

## SUMMARY

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Supported metal catalysts constitute an important class of catalysts due to their widespread applications in chemical industry and unique characteristics. Many of the successful catalysts are multimetallic in composition and exhibit a high level of activity, maximum selectivity and excellent stability during use for a variety of hydrocarbon reactions. The efficacy of supported metal catalysts are, in general, governed by the following five aspects, namely, (a) nature of active species, (b) type of support, (c) choice of promoters (d) preparation methods and (e) pretreatment procedures. For the design of a successful catalyst a judicious combination of all the above aspects is needed.

The work incorporated in this thesis is divided into two parts:

- (1) Studies on modification of properties of spheroidal gamma alumina and
- (2) Studies on the role of promoters in Pt/alumina catalysts for dehydrogenation of higher paraffins.

The method of preparation of spheroidal gamma alumina by sol-gel/oil drop technique was adopted and standardised. Attempts have been made to modify the pore structure of alumina spheroids by introduction of organic acids in the alumina sol itself. Carboxylic acids (mono, di & tri basic and hydroxy) were shown to have been incorporated in the sol matrix through IR spectroscopic and thermal analysis techniques. This method of

addition of acids in the sol preparation stage induces the growth of colloidal aggregates of hydroxides in the sol, thus modifying the fundamental nature of the polymeric sol matrix. The organic acid additives change the morphology, pore structure and mechanical properties of the alumina spheres. The investigation has thus resulted in a method, suitable for modification of pore structure of alumina, particularly in cases where microporosity is not desired and the proportion of meso and macro pores are to be increased.

The second aspect investigated in the present work was the role of promoters in platinum on alumina catalysts during the dehydrogenation of n-dodecane to monoolefins. Promoters were selected from groups IB(Ag), IIIA(In), IVA(Sn) and VA(Sb) so as to have a systematic variation in electronic configuration. Platinum to promoter atomic ratio was always maintained at 1:2 and similar methods of preparation and pretreatments were adopted. The catalysts were characterised by chemical analysis, dispersion, TPR, DRS and ESCA measurements to determine the possible interaction between the elements and to identify the surface species. The activity, selectivity and stability of these catalysts for dehydrogenation of n-dodecane were determined under atmospheric and high pressure conditions. Further, TPO experiments were carried out in order to understand the coking behaviour of these catalysts.

Results of TPR, DRS and ESCA experiments indicate strong interaction between promoters and platinum and resultant electronic modification (ligand effect). Dispersion experiments

provide strong evidence for the existence of ensemble effect. DRS studies show that these elements modify the electronic spectrum of platinum in the reduced state. Moreover, it is observed that the thermal reduction behaviour is also modified accordingly and to varying extents. Of these elements Sn shows maximum interaction with platinum and the interaction is in the order,



XPS results indicate a decrease in electron density around platinum in the presence of Sn, slight increase in the electron density in presence of Sb and more pronounced increase in the presence of Ag. Indium is not found to induce any significant changes in the electronic levels of platinum.

The activity and stability evaluation show that Pt-Sn combination is better than other systems studied. Though In and Sb enhance the activity to significant levels their stability is not found to be satisfactory. The observations have been explained in terms of the paraffin/olefin adsorption-desorption mechanism and complex formation involving back donation of electrons from platinum to adsorbed olefin. It has been found that both ensemble and ligand effects are operating favourably in the case of Pt-Sn combination whereas in the case of other promoters, possibly one of the effects predominate over the other or they operate in mutually opposite directions, resulting in marginal improvement in selectivity and stability. Moreover, it appears that the ensemble effect is mainly responsible for the increase in the activity whereas ligand effect governs the

stability of the catalyst.

Finally, the kinetics of n-dodecane dehydrogenation on Pt-Sn-Li/alumina catalyst was studied with an intention to get an insight into the mechanism of the reaction and the performance of the catalyst. The results of the kinetic study indicate that the rate of the overall reaction is controlled by the dual site surface reaction step. This in accordance with our earlier observation that the paraffin adsorption and olefin desorption are favoured in the case of Pt-Sn-Li/alumina due to the decrease in the electron density around platinum.

It is suggested that a more realistic picture about the catalytic action of promoted platinum catalysts could emerge only when the ligand and ensemble effects could be quantified and their influence with respect to specific reaction system/mechanism is well understood.