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VAPOR-PHASE CARBONYLATION OF METHANOL OVER LEAD ON ACTIVE CARBON CATALYST

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Lead supported on active carbon showed a catalytic activity for the vapor phase carbonylation of methanol under pressurized conditions in the presence of methyl iodide promoter.

1. Introduction

It is well known that the carbonylation of methanol is catalyzed in the liquid phase by complexes of cobalt, rhodium, nickel, or iridium metal [1]. The authors have already reported [2–5] that nickel and other group 8 metals on active carbon show an excellent activity for the vapor phase carbonylation of methanol under mild conditions.

In a previous work [6] we reported that a tin catalyst which had never been known to show catalytic activity for carbonylation reaction showed a high activity for the vapor phase carbonylation on methanol when it was supported on active carbon. In the present work, we report that lead supported on active carbon also showed an excellent activity for the reaction.

2. Experimental

The catalyst precursors were obtained by impregnating a commercially available active carbon (AC; Takeda Chemical, Shirasagi C, specific surface area 1200 m^2/g, particle size 20–40 mesh) with metal acetates from their aqueous solutions by a dry-up method. They were reduced in a hydrogen stream, 400 ° C, 3 hours in situ before reaction. The metal loading was 2.5 wt% as metal. A fixed bed flow type reactor apparatus was employed. The details of the reaction apparatus has been reported previously [3]. Reaction conditions were: temperature 250–325 ° C, pressure 11 atm, $W/F = 5$ g · h/mol (W: catalyst weight, F: reactant feed rate), $CO/CH_3OH/CH_3I = 100/19/1$ (molar ratio).

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3. Results and discussion

Figure 1 shows the experimental results over a variety of metals supported on AC. All metals showed carbonylation activity [6]. Main products were methyl acetate (AcOMe) and dimethyl ether (DME) and minor products were acetic acid (AcOH), methyl formate (MeF), methane (CH_4), and carbon dioxide (CO_2). Tin, lead, manganese, and molybdenum gave carbonylation products (AcOMe and AcOH) with yield higher than 5% and selectivity higher than 40%. Turnover rate of Pb/Ac was 20.1 calbonylated product-mol/supported Pb-mol · h.

Figure 2 shows the product yields and carbonylation selectivity on Pb/Ac as a function of the reaction temperature. The yields of the carbonylation products (AcOMe and AcOH) and CH_4 increased with a rise in the reaction temperature. The yield of DME was almost constant in the range of the examined temperatures. The selectivity to carbonylation increased with increasing reaction temperature to reach about 80% at 300 ° C. The apparent activation energy is calculated as 13.4 kcal/mol.

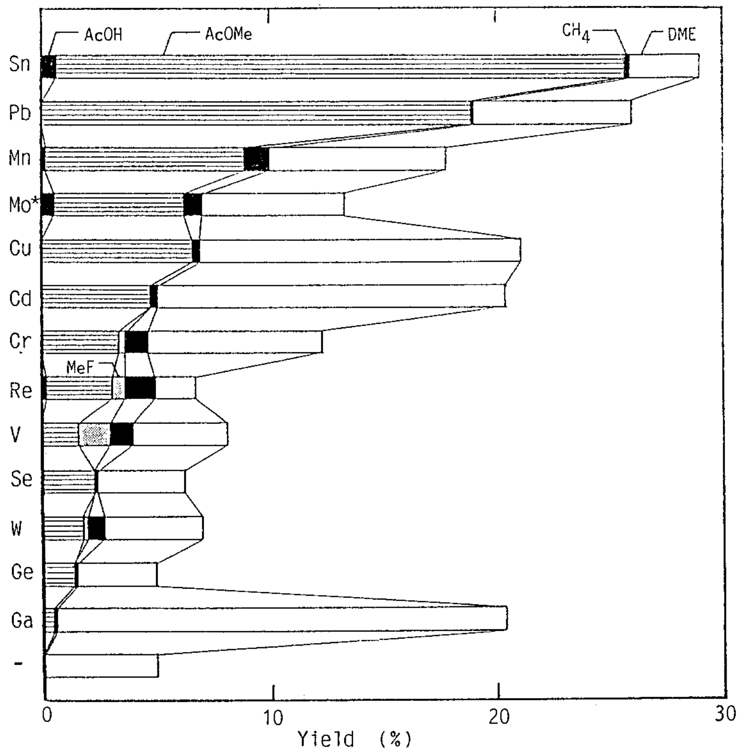

Fig. 1. Carbonylation of CH_3OH with supported catalysts. Support: AC loading: 2.5 wt% as metal, Reaction conditions: 250 ° C, 11 atm, $W/F = 5$ g·h/mol, $CO/CH_3OH/CH_3I = 100/19/1$ (molar ratio). * 230 ° C, $CO/CH_3OH/CH_3I = 60/19/1$ (molar ratio).

