Catalysis Letters 19 (1993) 247–255

Vapor-phase carbonylation of methanol on an active carbon supported iridium-catalyst

G. Zehl, S. Bischoff and B. Lücke [1]

Chemiezentren Adlershof in der KAI e. V., Zentrum für Heterogene Katalyse,
Rudower Chaussee 5, O-1199 Berlin, Germany

Received 17 December 1992; accepted 16 March 1993

Iridium on active carbon (Ir/A.C.) is an effective catalyst for the vapor-phase carbonylation of methanol. In contrast to rhodium-catalysts the reaction rate is nearly independent of the partial pressure of the methyl iodide promoter and the methanolysis of an iridium–acetyl species has been found to determine the rate. Undesired methane formation accompanying the carbonylation is suggested to proceed via proteolysis of iridium–methyl species by methanol or water. Methyl chloride has been found to be a less effective promoter than methyl iodide.

Keywords: Iridium catalyst; supported catalyst; vapor-phase carbonylation; methanol carbonylation; active carbon support

1. Introduction

The vapor phase carbonylation of methanol catalyzed by active carbon supported transition metals [1,2] could represent an interesting alternative to the established Monsanto process [3].

Analogous to the liquid phase reaction, rhodium on active carbon (Rh/A.C.) is the most active and selective of carbon supported transition metal catalysts for vapor-phase carbonylations [2]. Major drawbacks are the high price of rhodium and the high reaction order of the corrosive and expensive promoter CH_3I. The latter requires high CH_3I/CH_3OH ratios to achieve high conversions.

The less expensive Ni/A.C. catalysts exhibit lower, but still good activities [4]. Their disadvantage is excessive methane formation hindering an industrial application [5]. Iridium supported on active carbon was found to be less active than rhodium but more active than nickel [2]. Iridium is also an effective catalyst for the title reaction when it is supported on NaY by ion exchange. An interesting feature of these catalysts reported by Naccache [6,7] is that methyl chloride can be used as promoter instead of the more costly and corrosive methyl iodide.

---

[1] To whom correspondence should be addressed.

With exception of the comparison of activities as mentioned above, few data have been published on supported Ir-catalysts for the title reaction. In the present work we wish to report catalytic properties of these catalysts and to compare the efficiencies of CH_3Cl and CH_3I promoters.

2. Experimental

The catalyst was prepared by impregnating a commercially available technical activated carbon (Takeda Shirasagi C) with an aqueous solution of $Na_2[IrCl_6]$, followed by drying at 140°C for 12 h in an air oven. The metal loading was 1 wt% Ir. A catalyst with 5.0 wt% Ir loading for investigations on deactivation was prepared by a similar procedure.

The catalytic tests were carried out in a flow type fixed bed reactor with a capacity of about 1.2 ml and an inner diameter of 8 mm. Reaction orders were determined at 230°C and 1.0 MPa. The partial pressures of methanol, CH_3I and CO were varied in the following ranges: 0.0026–0.047, 0.00021–0.021 and 0.064–0.857 MPa respectively. Reactor space-time was held constant by adding Ar as balance gas to the feed. To avoid space-time fluctuations caused by CO-consumption, the CO/CH_3OH feed ratio was larger than 4/1 and the CH_3OH conversion level was kept below 15% by diluting the feed gas with Ar.

H_2-chemisorption was applied to determine the degree of metal dispersion. Before chemisorption the catalyst was kept in an Ar stream for 1 h at 400°C followed by a treatment with hydrogen for 1 h at the same temperature. The reduced catalyst was then treated again with Ar for 1 h at 400°C.

XRD measurements were conducted with an URD-6 instrument (Fa. Freiberger Präzisionsmechanik GmbH) at 40 kV and 35 mA using Cu K irradiation. The Scherrer equation was used to calculate the average crystallite size of Ir.

CH_3I or CH_3Cl was used as promoter.

3. Results and discussion

3.1. THE INFLUENCE OF REACTOR SPACE-TIME

Table 1 and results of other experiments show that the reaction over the highly porous catalyst is not controlled by external mass transfer. An increase of the contact time (W/F) at high conversion levels results in increasing acetic acid-yields at the expense of the methyl acetate formation (fig. 1). This supports the idea that methyl acetate is an intermediate in the formation of acetic acid. In that sense the Ir/A.C. system is quite similar to Ni/A.C. and Rh/A.C. catalysts [4,8].

