CHEMICALS FROM METHANOL AND CARBON MONOXIDE

1. Introduction

Methanol is a versatile, readily available C₁-compound made from synthesis gas. Large scale industrial methanol production from CO/H₂ was started up in 1925 by BASF using ZnO/Cr₂O₃ catalysts. The present methanol production capacity has been reported to be 21 mio t/a, while the actual demand is only in the range of 12 mio t/a. This overcapacity is mainly due to the build-up of new plants in the Middle East, Eastern Europe, New Zealand and Latin America, where surplus natural gas is available at a very low price [1, 2]. The ready supply as well as the low raw material costs will keep the price of methanol low in the near future. This will stimulate methanol demand and will help to introduce new methanol-based processes for motor fuels as well as for organic base chemicals [3].

The present industrial uses of methanol include the syntheses of formaldehyde, methyl esters, methyl amides and methyl halides. In addition, methanol or its derivatives find increasing interest as a substrate for carbonylation and dehydration reactions, which are summarized in Scheme 1. Some of these processes have already been commercialized, such as the synthesis of acetic acid, of acetic anhydride, or of methyl formate. The feasibility of the MTG (methanol-to-gasoline) process has been proved by pilot plant operation and a commercial unit of a capacity of 560,000 t/a of hydrocarbons had started up operation in New Zealand by 1985. In addition there is a variety of carbon monoxide-based reactions, which convert methanol mainly into C₂-oxygenated compounds.

These can potentially replace ethylene-based routes, e.g. in the case of ethanol, acetaldehyde, vinyl acetate, and ethylene glycol. With methanol from cheap natural gas becoming available in the near future, these processes, although uneconomic today, might become industrially attractive.

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2. Carbonylation of Methanol and of Methanol Derivatives

While the base-catalyzed carbonylation of methanol yields methyl formate, a versatile intermediate for formic acid and formamide synthesis, the transition metal-catalyzed carbonylation involves $\text{C}-\text{C}$ coupling, giving acetic acid derivatives as $\text{C}_2$ oxygenates.

2.1. TRANSITION METAL CATALYZED CARBONYLATION $[4-11]$ 

From the industrial point of view one of the major achievements of homogeneous catalysis has been the introduction of acetic acid processes via the carbonylation of methanol. These processes allow not only the use of methanol as a cheaper feedstock as compared to ethylene, but are also characterized by an extremely high selectivity.

The carbonylation of methanol to give acetic acid is catalyzed by Group VIII transition metal complexes, especially rhodium, cobalt, and nickel:

$$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{CO}_2\text{H}$$

(1)

Iodine compounds are essential cocatalysts, and the reaction is believed to proceed via methyl iodide, which alkylates the transition metal. At elevated pressures and temperatures both acetic acid and the iodine compounds are highly corrosive. Thus, the development of corrosion-resistant alloys such as Hastelloy C was a prerequisite to commercializa-