro-

carbonylation by promoting reduction steps on active Co sites. The close neighborhood of hydrogen activation sites and carbonylation centers appears as a necessary condition for the obtained synergisms and hydrogen-spillover over distances of millimeters can be neglected as an explanation for the experimental findings. Because of the high mobility of the metals on active carbon, a clear definition of the term close neighborhood between Pd, Ru and Co sites cannot be given.

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