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Studying of the Effective Parameters on Catalyst at Ethylene Dichloride Production

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Abstract

Commercial production of ethylene dichloride (EDC) employs bi-functional catalysts such as $CuCl_2$, which is prepared via impregnation. In this route the active agent penetrates the catalyst base (γ-alumina). The purpose of this work is the preparation of a catalyst for oxychlorination reaction. The active agents of this catalyst are KCl and $CuCl_2$ of which the latter has the role of catalyst and the former is used to prevent sublimation of $CuCl_2$ at the elevated temperatures.
In addition to the preparation of the catalyst with different degrees of activities a fixed bed reactor was employed to compare the kinds of produced catalyst. The effect of different variables (concentration, PH, temperature of solution and time of impregnation) on the penetration of the active agents into the catalyst base was studied. Cu/K ratio influence on $CuCl_2$ sublimation and reaction yield was also considered. The results that are reflected as graphs have been used to prepare suitable catalysts for EDC production.

Key words: Ethylene Di chloride; CuCl2; KCl; impregnation; catalyst; oxychlorination

Introduction

Production of EDC employs $CuCl_2$ catalyst as following reaction:

$$C_2H_4 + 2HCl + 0.5O_2 \xrightarrow{CuCl_2} C_2H_4Cl_2 + H_2O \qquad \Delta H = -56.6\ kcal/mol$$

The mechanism of above reaction is as follow:

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + Cu_2Cl_2$$

$$Cu_2Cl_2 + 0.5O_2 \rightarrow CuO.CuCl_2$$

$$CuO.CuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

By Cracking of EDC, vinyl chloride is produced, and then P.V.C. will be prepared.
Above catalyst is prepared via impregnation. The active agents of this catalyst are $CuCl_2$ and KCl, that copper chloride has the role of catalyst and potassium chloride is used to prevent sublimation of $CuCl_2$ at the elevated temperature.

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 2CuCl \uparrow$$ Sublimate

$$2CuCl_2 - KCl + C_2H_4 \rightarrow C_2H_4Cl_2 + 2CuCl - KCl$$ Non-Sublimate

Experimental tests

Catalyst is prepared as following procedure:

- Catalyst base selection
- Impregnation
- Drying and calcination

Selected base analysis is as follow:

SiO_2	0.02%
TiO_2	0.002%
Fe_2O_3	0.02%
Na_2O	0.35%
Al_2O_3	93.6%
Loss on Ignition	6%

Specific Surface	325 m^2/g
Porosity	0.5 cm^3/g
Bulk Density	769 kg/m^3
Crushing Press	703 kg/m^2
Macro Porosity	0.3 cm^3/g
Abrasion Loss	0.3

The active agents KCl and $CuCl_2$ are selected and solution are prepared. The effect of concentration, PH, temperature and time on the impregnation of the active agents into the catalyst base is studied. Results are shown in Figs.1-7 and the effect of temperature was negligible.
After impregnation, catalyst is dried at 130^{o}C. And after 150minutes, moisture is decrease to 0.2 %wt. For calcination, temperature is increased to 300^{o}C with rate 2^{o}C/min.
In 2nd Experiments, produced catalysts at 400^{o}C are tested and $CuCl_2$ sublimation versus Cu/K ratio is considered as shown in Fig 9. In 3rd series of experiments a fixed bed reactor was employed to test the bellow parameters (Fig.8).

- Specification activity versus $CuCl_2$ wt%
- EDC selectivity and HCl conversion versus Cu/K ratio.

Discussion and results:

The effect of different concentration, time and PH on $CuCl_2$ penetration is shown in Fig 1,2,3. As it is seen, effect of PH on penetration of $CuCl_2$ is negligible, but concentration and time variables are important. At concentration more than 90 g/l and time more than 20hr, $CuCl_2$ weight percent is approximately constant.
The effect of different parameters on KCl penetration is shown in Fig 4,5,6. As it is seen, with increase penetration of KCl, PH is increased but range of variation is negligible. At concentration more than 90 g/l and time more than 7 hr, KCl penetration is approximately constant.
Specific activity of catalyst is considered and shown in Fig 7.By increasing $CuCl_2$ weight percent, specific activity of catalyst is increased and when $CuCl_2$ concentration reaches to 8wt%, specific activity will be approximately constant. Sublimation of $CuCl_2$ is considered as shown in Fig 9 .As it is seen amount Cu/K less than 1.6 is good and we don't have sublimation. Reaction yield is considered in Fig 8. With Cu/K ratio less than 2, EDC selectivity is increased but HCl conversion will be decreased. Therefore the cross point of two curves shows that the best ratio of Cu/K is 1.18. Finally drying curves for catalyst versus time is drawed in Fig 10.

