Supported Liquid-phase Rhodium Catalyst for Acetylene Hydrochlorination

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A novel, highly active, supported liquid-phase, rhodium catalyst for acetylene hydrochlorination for mercury free production of vinyl chloride is described.

Acetylene hydrochlorination is used in vinyl chloride (VC) manufacture, but requires mercury chloride as a catalyst. The search for a nonmercuric catalyst is divided into searches for homogeneous and heterogeneous catalytic systems. Complexes of various transition metals are known to catalyse the addition of HCl to acetylene under homogeneous conditions: Cu,[1] Pt,[2,3] Au,[4] Pd[5,6] and Rh.[7] Platinum and palladium complexes, with high activity, are too unstable, but in organic solvents, rhodium catalysts are the most stable. Under heterogeneous conditions, complexes of Pt and Au[8,9] display activity. However, the activity of $HAuCl_4/C$ is highest.

We determined that supported liquid-phase catalysts (SLPC) are active and sufficiently stable in acetylene hydrochlorination.[11] The catalytic system was an *N*-methylpyrrolidone (MP) solution of $RhCl_3$ supported on activated carbon. The rhodium complex was dissolved in *N*-methylpyrrolidone and a volatile solvent such as acetone, alcohols and dichloromethane. Activated carbon was impregnated by such a two-component solution, and the volatile solvent was removed by distillation. Specific solvent effects were not observed.

The experiments were performed in a gas-flow reactor; ($HCl:C_2H_2 = 1.1:1$). Concentration of $RhCl_3$ was 0.01 mol dm^{-1} MP. The volume rate of the reagent feed varied in the range 625–2250 h^{-1}. The results are summarized in Table 1.

Table 1 Acetylene hydrochlorination in various catalytic systems

Catalytic system	Metal content/ wt%	Volume rate/h^{-1}	T/°C	Activity/ h^{-1}	Activity drop/ % h^{-1}	Ref.
$RhCl_3$-MP/C	0.014	2250	170	17500	0.23	
$RhCl_3$/C	4.7	1080	180	79.2	15.4	9
$HgCl_2$/C	1.9	1180	180	3500	14.8	10
$HAuCl_4$/C	2.0	1190	180	5400	9.9	10

The experimental data obtained obeys eqn. (1) at 150 °C,

$$r_{VC} = \frac{k_1 \, RhCl_3 \, P_{C_2H_2} P_{HCl}}{I + k_2 \, P_{HCl}} \tag{1}$$

where $k_1 = 4.6\ 10^6\ MPa^{-2}h^{-1}$, and $k_2 = 12\ MPa^{-1}$

Kinetic study with rhodium SLPC showed that the rate of VC formation is first order in the catalyst concentration (the content of the active species on the support), first order in the acetylene partial pressure, and below first order in the partial pressure of HCl.

Received, 1st November 1993; Com. 3/06527H

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