Table 1
Influence of reactor space-time on CH_3OH-conversion and formation rate of CH_3COOCH_3 [a]

W/F (g-cat h/mol)	CH_3OH-conversion (%)	Formation rate of CH_3COOCH_3 (mmol/g-Ir h)
0.73	13.3	389.0
0.87	15.6	382.5
1.08	18.7	369.5
1.43	24.0	362.5

[a] Reaction conditions: 1.0 wt% Ir/A.C., 230°C, 0.5 MPa, $CO/CH_3OH/CH_3I = 400/19/1$.

3.2. TEMPERATURE EFFECTS

Fig. 2 shows the influence of the reaction temperature on the product spectrum. As on Ni- or Rh-catalysts, the formation of carbonylated products is enhanced with increasing temperature. This is accompanied by increased formation of methane rendering the process less selective. A maximum of carbonylation activity was reached at 310°C. Higher temperatures led to a sharp decrease of the carbonylation activity and to a dramatic increase of the methane selectivity.

At 350°C and a low CH_3I- and CO-partial pressure in the gas feed ($CO/CH_3OH/CH_3I/Ar = 50/199/1/100$) catalyst deactivation was observed. During the deactivation the methane selectivity rose from 64 to 72% and the methyl acetate selectivity declined from 26 to 14%. The deactivated catalyst remained less active when it was exposed to the standard conditions again (250°C, 2 MPa).

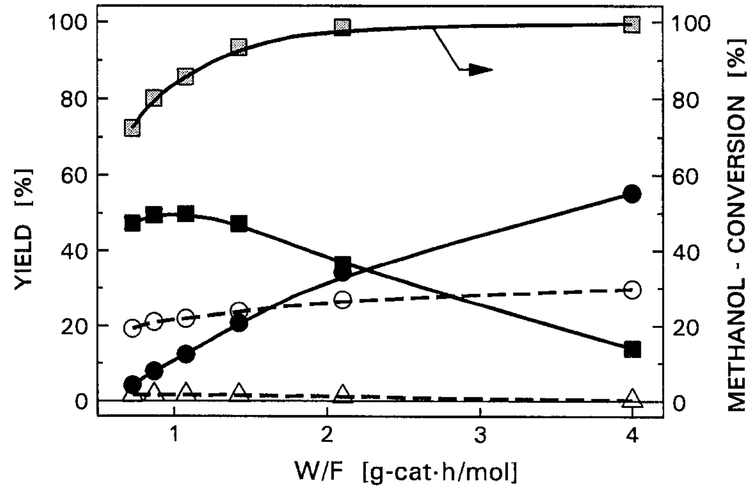

Fig. 1. Influence of the reactor space-time on the yields of CH_3COOH (●), CH_3COOCH_3 (■), CH_4 (○), CH_3OCH_3 (△) at high CH_3OH-conversions (▨); 1.0 wt% Ir/A.C., 2.0 MPa, 230°C, $CO/CH_3OH/CH_3I = 400/19/1$.

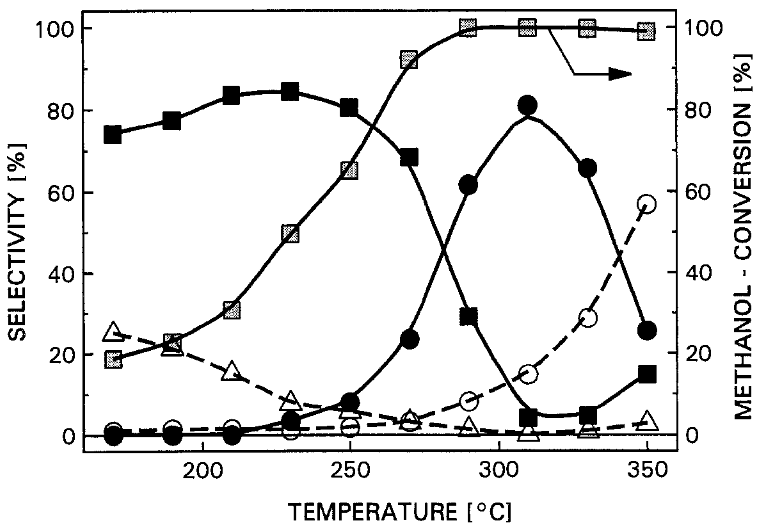

Fig. 2. Influence of the temperature on the selectivities of CH_3COOH (●), CH_3COOCH_3 (■), CH_4 (○), CH_3OCH_3 (△) and the CH_3OH-conversion (▨); 1.0 wt% Ir/A.C., 2.0 MPa, $W/F = 2.9$ g-cat h/mol.

