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PREPARATION OF NICKEL-ON-ACTIVE CARBON CATALYST BY CVD METHOD FOR METHANOL CARBONYLATION

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Chemical vapor deposition on nickel, nickel on carbon for carbonylation.

The nickel on active carbon (Ni/A.C.) catalysts prepared by a simple chemical vapor deposition (CVD) method showed comparable catalytic activities for the vapor phase carbonylation of methanol to those of the catalysts prepared by impregnating A.C. with nickel nitrate and activating by hydrogen treatment. The CVD method was successfully applied to the in situ catalyst preparation.

1. Introduction

The production of acetic acid by carbonylation of methanol has been performed industrially in the liquid phase using carbonyl complexes of cobalt [1] or rhodium [2] and iodide promoter. The authors have already reported that nickel on carbonaceous materials exhibits excellent catalytic activity for the title reaction under moderately pressurized conditions in the presence of methyl iodide promoter [3–5].

The nickel catalyst has been prepared by impregnating active carbon with nickel nitrate or acetate from their aqueous solution, which is followed by the activation with hydrogen treatment. A more simple method of catalyst preparation has been required.

Chemical Vapor Deposition (CVD) method is a typical method for preparing thin film. Recently, the method has been applied to prepare supported metal catalysts using metal organics [6]. Since the active carbon used as the catalyst support is characterized by the huge surface area and is well-known as an excellent absorbent for metal carbonyls, it would be suitable for catalyst preparation by the CVD method. In the present study, a CVD method using nickel carbonyl ($Ni(CO)_4$) as a catalyst precursor was studied and the method was applied for the in situ catalyst preparation.

2. Experimental

The vapor phase deposition of nickel carbonyl was conducted using an apparatus shown in fig. 1 under atmospheric pressure. Nickel carbonyl was synthesized according to the procedure described by Mayer and Wibaut [7]. The carbonyl vapor was introduced with N_2 carrier into a fluidized bed of active carbon granules (A.C., Kureha BAC, made of petroleum pitch, microsphere type) to be adsorbed on it at 50 °C or 180 °C, then it was decomposed therein at 250 °C in N_2 atmosphere. The catalysts were subjected to the reaction without any additional treatment. The reference catalysts were prepared by impregnating A.C. in aqueous solution of nickel acetate. The precursor was dried in air at 120 °C for 24 h and then reduced in flowing hydrogen at 400 °C for 1 h. In situ preparation of a Ni/A.C. catalyst was performed using a carbonyl generator containing nickel oxide which was connected to the top of the reactor. Through the generator, which was kept at 250 °C and 11 atm, carbon monoxide was fed to the reactor after mixing with methanol and methyl iodide which were supplied below the generator. The reaction was carried out in a fixed bed flow type reactor under pressurized conditions (11 atm and 250 °C).

3. Results and discussion

Figure 2 shows that the nickel particle on active carbon differ greatly from each other. Especially, the size of nickel metal which was prepared by CVD was much larger than in the other case. Although the mechanism of metal deposition is not clear, the carbonyl might be decomposed at the outer surface of A.C. at 50 °C.

The activities of the Ni/A.C. catalysts, prepared by both the CVD and the impregnation method for the vapor phase carbonylation of methanol, are il-

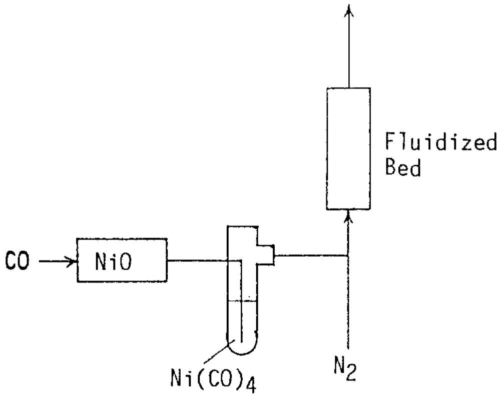

Fig. 1. Flow-sheet of CVD apparatus.

