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Superior Mercury-free Catalysts for Acetylene Hydrochlorination to VCM: Achieving High Productivities and Long Catalyst Life-Time

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Abstract

New mercury-free catalytic systems based on the use of ionic liquids (IL) and noble metals (e.g. Pd, Au) have been evaluated for the hydrochlorination reaction of acetylene to produce Vinyl Chloride Monomer (VCM). Two different approaches have been investigated: gas-liquid homogeneous catalytic systems in the presence of molten IL/Metal and heterogeneous gas-solid ones using solid materials. For the latter case, very positive results have been obtained using SILP-type catalysts (SILP: Supported Ionic Liquid Phase) where IL/Metal were deposited onto a solid mesoporous support. Remarkably, both systems display very high Space Time Yield (STY) and breakthrough life-time stability. No deactivation is observed even after 500 h on stream indicating the strong advantages of these new materials compared to most investigated Au/C supported systems. The development of heterogeneous catalysts was preferred as the scale-up of gas-liquid technology implies important CAPEX investments to convert current plants from gas-solid to gas-liquid equipment.

Introduction

Poly Vinyl Chloride (PVC) has become the third most used plastic worldwide after polyethylene and polypropylene and its demand continues increasing. The global installed capacity is estimated around 47.5 million tons per year and its production has grown from 24.7 million tons in 2000 to 32.3 million tons in 2009[1]. PVC is produced by polymerizing the VCM which is manufactured industrially via two distinct processes (figure 1):

- acetylene-based hydrochlorination process
- ethylene-based ‘balanced-process’ (chlorination / oxychlorination / pyrolysis)

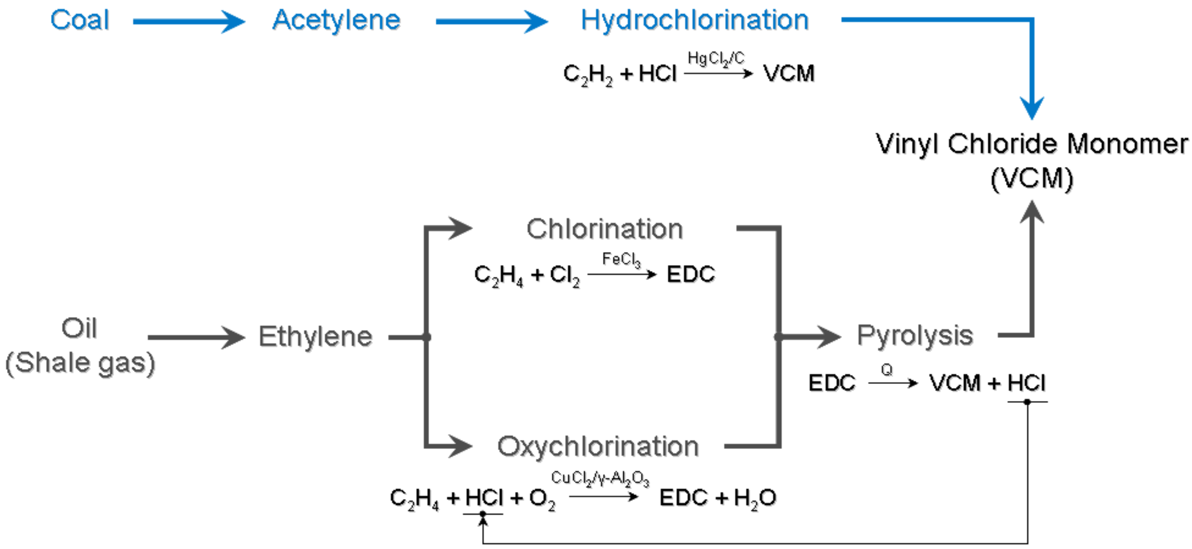

Figure 1: Industrial processes for the production of VCM.

Whilst the latter process finds application worldwide, the former is limited to countries where affordable access to large coal resources is possible namely, China where in 2010 statistics revealed that ~80% of the PVC domestic gross capacity was made up acetylene-based plants[2]. Although the acetylene-based process is significantly simpler compared to the ethylene-based route, there is a major drawback. Standard catalysts contain mercury salts that, under reaction conditions, tend to sublime leading to important environmental and health concerns as well as limited catalyst life-time. It was estimated that ~ 10 ktons of mercury catalyst were used in 2010 implying a pure mercury consumption of about 800 tons. Besides these extremely important issues, it is also worth mentioning that, according to industrial forecasting, important mercury mine capacity is expected to be exhausted within 5-10 years[2].