The irreversibility of the deactivation is in contrast to results obtained for nickel [5] and is not fully clear yet. Electron micrographs of an active and a deactivated Ir/A.C. catalyst (figs. 3a, 3b) indicate that the deactivation proceeds via metal aggregation, which has already been proved for Ni/A.C. catalysts [5]. Furthermore, the XRD-spectrum of the active catalyst did not contain Ir-peaks suggesting small crystallite sizes. Sharp signals at $2\theta = 40.94°$ and $2\theta = 41.3°$ appeared in the XRD-plot of the deactivated catalyst and are assigned to Ir-crystallites with average crystallite sizes of about 35 nm [1, 1, 1] and 50 nm [2, 0, 0] respectively. Ir dispersities (H/Ir) of 0.31 and 0.12 for the active and the deactivated catalyst respectively support the concept of active site loss caused by sintering.

3.3. REACTION ORDERS

Estimating reaction orders n_i by the formal model $r = kc_i^{n_i}$ (r: rate(mmol/h), n_i: reaction order, p_i : partial pressure of compound i) has been shown to give useful information on the reaction mechanism [5]. Table 2 summarizes the reaction order of CO, CH_3OH, CH_3I, and H_2O relative to the carbonylation and side reactions like CH_4 or CH_3OCH_3 formation.

The high reaction order of CH_3OH related to the formation of CH_3COOCH_3 (0.7) shows that CH_3OH is involved in a rate-determining step of the reaction. This is in contrast to the Rh-catalyzed methanol carbonylation, where a reaction order of about zero has been found in the liquid-phase [3] and in the vapor-phase reaction

[8] as well. Because the methanolysis of free acetyl iodide is not rate determining at the more active Rh-catalyst, we conclude that the rate determining step on Ir/A.C.-catalysts is the methanolysis of Ir–acetyl species. The reaction order of CO (0.4) differs clearly from those known for Rh- or Ni-catalysts (~ 0 or 0.7 respectively [8,9]).

The low reaction order of CH_3I suggests that the formation of Ir–methyl species via oxidative addition proceeds rather quickly, while the subsequent CO-insertion and the methanolysis of the resulting Ir–acetyl species determine the carbonylation rate. The fact that some reaction orders (CO on CH_3COOCH_3 and CH_4) depend on the stoichiometric gas composition hints at a complex reaction network similar to that for Ni/A.C. catalysts [5].

Runs with the unloaded active carbon have shown that the formation of CH_3OCH_3 is catalyzed by the carbon support itself. Declining CH_3OCH_3 yields with catalyst deactivation, as found for Ni [5], support the idea of a metal catalyzed ether formation occurring simultaneously with the carbon catalyzed reaction. The above side reaction is suppressed by CO, which can be explained by the competition of methanol and CO for Ir–methyl species yielding the ether or carbonylated compounds respectively.

It has already been shown that the methane formation over Ni/A.C.-catalysts results from proteolysis of Ni–methyl species by CH_3OH or H_2O [5]. The low reaction order of CH_3I and the high reaction order of methanol relative to the methanation also obtained for iridium hint at a similar reaction path for Ir–methyl species. Consequently, adding H_2O to the feed gas led to an enhanced methane formation at the expense of dimethyl ether (table 2). This suggests that Ir–methyl species can form both methane or dimethyl ether.

3.4. CH_3Cl AS ALTERNATIVE PROMOTER

The role of promoters in the title reaction is in the formation of metal–methyl species which can be transformed to acetyl species by CO-insertion. CH_3Cl could represent an alternative to the commonly used CH_3I, the latter being rather corrosive and expensive.

