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Promotion Effect of Hydrogen on Vapor Phase Carbonylation of Methanol over Nickel on Active Carbon Catalyst

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In the vapor phase carbonylation of methanol by carbon monoxide on a nickel on active carbon catalyst, co-existence of hydrogen greatly enhanced the rate of acetic acid production but with a slight increase in methane formation.

Carbonylation of methanol to acetic acid has been performed in industrial scale using iodide-promoted cobalt or rhodium catalyst in liquid phase.[1,2] The authors have found that nickel supported on active carbon (Ni/A.C.) has excellent activity and selectivity for the above reaction in vapor phase.[3,4] The Ni/A.C. catalysts show invariant activity for the carbonylation irrespective of the preparation method, pretreatment of precursor or additives.

Since commercially available carbon monoxide usually contains a small amount of hydrogen and it is costly to produce hydrogen-free carbon monoxide, the authors studied the effects of hydrogen on the reaction, finding that it accelerates markedly the carbonylation reaction.

The experiments were conducted in a fixed bed flow type reactor under pressurized conditions as have been reported in detail elsewhere.[3] Methanol (MeOH) and methyl iodide (MeI) were mixed and fed with a high-pressure type microfeeder. Catalysts were prepared by impregnating a commercially available granular active carbon (A.C., Takeda Shirasagi C, 20-40 mesh) with an aqueous solution of nickel acetate and drying at 120 °C for 12 h in an air oven. The catalyst was used without any further pretreatment. The nickel content was 0.1, 2.5, and 10 wt% as metal. The carbonylated products were acetic acid (AcOH) and methyl acetate (AcOMe). Small amounts of dimethyl ether (DME), methane (CH_4), and carbon dioxide (CO_2) were also formed.

The effects of hydrogen on the reaction are illustrated in Fig. 1. The abscissa shows the molar ratio of hydrogen to carbon monoxide in the feed gas. Both methanol conversion and yield of AcOH are increased with increasing the partial pressure of hydrogen. It is noteworthy that AcOH selectivity in the carbonylated products is largely increased. The yield of AcOH reaches the maximum level at the H_2/CO ratio of 0.1 or above. On the other hand, the higher H_2 pressure gives also an undesirable increase in CH_4 yield. It should be also noted that hydrogen in the feed gas suppresses the formation of DME and CO_2. While DME is supposed to be converted into AcOMe and successively into AcOH at high conversion level of MeOH, it is not easy to understand the mechanism of CO_2 suppression. Moreover, since the Ni/A.C. catalyst exhibits no activity for producing methane from carbon monoxide and hydrogen,[5] the increase in methane formation with the addition of hydrogen in the feed gas is probably attributed to the hydrogenolysis of methyl iodide used as a promoter.

In Fig. 2 are shown the activities of AcOH synthesis of Rh/A.C. (full line), Ni/A.C. (dotted line), and Ni/A.C. in the presence of hydrogen in the feed gas (broken line) as a function of temperature. AcOH yield is calculated assuming that AcOMe consists of AcOH and MeOH. The addition of hydrogen into the feed

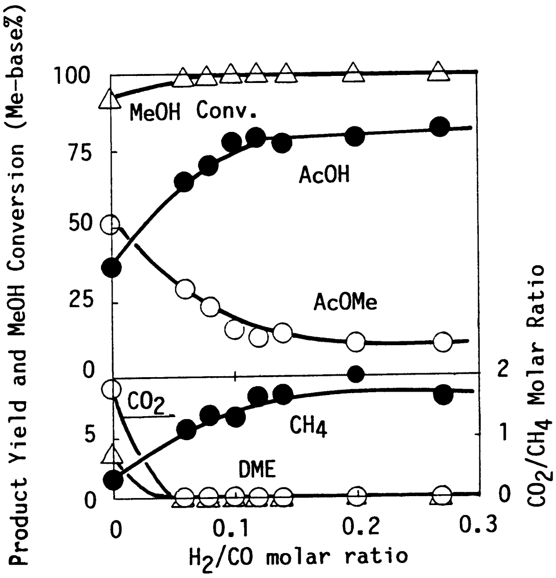


Fig. 1. Effect of H_2/CO ratio on product yield. 250°C, 11atm, W/F=5 g·h/mol, CO/MeOH/MeI=100/19/1.