All these factors stress even further the importance of finding solutions in a relative short time. Although much work has been done on decreasing the loading of mercury in current type of catalysts, the development of mercury-free systems would be the sole solution for putting an end to this problem.

Many mercury-free systems have been studied so far but to the best of our knowledge no industrial solutions has been applied yet. Here we present for the first time, new experimental results on innovative mercury-free systems based on the use of ionic liquid/noble metals that display promising performances. We believe these materials may be candidates for solving all the issues above mentioned letting the acetylene-based route be a much greener and sustainable process.

Homogeneous Ionic Liquid systems

Acetylene hydrochlorination is highly exothermic (ΔH ~ -100 kJ / mol) and it is carried out industrially using multi-tubular packed reactor. However, local hot-spots formation can not be entirely avoided leading to fast mercury volatilization and deactivation rates. A possible solution to obviate this problem may be to carry out the reaction in a liquid medium that would favour heat removal improving temperature control. Cao *et al.* already suggested that the use of IL may be beneficial for this potential application since such organic compounds display very low partial pressure, excellent solvent capabilities, good thermal stability and heat conductivity[3]. Herein, we present our recent results using different inorganic salt catalysts and IL. Figure 2 shows catalytic activities for different metals.

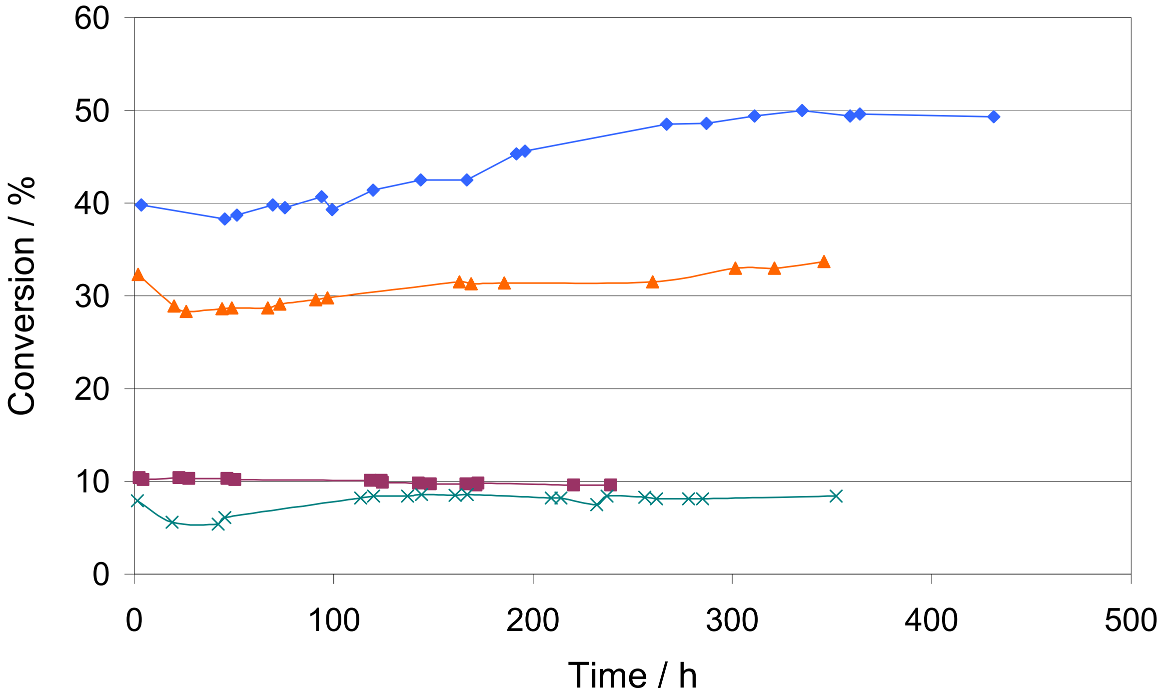

Figure 2: Acetylene conversion as a function of time on stream for different inorganic salt catalysts. Experiments conditions: 1-Butyl-3-Methyl-imidazolium chloride (BMIM Cl), T = 150°C, C_2H_2 = 5 NL/h, HCl = 6 NL/h. VCM selectivity always > 99.8%. Legend: ♦ $PdCl_2$, ▲ $AuCl_3$, x $PtCl_4$, (■ $HgCl_2$ for comparison).