Table 3 compares the catalytic features of Ir/A.C. catalysts with CH_3I or CH_3Cl as promoter. CH_3Cl is obviously a less effective promoter, which has also been shown for Ir/NaY catalysts [6]. The substitution of the CH_3I promoter led to a lower methyl acetate and higher dimethyl ether selectivity. The reaction order of about 0.8 on the methyl acetate formation is higher than the reaction order of CH_3I indicating that CH_3Cl is added more slowly to the supported Ir.

4. Conclusions

Iridium supported on activated carbon is an effective and reasonably selective

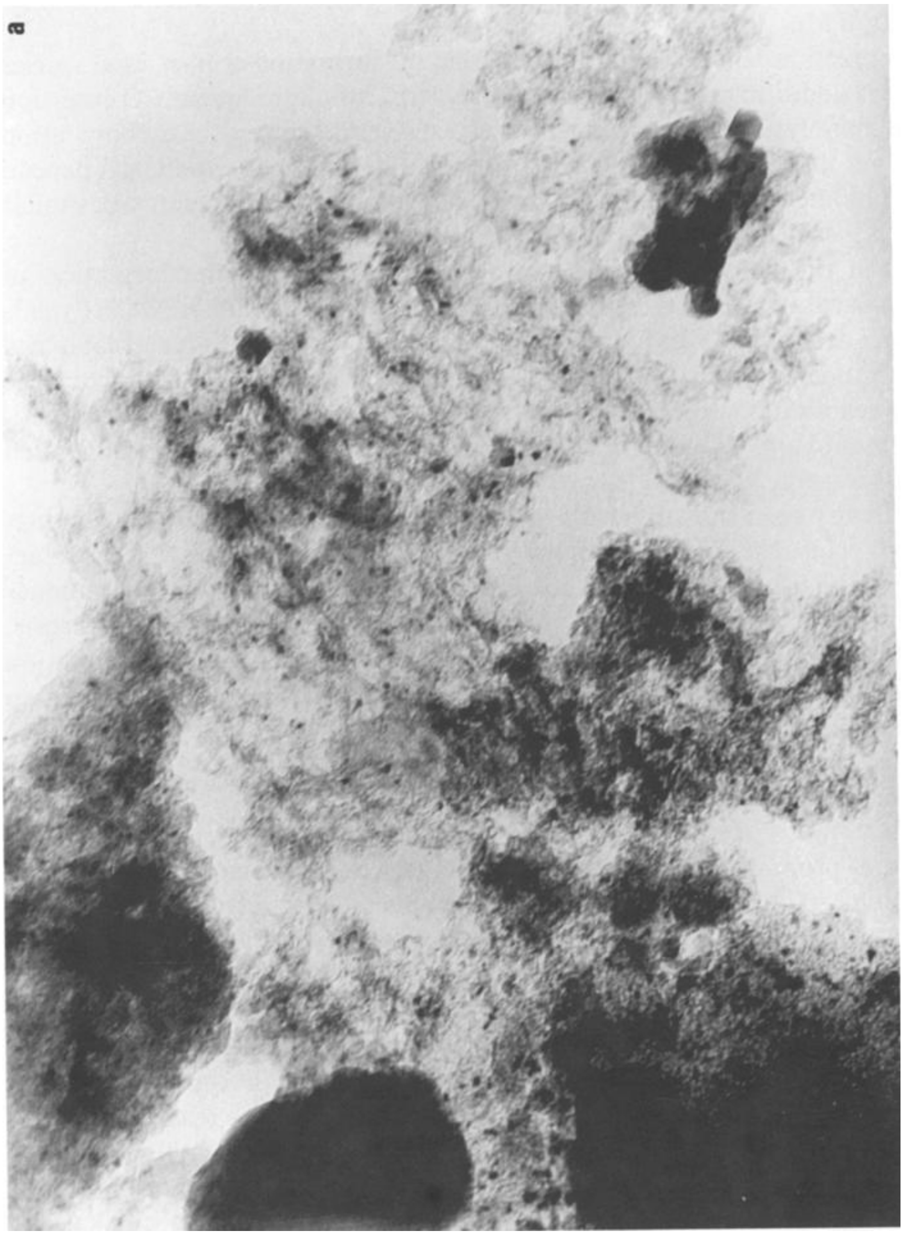

Fig. 3.(a) Electron micrograph of an active Ir/A.C. catalyst used for 30 h at 250°C, 2.0 MPa, $W/F = 2.9$ g-cat h/mol, $CO/CH_3OH/CH_3I = 40/19/1$, enlargement: 162000. (b) Electron micrograph of an deactivated Ir/A.C. catalyst, deactivation temperature: 350°C, enlargement: 162000.

