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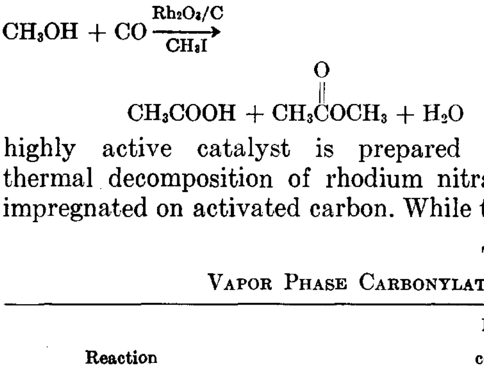
Received October 1, 1968

Vapor Phase Carbonylation of Methanol to Acetic Acid

Low pressure carbonylation of methanol using a soluble rhodium catalyst in the liquid phase has recently been reported (*1*). We wish to report that the vapor phase carbonylation of methanol to acetic acid using a supported rhodium catalyst and a methyl iodide promoter has now been effected at atmospheric pressure Eq. (1). A highly active catalyst is prepared by thermal decomposition of rhodium nitrate impregnated on activated carbon. While the active catalytic species has not been fully defined, the results obtained with this system are similar to those found in liquid phase studies (*1*, *2*). This catalyst (3% rhodium content) is effective at low temperatures (175–250°C) and low pressures (15–300 psia) with very high selectivity (>99%).



$$CH_3OH + CO \xrightarrow[CH_3I]{Rh_2O_3/C} CH_3COOH + CH_3\overset{\overset{O}{\|}}{C}OCH_3 + H_2O \quad (1)$$

Some typical results obtained with a 10 cc catalyst charge (4.5–5.0 g) in fixed bed flow reactor system are presented in Table 1. It may be seen that even at atmospheric pressure (runs 1–3) reasonable conversions of methanol are obtained. (At these conversions methyl acetate is the major product obtained due to esterification of the

TABLE 1

Vapor Phase Carbonylation of Methanol to Acetic Acid[a]

Run no.	Reaction		Feed rate (moles/hr)			Methanol conversion[b] (mole %)	Product analysis (weight %)					
	Pressure (psia)	Temp. (°C)	CH_3OH	CH_3I	CO		$[CH_3]_2O$	CH_3OH	CH_3I	CH_3OAc	HOAc	H_2O
1	15	175	0.25	0.02	0.50	9.5	0.5	59.1	20.3	15.3	0.7	4.1
2	15	210	0.25	0.02	0.50	14.8	0.5	50.9	19.1	21.4	2.4	5.7
3	15	245	0.25	0.02	0.50	21.5	0.5	42.0	17.3	26.6	6.4	7.2
4	215	200	0.25	0.006	0.50	92.6	0	0.2	1.0	9.0	87.6	2.2
5	215	200	0.25	0.002	0.50	88.3	0	0.4	1.1	14.2	80.7	3.6
6	135	205	1.18	0.035	1.98[c]	15.4	0.3	53.9	9.1	27.9	1.4	7.4
7	175	205	1.18	0.035	1.98[c]	20.8	0.4	45.6	8.7	33.7	2.4	9.2
8	215	205	1.18	0.035	1.98[c]	22.2	0.4	42.9	8.7	35.8	2.4	9.8

[a] 10 cc catalyst (4.5–5.0 g) used in a fixed bed flow reactor system.

[b] Calculated as moles $\left[\dfrac{CH_3OAc + HOAc}{2[CH_3]_2O + CH_3OH + 2CH_3OAc + HOAc}\right] \times 100.$

[c] Feed diluted with 1.52 moles/hr of hydrogen.

formed acetic acid with the excess methanol present.) Little conversion of the methyl iodide promoter is found.

At higher pressures (runs 4 and 5) essentially total conversion of methanol is obtained even at only 10–30% of the methyl iodide levels used in the runs at atmospheric pressure. At high methanol conversions, some consumption of the methyl iodide promoter to form acetic acid and hydrogen iodide occurs. Hydrogen iodide can be used in place of methyl iodide as the promoter. The carbonylation reaction is also effective in the presence of a hydrogen diluent (runs 6–8). No reduction products such as acetaldehyde or ethanol are found in any of these runs. The increased feed rates used in runs 6–8 could account for the decreased conversions observed.

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Received November 11, 1968

On the Mechanism of the Synthesis $CO + 2H_2 \rightarrow CH_3OH$

The catalytic synthesis of methanol from hydrogen and carbon monoxide has been the subject of many investigations (*1*), first with regard to the equilibrium constant of the reaction and later with regard to the rate and mechanism (*2*).

Rate measurements have led to various conclusions as to the rate determining step in the reaction. Temkin *et al.* (*3*) suggested that the rate of adsorption of the reacting gases on the catalyst determined the rate of production of methanol, while Natta *et al.* (*4*) postulated that the surface reaction was rate determining. Ogino *et al.* (*1*) based their rate equation on the assumption that the desorption of the product methanol was rate determining. Saida and Ozaki (*2*) found that their data could be explained equally well by at least two mechanisms: One mechanism requires the attack of a hydrogen molecule on formaldehyde, while in the second a CH_3O radical is formed from chemisorbed hydrogen and CO, and then reduced to methanol by another chemisorbed hydrogen atom, the latter step being rate determining.

Tsuchiya and coworkers (*5*) also suggested the formation of a CH_3O radical on the catalyst, having found that H_2 and CO are adsorbed on the catalyst in a mole ratio of 3:2. This would require a rate determining step in which the radical is attacked by a hydrogen molecule, forming methanol and a chemisorbed hydrogen atom:

$$CH_3O(a) + H_2 \rightarrow CH_3OH + H(a)$$

It thus appears that data specifically indicating the rate determining step can help clarify the mechanism of the synthesis.

In the course of synthesizing methanol (for vapor pressure measurements) on a commercial catalyst (*6*), a system, previously saturated with CO and H_2, was used to produce CD_3OD. The synthesis was carried out at 250°C and a pressure of 60 psia, in a glass system similar to that described by Beersmans and Jungers (*7*). The CO and D_2 were supplied to the system from cylinders of the compressed gases (*8*); the D_2:CO ratio was 2:1. Circulation was maintained by thermal convection and the product was collected in a liquid air-cooled trap.

The catalyst vessel was first evacuated