As it can be seen in the graph, $PdCl_2$ catalyst performs the best and, remarkably, all systems display no deactivation even after 10 days. For some metals, in particular Pd, a stabilization time seems necessary before obtaining stable conversion. VCM selectivities were always > 99.8% with trace formations of 1,1 and 1,2 Dichloroethane (DCE) with the Markovnikov adduct being more abundant.

Although not included in the plot, other salts were tried but conversions lower than 10% were observed, namely CuCl, WCl_6, WCl_4, $MnCl_2$, $SnCl_2$, $SnCl_4$, VCl_3, $SbCl_3$, $CeCl_3$ and $CuCl_2$.

Hutchings[4] proposed that Au should be the most active metal due to its high redox potential. However, results show that under these conditions Pd outperform Au. Nevertheless, the involvement of the IL on the catalysis mechanism is not yet well understood. We believe IL-interactions with the metal play a fundamental role that may explain why Pd displays superior activity.

In view of the experimental results obtained, $PdCl_2$ was chosen for a follow-up screening of different IL as it displayed the highest conversion rates (results are shown in Figure 3).

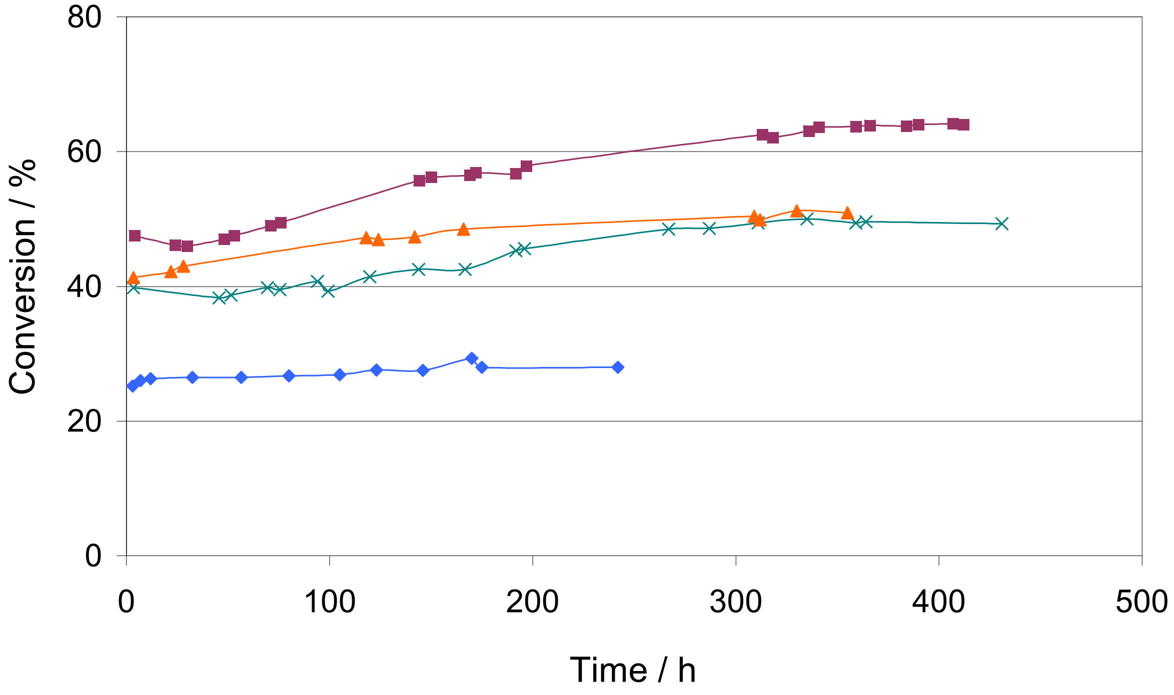

Figure 3: Acetylene conversion as a function of time on stream and different IL. Experiments conditions: IL + $PdCl_2$, T = 150°C, C_2H_2 = 5 NL/h, HCl = 6 NL/h. VCM selectivity always > 99.8%.
Legend: ♦ Tri-hexil-tetradecyl-phosphonium chloride, ▲ 1-Ethyl-3-methyl-imidazolium chloride, x 1BMIM Cl, ■ 1-Butyl-imidazole.