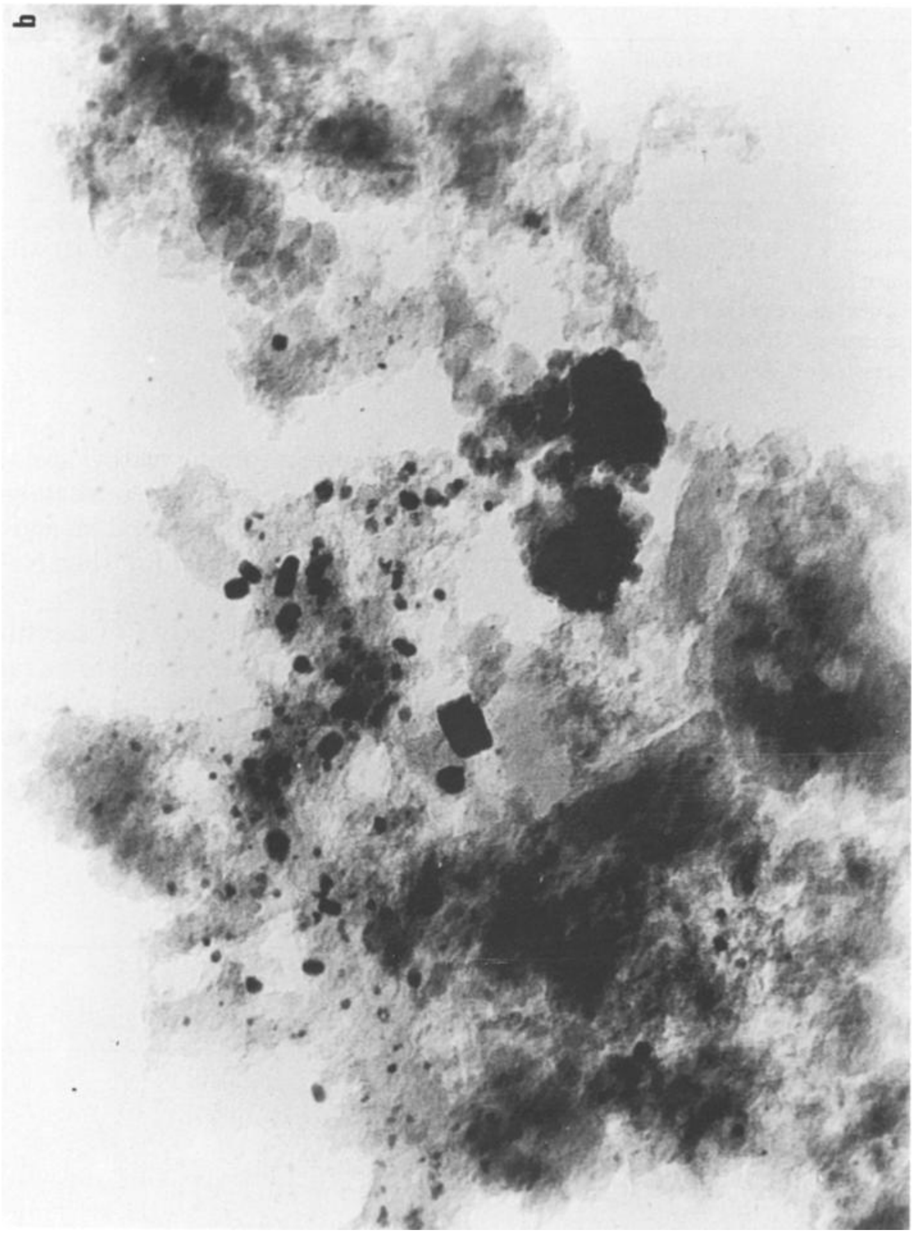

Fig. 3. (continued).