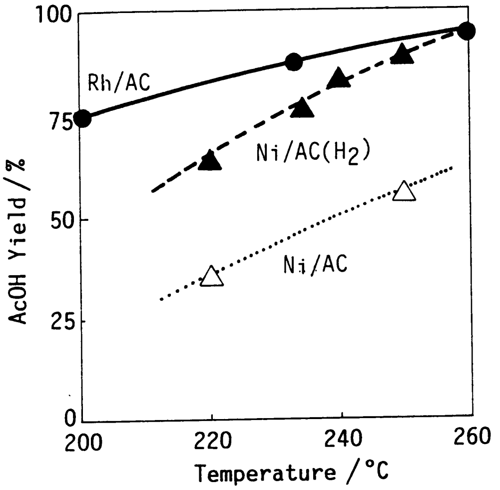
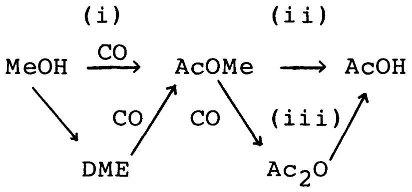


Fig. 2. Effect of temperature on carbonylation. 11atm, W/F=5 g·h/mol, CO/MeOH/MeI/(H_2)=100/19/1/(27).

gives the higher AcOH yield which is equal to that obtained at temperature 40-60 °C higher in the case of hydrogen-free system. Moreover, at the same level of yield of the carbonylated products, selectivity to CH_4 is lower in the reaction with H_2 (5.4% at 230 °C with H_2 and 6.4% at 290 °C without H_2). The results also suggest that the performance of the nickel catalyst in the presence of hydrogen is so excellent as that of rhodium catalyst without hydrogen.

The reaction network from MeOH to AcOH on this catalyst has been proposed as shown in Scheme 1.[4)] Several experiments have been conducted to clarify which one of the reaction path ways is promoted by the added hydrogen.



Scheme 1.

The primary product of MeOH carbonylation is AcOMe, which appears almost exclusively at low conversion level of MeOH. The comparison of experiments No.1 and No.2 in Table 1 shows that hydrogen enhances the reaction path way (i) in Scheme 1 by a factor of about 3. Table 2 shows that the conversion of AcOMe to AcOH via carbonylation was increased by hydrogen. The result indicates that hydrogen also promotes the path way (ii).

Table 1. Effect of H_2 on Carbonylation of MeOH[a)]

No.	1	2	3	4
Ni loading/wt%	0.1	0.1	10	10
Pressure/atm	11	11	10	10
W/F /g-cat·h/mol	2[b)]	2	4.6[c)]	4.6
H_2/CO	0	0.3	0	0.14
MeOH Conv./%	13.6	38.6	57.7	85.0
Yield/%(Me-base)				
AcOMe	10.3	36.0	47.6	60.6
AcOH	0	0	0	10.8
DME	3.3	1.8	6.5	0
CH_4	0	0.8	3.6	13.6
AcOH STY[d)] /mmol/h·g	3.9	13.5	7.5	13.0

a) temperature=250 °C. b) CO/MeOH/MeI=50/9/1. c) CO/MeOH/MeI/N_2=50/36/2/150. d) Total STY of AcOH and AcOMe.

Table 2. Effect of H_2 on Carbonylation of AcOMe[a)]

No.	1	2
H_2/CO	0	0.15
AcOMe Conv./%	58.7	85.9
Yield/%(Me-base)		
AcOH	55.1	80.0
MeOH	1.5	0.3
CH_4	2.1	5.6
AcOH STY /mmol/h·g	18.6	27.0

a) catalyst:2.5 wt%Ni/AC, temperature=250 °C, CO/AcOMe/MeI/H_2O(/H_2)= 100/9/1/10(/15), pressure=11atm.

Generally speaking, catalytic activity per metal atom of supported heterogeneous catalyst is smaller than homogeneous catalyst. It can be explained by the fact that only small part, or outer surface, of metal of the heterogeneous catalyst contributes to the reaction. It was attempted in this study to measure the fraction of nickel on active carbon which contributed to the carbonylation. Namely, the used catalysts were extracted with methanol in a Soxhlet extractor to remove the ionic nickel. In the case of 10wt% Ni/A.C., 1.5wt% Ni remained on A.C. after the extraction and the extracted catalyst showed the same activity as the fresh one. The 2.5wt% Ni/A.C. from which 1.3wt% Ni was removed also showed the same activity as that of the fresh catalyst. Since the strong ligands to nickel such as iodide ion or acetate ion should weaken the metal support interaction, the ionic nickel might be liberated easily from support by the above extraction. It is suggested that nickel removed by the extraction is inactive for the carbonylation, whereas the residual nickel is responsible for carbonylation.

The above extraction was also applied to the catalyst after the use with hydrogen in the feed. The activity is shown in Table 1 (No.3, 4). The fresh catalyst contained 10wt% Ni before the reaction. While the STY of AcOH increased from 7.5 to 13.0 mmol/h·g by the addition of hydrogen, the residual nickel increased from 1.5 to 3.7 wt% by added hydrogen. Hydrogen evidently increases the amount of active nickel.

It is suggested that the addition of hydrogen does not accelerate any particular reaction path in the reaction network, but increases in the number of active site on the catalyst.

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