As previously mentioned, Pd seems to require a stabilization time in particular when imidazolium salts are used (1-Butyil-imidazole reacts with HCl under reaction conditions to yield 1-Butylimidazolium chloride). However, during such time, conversion does not decrease but it rather increases of about 20 % (~ 30% for 1-Butylimidaole). Remarkably, in all the experiments, VCM selectivity still remained always > 99.8%. Under best conditions, STY was estimated to be around 0.4 ton_{VCM} / ton_{IL} / h.

Heterogeneous Ionic Liquid systems

Homogeneous IL-based system displayed promising performances featuring high STY and long life-span. However, it can not be forgotten that the scale-up of such technology would imply important CAPEX investments to convert current plants from gas-solid to gas-liquid equipment. Inspired by the positive results already obtained, a ‘drop-in’ catalytic solution was developed in order to be closer to current industrial needs. The focus was to develop a heterogeneous catalyst capable of directly replacing the current $HgCl_2$/C system.

Therefore, we had the idea of using SILP catalysts where IL/Metal are deposited onto a mesoporous solid support. This approach would have the advantage of marrying the benefits of the homogeneous catalysis (high turn over frequencies) with the ones of the heterogeneous (easy recover of the catalyst). Surprisingly, we found that such materials were active for the hydrochlorination reaction.

In view of previous results, $PdCl_2$ and BMIM Cl were chosen for initial tests where different SILP-catalysts were synthesized with increasing IL loading. Figure 4 shows their catalytic performances as function of time and temperature.

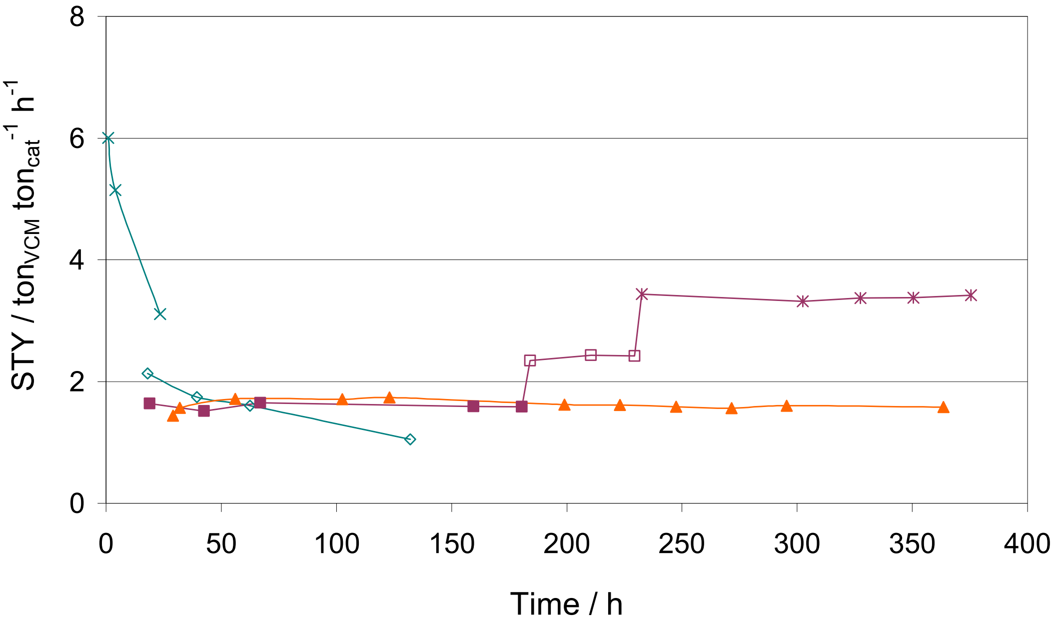

Figure 4: VCM STY as a function of time on stream for different Pd/BMIM Cl SILP-catalyst. Experiments conditions: C_2H_2 = 5 NL/h, HCl = 6 NL/h. VCM selectivity always > 99.8%
Legend: Pd/SILP with 50 wt% BMIM Cl: ▲, T = 110°C
Pd/SILP with 30 wt% BMIM Cl: ■ T = 110°C, □ T = 130°C and ✕ T = 150°C
Pd/SILP with 10 wt% BMIM Cl: x T = 150°C and ◊ T = 110°C
(Only for this particular catalyst selectivities dropped to values ~98% after first hours due to formation of 1,1- and 1,2-dichloroethane and other side products).