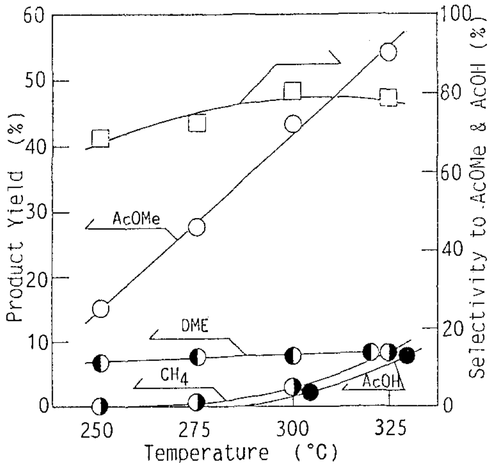

Fig. 2. Effect of reaction temperature. Reaction conditions: 11 atm, $W/F = 5$ g·h/mol, $CO/CH_3OH/CH_3I = 100/19/1$ (molar ratio).

Figure 3 shows that the activity increases with the process time for either a reduced or unreduced catalyst. The reduced catalyst was more quickly activated. The Pb/AC XRD data of supported catalysts (fig. 4) show that while the unreduced catalyst was composed of basic lead carbonate the reduced catalyst was composed of the mixture of lead carbonate and metallic lead and that no crystalline compound was formed during the methanol carbonylation. It suggests

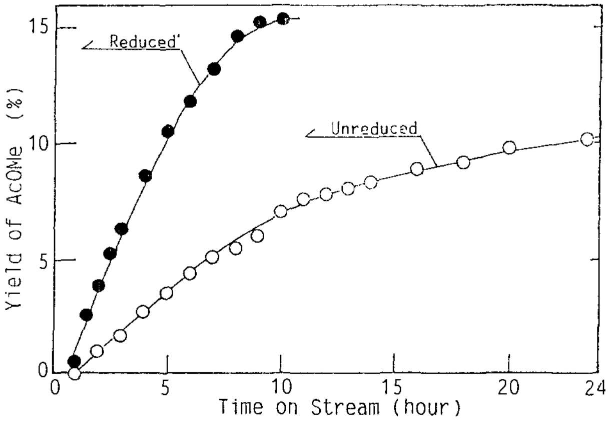

Fig. 3. Activity change with process time. Reaction conditions: 250 ° C, 11 atm, $W/F = 5$ g·h/mol, $CO/CH_3OH/CH_3I = 100/19/1$ (molar ratio).

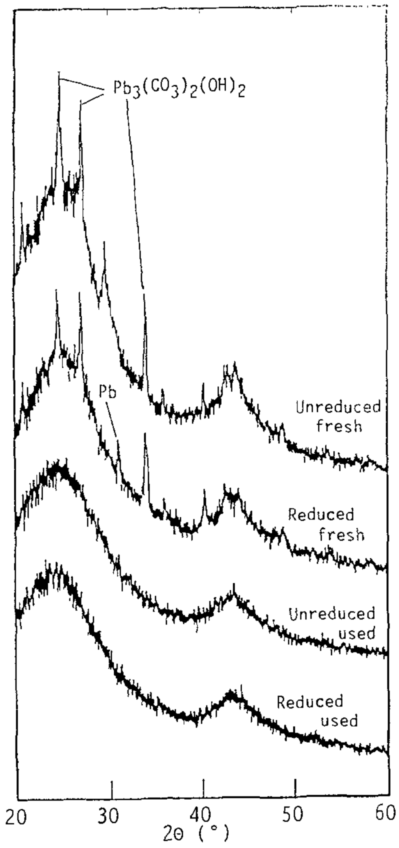

Fig. 4. XRD pattern of Pb/AC.

that reduced lead is a precursor of the active species of methanol carbonylation. However, the active species of this lead catalyst are not clear yet.

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