BF₃-Catalyzed High Pressure Synthesis of Acetic Acid from Methanol and Carbon Monoxide

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ABSTRACTS

Preparation of Crystalline Polyaldehydes

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We found that some organometallic compounds and metal alkoxides polymerized aldehydes including acetaldehyde, propionaldehyde and trichloroacetaldehyde (anhydrous chloral) to give crystalline polyaldehydes. Crystalline polyacetaldehyde was much less soluble in organic solvents than the amorphous one.

Active species of this polymerization was supposed to be metal alkoxide and the mechanism of polymerization was considered in connection with several synthetic organic reactions which involve metal alkoxides and carbonyl compounds. It was assumed that the coordination of aldehyde to the metal alkoxide was essential in propagation reaction which determined the stereospecificity of the polymer produced.

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Yoshimasa Takezaki, Tsuneo Kawatani, Nobuyuki Sugita, Sachio Yuasa, Minoru Osugi and Yoshiko Suzuki

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The reaction of acetic acid synthesis from MeOH and CO has been investigated kinetically in the presence of BF₅•4H₂O as catalyst, as shown by

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{BF}_5} \text{CH}_3\text{COOH}. \quad (1)
\]

The following results have been found out:

1) Preliminary experiments on the system BF₅/H₂O/MeOH/AcOH: On atmospheric distillation of the mixture MeOH/BF₅/H₂O/AcOH (mole ratio 1/0.25/1/0.8) with a Widmer column, AcOH, MeOH and H₂O are distilled out until 106°C and the residue is of the composition (0/0.5/1/0.1).

When the mixture of MeOH/BF₅/H₂O(1/0.5/1) is heated in the autoclave up to 335°C, vapor pressure reaches 66 atm., and both of BF₅ and H₂O remain in the liquid phase, and free MeOH is in the dehydration equilibrium with MeOMe and each gaseous component (MeOH and MeOMe) is also in equilibrium with each dissolved in the liquid phase. The dehydration equilibrium constant K and Henry’s constants, K’ₘ and K’ₑ, have been obtained at 335°C as below:

\[
\text{CH}_3\text{OH} \rightleftharpoons \frac{1}{2}\text{MeOMe} + \frac{1}{2}\text{H}_2\text{O} \quad \text{(gas phase)}, \quad K = P_{\text{H}_2\text{O}}^{1/2}P_{\text{MeOMe}}^{1/2}/P_{\text{CH}_3\text{OH}} = 2.13 \quad (2)
\]

\[
M'ₘ/Vₐ = k'ₘₙ P, \quad k'ₘ = 4.56 \times 10^{-4} \quad \text{(mol. c.c.-¹ atm.⁻¹)} \quad (3)
\]

\[
M'ₑ/Vₐ = k'ₑₙ P, \quad k'ₑ = 7.25 \times 10^{-5} \quad \text{(mol. c.c.-¹ atm.⁻¹)} \quad (4)
\]

where, suffix m stands for MeOH and e for MeOMe.

\[M' = \text{moles in liq.}, \quad Vₐ = \text{liq. volume}, \quad P = \text{pressure.}\]
SYNTHESIS OF DIMETHYLFORMAMIDE FROM METHANOL, AMMONIA AND CARBON MONOXIDE UNDER HIGH PRESSURE

Yoshimasa Takezaki, Yoshiharu Kitahama, Yoshiko Suzuig, Nobuyuki Sugita and Sachio Yuasa

Kogyokagaku Zasshi (Journal of the Chemical Society of Japan, Industrial Chemistry Section), 63, 1739 (1960)

The effects of reaction conditions on the one step synthesis of dimethylformamide from MeOH, NH₃ and CO have been studied under high pressure in the presence of AcOK as a catalyst. Stoichiometrically the reaction is represented as below, but it is very interesting to know whether the reaction proceeds in one step or in two steps, i.e. methylation followed by formylation.

\[
\begin{align*}
&\text{NH}_3 + 2\text{MeOH} + \text{CO} \xrightarrow{\text{AcOK}} (\text{CH}_3)_2\text{NCHO} + 2\text{H}_2\text{O} \\
&\text{NH}_3 + \text{MeOH} + \text{CO} \xrightarrow{\text{AcOK}} \text{CH}_2\text{NHCHO} + \text{H}_2\text{O} \\
&\text{NH}_3 + \text{CO} \xrightarrow{} \text{NH}_2\text{CHO}
\end{align*}
\]

1) The effect of reaction temperature (220~340°C): The increase of DMA yield and the decrease of MMF and DMF above 280°C are due to the instability