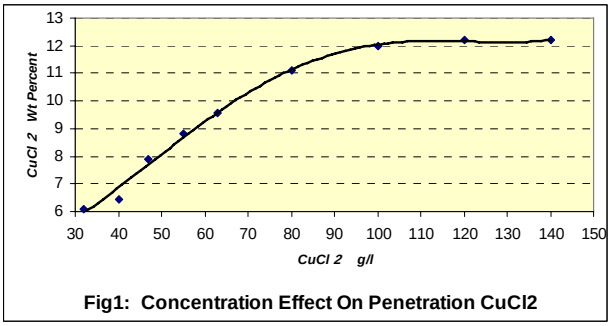

Fig1: Concentration Effect On Penetration CuCl2

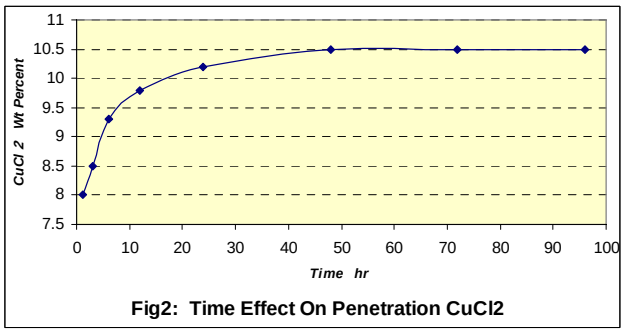

Fig2: Time Effect On Penetration CuCl2

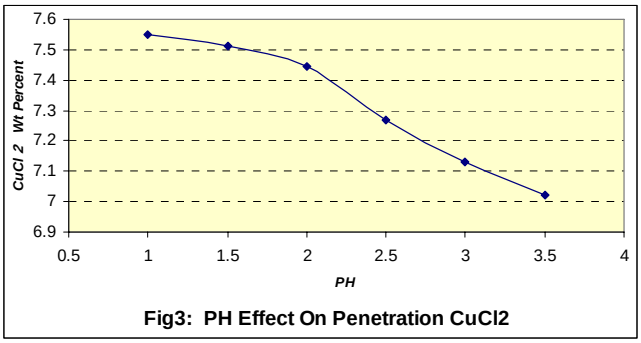

Fig3: PH Effect On Penetration CuCl2

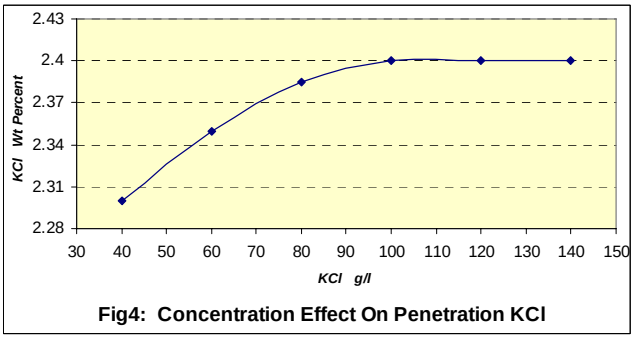

Fig4: Concentration Effect On Penetration KCl

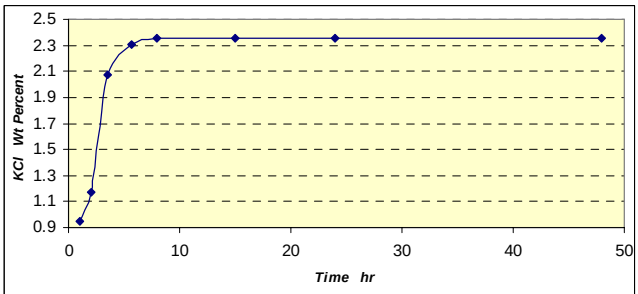

Fig5: Time Effect On Penetration KCl

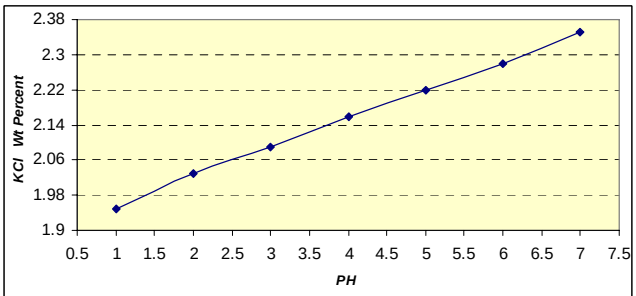

Fig6: PH Effect On Penetration KCl

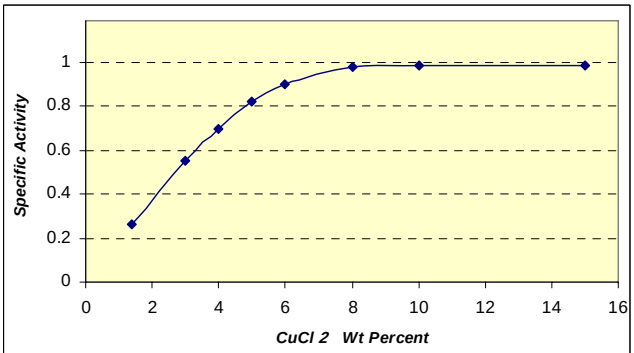

Fig7: CuCl2 Effect On Specific Activity

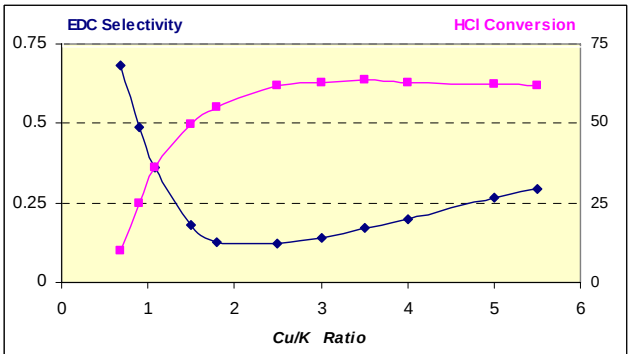

Fig8: Cu/K Ratio Influence

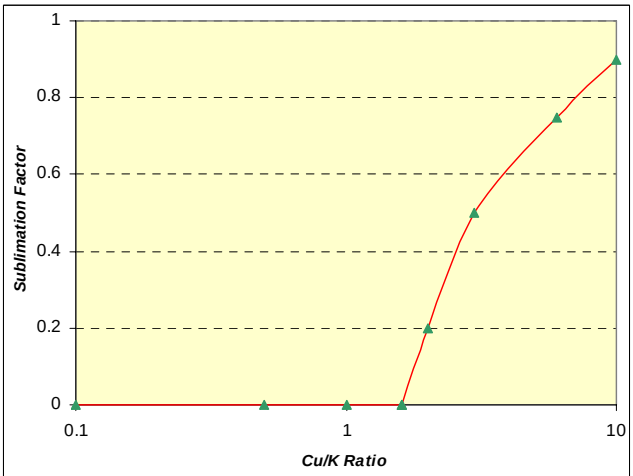

Fig9: Cu/K Ratio Effect on CuCl2 Sublimation Factor (400 Deg. C)

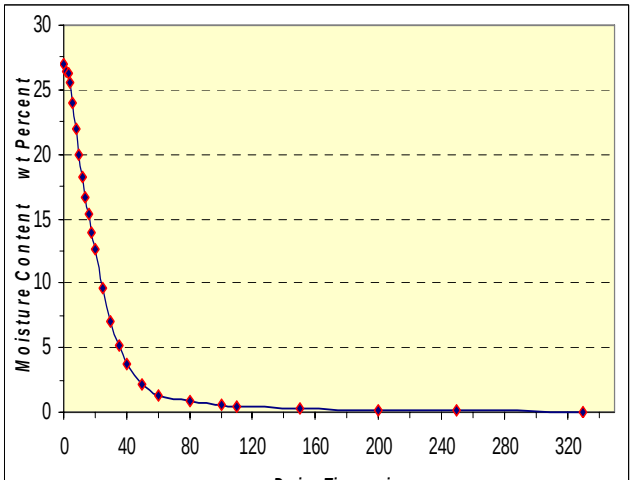

Fig10: Catalyst Drying Curve

References:

[1] James w. Fulton, Making the Catalyst, Chem. Eng., July 7, 1986, P59
[2] Trimm, D.L., Design of Industrial Catalysts, Elsevier Scientific Pub. Co., Amsterdam, 1980
[3] Moss, R.L., Preparation and Characterization of Supported Metal Catalysts Experimental Method in Catalytic Research, Vol. II, Anderson, R.B., and Dawson, P.T., eds, Academic Press, New York, 1967
[4] Shingu, H., and Inui, T., Some Mechanistic Correlations Between Impregnation and Activation Operations for the Preparation of High-selectivity Supported Metal Catalysts, Preparation of Catalysts II, Delmon, B., Grange, P., Jacobs, P.A. and Poncelet, G., Eds, Elsevier Scientific Pub. Co., Amsterdam, 1979
[5] Acres, G.J.K., Bird, A.J., Jenkins, J.W. and King, F., The Design and Preparation of Supported Catalysts, Catalysis, Vol.4, Kemball , C., and Dowden, D.A., Eds, Alden Press, Oxford, 1981
[6] James W. Fulton.,Selecting the Catalyst Configuration, Chem. Eng., May 12, 1986, pp 97-99
[7] Sittig, M., Handbook of Catalyst Manufacture, Noyes Data Corp., Park Ridge, N.J., 1978