

Quantitative study by Raman spectroscopy of the stability of 1-methyl-3-butylimidazolium chloride/ AlCl_3 /Ethyl AlCl_2 mixed molten salts in presence of an aliphatic hydrocarbon.

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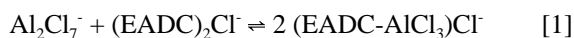
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The major application of acidic 1-methyl-3-butylimidazolium chloride (MBIC) - Ethyl AlCl_2 (EADC) and MBIC- AlCl_3 -EADC mixtures is their use as solvent for catalytic reactions such as the dimerization of olefins catalyzed by nickel complexes (Difasol[®] process) (1-3). These ionic liquids indeed proved to be particularly effective for a two-phases catalysis process since the products are not soluble in the molten phase and can be extracted by an aliphatic hydrocarbon phase. However, the main difficulty is to suppress or limit catalyst leaching in the organic phase and to avoid the loss of the ethylaluminum necessary for the alkylation of the nickel catalyst. A thorough quantitative investigation of the behavior of the molten salt phase as well as the organic phase has then been undertaken by Raman spectroscopy. Since the mixed mixture, containing EADC together with AlCl_3 , is the one used in the industrial process it has received most of our attention.

If the structure of MBIC- AlCl_3 and MBIC-EADC mixtures is well known (4-5), new Raman spectra confirm that the MBIC- AlCl_3 -EADC mixtures exhibit an additional mixed (EADC- AlCl_3) Cl^- species which seems to play an important role in the catalytic process. The formation of such species is not quantitative and is related through an equilibrium:



For the dynamic extraction of the molten phase by an aliphatic hydrocarbon (cyclopentane), the same apparatus as we have described previously (6) has been used. It allows to record Raman spectra of all phases, as a function of time. Measurements have been performed on a large number of MBIC-x AlCl_3 -y EADC compositions where x and (or) y varied while keeping the sum (x+y) such as the melt stays acidic. The present results show that the dynamic extraction process is more complicated than initially thought (6). Two extraction reactions must indeed be taken into account simultaneously:



where DEAC is the (Ethyl) $_2$ AlCl. An interesting conclusion is that the extent of each reaction was found melt composition dependent: the proportion of EADC versus DEAC increases with the acidity level of the initial melt, mainly determined by its AlCl_3 content.

Since the extraction process mechanism is now fully understood, conclusions could be drawn to propose a melt composition exhibiting the lowest loss in ethylaluminum while keeping the acidity level compatible with the catalysis process.

Other ways to further decrease the ethylaluminum extraction will be presented.

Acknowledgments

The F.N.R.S. of Belgium is gratefully acknowledged for a grant to S. Dechamps. The Institut Français du Pétrole is also acknowledged for financial support

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