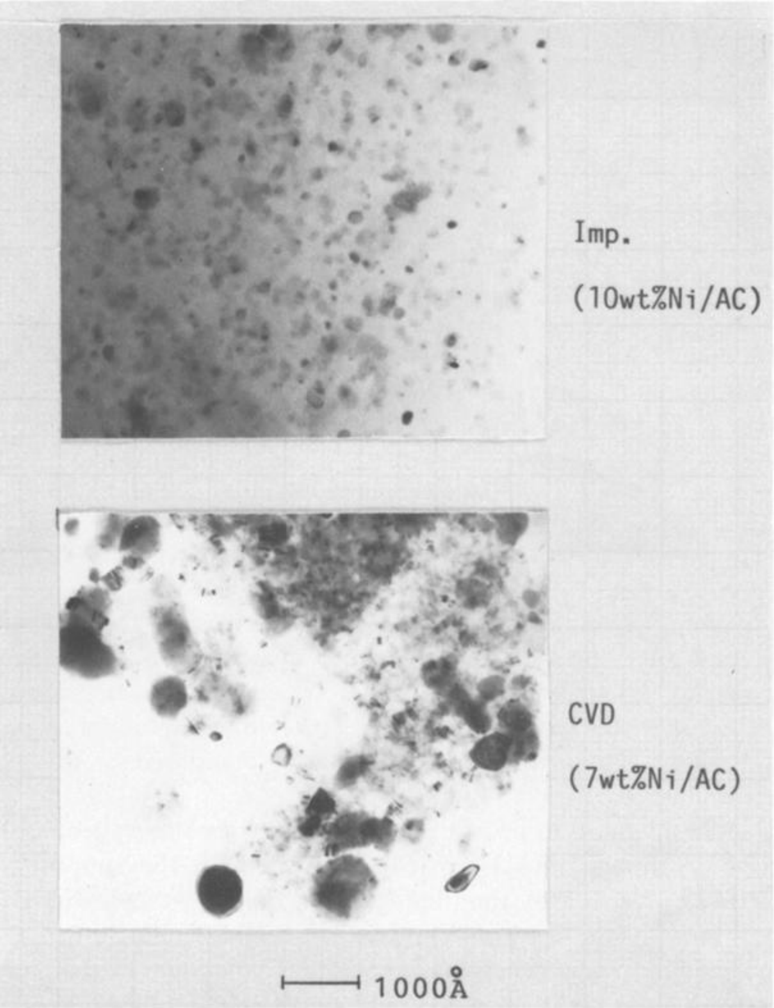

Fig. 2. TEM of fresh catalysts prepared by the CVD and the impregnation method.

lustrated in fig. 3 as a function of nickel loading. The carbonylated product was mainly methyl acetate. Figures in the parentheses are the temperatures of the carbonyl deposition. An activation step such as hydrogen reduction was not necessary for the CVD method. No difference in the activity arising from the preparation methods was observed, whereas the TEM picture of fresh Ni/A.C. showed a significant difference between the two catalysts in terms of the particle size and the distribution of nickel metal (fig. 2). It is therefore suggested that any nickel loaded on the catalyst was converted into some type of active species on the surface of A.C. during the reaction.

The change in the activity of Ni/A.C. catalysts with reaction time, for the in situ preparation, is illustrated in fig. 4. While the activity of the Ni/A.C. prepared by the impregnation method reached a steady state quickly (dotted

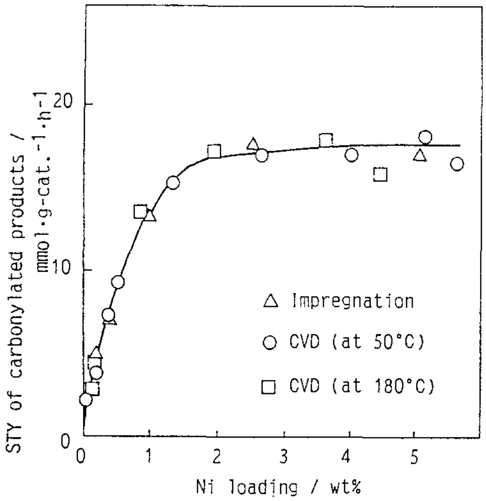

Fig. 3. Catalytic activity as a function of Ni loading: 250 °C, 11 atm, W/F = 5 g.h/mol, CO/MeOH/MeI = 100/19/1, Carrier: Kureha BAC.

line), that of the CVD catalyst increased slowly to reach a steady level after 300 min, suggesting that the rate of either the nickel carbonyl formation or its deposition on A.C. is rather slow. However, once nickel is decomposed on the carbon surface, it works well as the active center of the reaction. The reason of the lower catalytic activity of the CVD catalyst compared to the impregnated catalyst is not clarified.

A.C. was demonstrated to be a suitable support for catalyst preparation by the CVD method. Although nickel particles deposited on the support were much larger than those prepared by the impregnation method, they exhibited activities equivalent to those of the conventional Ni/A.C. catalyst. No activation step such as hydrogen reduction was necessary for the CVD method and an active catalyst was prepared by applying the method even under reaction conditions.

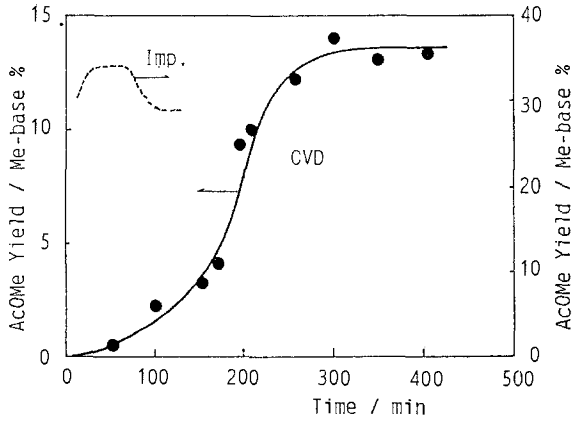

Fig. 4. Changes of MeOH carbonylation activity: 250 °C, W/F = 5 g.h/mol. CO/MeOH/MeI/N2 = 27/19/1/77, 11 atm.

Acknowledgment

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References

[1] H. Hohenschutz, N. von Kutepow and W. Himmele, Hydrocarbon Process. 45 (1966) 141.
[2] J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, Chemtech. (1971) 600.
[3] K. Fujimoto, T. Shikada, K. Omata and H. Tominaga, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 429.
[4] T. Shikada, K. Fujimoto, M. Miyauchi and H. Tominaga, Appl. Catal. 7 (1983) 361.
[5] K. Omata, K. Fujimoto, T. Shikada and H. Tominaga. Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 234.
[6] D. Bailey and S. Langer, Chem. Rev. 81 (1981) 110.
[7] K. Mayer and I.P. Wibaut, Rec. Trav. Chim. 56 (1937) 356.