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SYNTHESIS OF ACETIC ANHYDRIDE BY VAPOR PHASE CARBONYLATION OF METHYL ACETATE WITH A NICKEL-ACTIVE CARBON CATALYST

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Vapor phase carbonylation of methyl acetate on nickel-active carbon catalyst was studied under pressurized conditions in the presence of methyl iodide as a promoter. High pressure was essential for the acetic anhydride formation. A fairly large amount of acetic acid, by-product, was also formed under the water-free reaction condition.

It has been reported in many patents that acetic anhydride is synthesized from dimethyl ether or methyl acetate by a homogeneous catalyst system which is composed of rhodium complexes and methyl iodide under mild reaction condition.[1)] The kinetics and mechanism of the reaction have been also reported.[2)] A commercial plant which produces 5 million ponds of acetic anhydride from acetic acid, methanol and carbon monoxide utilizing that technology is now under construction.[3)] Metal carbonyls such as cobalt carbonyl or nickel carbonyl which are less expensive and richer in the natural abundance have also been known to have catalytic activities for the carbonylation of ethers or esters to give corresponding acid anhydrides.[4-7)]

The authors have already reported that nickel metal supported on active carbon exhibits an excellent activity for the vapor phase carbonylation of methanol to form acetic acid and methyl acetate.[8-10)] In the present work, vapor phase carbonylation of methyl acetate with a nickel on active carbon catalyst was studied, and it was found that the catalyst exhibited a high activity for the formation of acetic anhydride. The details of the catalytic feature of nickel on active carbon are described here.

The catalyst was prepared by impregnating a commercially available granular active carbon (Takeda, Shirasagi C, specific surface area 1200 m^2/g, particle size 20-40 mesh) with nickel acetate aqueous solution, followed by drying in an air oven at 120°C for 24 h. The nickel content in the catalyst was 10 wt% as metal. A continuous flow type reaction apparatus with a fixed catalyst bed was employed at pressurized conditions. The reactor was made of stainless steel tube with an inner diameter of 14 mm. Liquid methyl acetate was mixed with methyl iodide promoter and was introduced into the reactor with a microfeeder. Reaction conditions adopted were as follows: reaction temperature, 250°C; reaction pressure, 31-51 atm; time factor (W/F), 5-15 g-cat h/mol; MeI/(MeI+AcOMe), 0.05-0.20 mol ratio; CO/(MeI + AcOMe), 5.4 mol ratio. Products eluted from the reactor were collected by absorption in a methyl isobutyl ketone solvent at 0°C, to be analyzed by a gas chromatograph using 1,4-dioxane as an internal standard. The analysis of unabsorbed products was also made with gas chromatograph. Methyl acetate, methyl isobutyl ketone, and 1,4-deoxane used in this experiment were reagent grade and were dehydrated over Molecular Sieve 5A before use. Product yields were calculated by the following equation:

$$\text{Yield (\%)} = \frac{\text{(product, mol/h)x(no. of methyl groups in molecule)}}{\text{(methyl acetate fed, mol/h) x 2}} \quad \text{X 100} \qquad (1)$$

This implies that all methyl groups in the molecules of acetic anhydride, acetic acid and methane are derived from methyl acetate.

The main products of this reaction were acetic anhydride and acetic acid. Small amounts of methane and carbon dioxide were formed. The molar ratio of carbon dioxide and methane in the products was from 0.7 to 1.3. It is not clear whether carbon dioxide is formed from methyl acetate or carbon monoxide.

Experimental results are summarized in Table 1. The effect of reaction pressure on the product yields is shown by Runs 1-3. While both the yields of acetic anhydride and acetic acid increased with an increase in the reaction pressure, the selectivity to acetic anhydride increased slightly with increasing pressure. The selectivity to methane was mostly less than 5%.

The effect of time factor (W/F) on the reaction was shown by Runs 2,4,and 5. The yield of acetic anhydride increased with increasing contact time and those of

Table 1. Product yield in vapor phase carbonylation of methyl acetate over Ni/A.C. catalyst[a)]

Run No.	Reaction conditions			Yield (%)			CO_2/CH_4
	Pressure (atm)	W/F (g·h/mol)	MeI/(MeI + AcOMe) (molar ratio)	Ac_2O	AcOH	CH_4	(molar ratio)
1	31	10.1	0.05	7.0	4.1	1.2	0.7
2	41	10.1	0.05	10.6	4.7	1.1	0.9
3	51	10.1	0.05	12.1	5.6	1.2	1.2
4	41	4.9	0.05	5.8	1.7	0.5	0.9
5	41	14.8	0.05	12.1	6.6	2.2	0.7
6	41	10.1	0.10	20.0	11.2	1.9	0.9
7	41	10.1	0.20	20.5	17.5	2.1	0.8

a) Reaction temperature, 250°C; CO/(MeI + AcOMe), 5.4 molar ratio.

acetic acid and methane increased also. The selectivity to acetic anhydride decreased with an increase in the time factor because of the increases in the yields of acetic acid and methane, which suggested the successive formation of acetic acid from acetic anhydride.

Effect of the partial pressure of methyl iodide on the reaction was shown by Runs 2,6,and 7. The yield of acetic anhydride increased with an increase in the partial pressure of methyl iodide up to 0.6 atm. On the other hand, the yields of acetic acid and methane increased with increasing methyl iodide pressure up to at least 1.2 atm. Thus, it can be deduced that the promoting effect of methyl iodide saturates at its fairly low pressure level, and thereafter its increase gives rise to the enhanced by-product formation.

For the formation of acetic anhydride the CO/AcOMe ratio in the feed was also an important factor. When the ratio was 1, little acetic anhydride was formed. However, acetic anhydride comprised one of the main products when the CO/AcOMe ratio was raised up to 10.

In spite of the reaction under water-free condition, a fairly large amount of acetic acid was formed. The formation of acetic acid might be attributed to hydrolysis of acetic anhydride or methyl acetate by water which is formed from methyl acetate or acetic anhydride accompanied by the carbon formation.$^{7)}$

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