Table 2
Reaction orders of CO, CH_3OH, CH_3I and H_2O [a]

Reactant	Reaction order [b] relative to formation of		
	CH_4	CH_3OCH_3	CH_3COOCH_3
CO	0.08 (0.07)	−0.3 (0.06)	0.37 (0.08)
CH_3OH	0.7 (0.05)	1.1 (0.14)	0.69 (0.05)
CH_3I [c]	0.08 (0.06)	0.5 (0.09)	0.07 (0.06)
CH_3I [d]	0.06 (0.04)	0.66 (0.11)	0.2 (0.08)
H_2O	0.22 (0.04)	−0.26 (0.09)	0.08 (0.09)

[a] Reaction conditions: 1.0 wt% Ir/A.C., 230°C, $W/F = 0.39$ g-cat h/mol, total pressure: 1 MPa, partial pressures: CO: 0.064–0.857 MPa; CH_3OH: 0.0026–0.047 MPa; CH_3I: 0.00021–0.021 MPa; Ar: balance gas.

[b] Standard deviations of the reaction orders in parentheses.

[c] Partial pressure of CO: 0.043 MPa.

[d] Partial pressure of CO: 0.857 MPa.

catalyst for the vapor-phase carbonylation of methanol affording methyl acetate and acetic acid. In accord with studies on heterogeneous and homogeneous catalyst systems [2,10] Ir exhibits a lower activity than Rh when it is supported on active carbon. On the other hand, Ir was reported to be more active than Rh when NaY was used as support [6].

Oxidative addition of the MeI promoter to Ir-sites and subsequent CO insertion form the essential Ir–acetyl species. Their methanolysis has been found to be rate determining, in contrast with results obtained for Rh/A.C., where the oxidative addition of MeI controls the rate. The undesired methane formation is attributed to the proteolysis of Ir–methyl species by CH_3OH or H_2O.

Methyl chloride is a less efficient but still a moderate promoter in the Ir/A.C.-

Table 3
Promoter influences on activity and selectivity [a]

	Promoter	
	CH_3I	CH_3Cl
formation rate (mmol/g-Ir h)		
CH_4	84.6	17.3
CH_3OCH_3	140.8	32.7
CH_3COOCH_3	815.8	94.2
selectivity (%)		
CH_4	4.2	6.4
CH_3OCH_3	14.1	24.0
CH_3COOCH_3	81.7	69.6

[a] Reaction conditions: 1.0 wt% Ir/A.C., 230°C, 0.5 MPa, $CO/CH_3OH/CH_3I = 400/19/1$.

catalyzed vapor-phase carbonylation of methanol. The advantage of the lower costs of CH_3Cl is compensated by its lower promoter efficiency.

Acknowledgement

Thanks are given to the BMFT (Federal Ministry for Science and Technology) Project-No. 30J1014P4 and FCI (Fonds der Chemischen Industrie im Verband der Chemischen Industrie e.V.) for financial support. We also want to thank Professor Dr. U. Steinike for XRD-measurements and Dr. E. Schierhorn for the electron micrographs.

References

[1] K. Fujimoto, T. Shikada, K. Omata and H. Tominaga, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 429.
[2] K. Fujimoto, K. Omata and H. Tominaga, in: *Industrial Chemicals via C_1 Processes*, Vol. 3, Am. Chem. Soc. Symp. Ser., ed. D.R. Fahey (Am. Chem. Soc., Washington, 1987) p. 208.
[3] J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, Chem. Technol. (1971) 600.
[4] K. Fujimoto, T. Shikada, K. Omata and H. Tominaga, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 436.
[5] K. Fujimoto, S. Bischoff, K. Omata and H. Yagita, J. Catal. 133 (1992) 370.
[6] P. Gelin, C. Naccache and Y. Ben Taarit, Pure Appl. Chem. 60 (1988) 1315.
[7] P. Gelin, Y. Ben Taarit and C. Naccache, Stud. Surf. Sci. Catal. (1981) 898.
[8] K.K. Robinson, A. Hershman, J.H. Craddock and J.F. Roth, J. Catal. 27 (1972) 389.
[9] K. Omata, K. Fujimoto, T. Shikada and H. Tominaga, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 234.
[10] D. Forster, Adv. Organomet. Chem. 17 (1976) 255.