The results indicate that IL loading is of paramount importance for obtaining stable catalysts. Catalysts with 10% IL loading display a very rapid deactivation. Analysis done on spent catalysts showed the formation of large amount of carbonaceous species indicating the tendency of these materials to coking. On the other hand, no formations of carbonaceous species were found on catalyst with 50% IL. This finding is of fundamental importance as coking is almost every time observed on heterogeneous hydrochlorination catalysts and it is usually assumed to be the main reason for catalyst deactivation.

The effect of the metal on the catalytic activity was also evaluated. As it can be seen in Figure 5, Pd has been found the most active in agreement with previous experiments on homogeneous liquid systems.

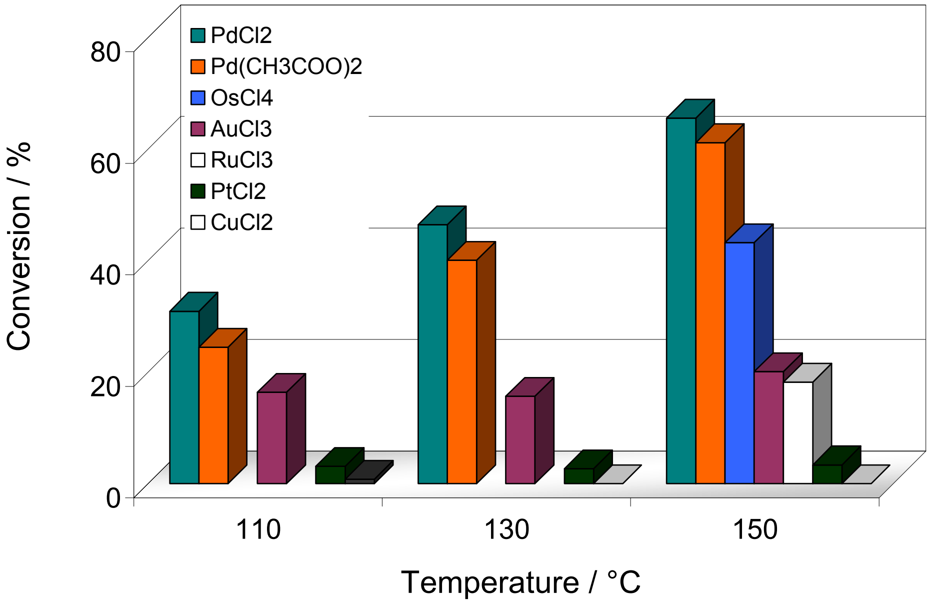

Figure 5: Acetylene conversion as a function of reaction temperature for different noble metals. Experiments conditions: 50 wt% BMIM-Cl SILP catalysts, C_2H_2 = 5 NL/h, HCl = 6 NL/h. VCM selectivity always > 99.8%

Conclusions

Two different types of catalytic systems based on the use of IL have been tried successfully for carrying out the hydrochlorination of acetylene: a homogeneous IL liquid system and a heterogeneous one. Both systems perform extremely well displaying high STY, long life-span and VCM selectivities > 99.8%. However, the heterogeneous system based on the SILP-concept may represent the way for a ‘drop-in’ solution much closer to current industrial needs.

Ongoing R&D focuses on achieving catalyst systems that fully meet ‘drop-in’ requirements meaning a straightforward replacement of current mercury catalyst within existing industrial equipments avoiding any further CAPEX investments. As a conclusion, we strongly believe these new materials are industrial candidates for replacing the current $HgCl_2$/C catalyst in the near future making the acetylene-based PVC production a more environmental benign and sustainable process.

References

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