CHAPTER 8

SUMMARY AND CONCLUSIONS

8. Summary and Conclusions

- Alumina samples with desired textural properties have been obtained by varying the preparation conditions/parameters via sol-gel process. The effect of various parameters viz. nature of hydrolysant (protic and aprotic), hydrolysis level "h" (molar ratio of water to alkoxide), acid and base catalysis (influence of pH) of the hydrolysis step, rate of addition of hydrolysant, aging and calcination conditions were investigated. The materials were characterized through various techniques viz. N_2 adsorption, SEM, XRD, IR and Thermogravimetry. For comparison, an alumina sample has been prepared by oil drop technique and evaluated.
- Sol-gel (SG) alumina possesses high surface area, pore volume and mean pore radius and is meso porous in nature. Alumina through oil drop (OD) route has medium surface area, comparable pore volume and mean pore radius and is also meso porous. While SG alumina is highly amorphous with smaller crystallite size, OD alumina is more crystalline with larger crystallite size.
- SG technique is highly versatile and useful for preparation of tailor made supports/catalysts.
- Sol-gel method of preparation of Pt-Sn/Al_2O_3 catalysts (mono and bifunctional) by single step method has been studied by varying preparation conditions like pH (pH 3 and 9) during hydrolysis and mode of solvent removal from the gel (distillation/filtration).
- Active elements (Pt and Sn) at measurable levels are lost during preparation of SG catalysts. Weak interaction of pseudo boehmite with metal precursors, adsorption behaviour of alumina based on its zeta potential; especially under SG preparation conditions and mode of separation of the gel from the solvent are responsible for the loss. Such losses are not observed in conventional catalysts.
- It is observed that subtle variations in preparation methods significantly affect the textural properties of the catalysts as revealed by surface area, pore volume, pore size distribution, pore shape and nitrogen adsorption-desorption isotherms and hystersis loop analysis data.

- Solvent removal by distillation yields better textural properties and better retention of active metals compared to filtration.
- Sn/Pt atomic ratio and residual chloride levels in the SG catalysts play a major role in governing the acidity of SG catalysts as investigated by butene-1 isomerization and temperature programmed desorption of ammonia.
- Variations in preparation methods significantly influence the Pt metal dispersion, Pt-Sn interaction and Sn-support interactions as revealed by metal dispersion measurements by chemisorptive titration and temperature programmed reduction studies.
- Pt dispersion for SG catalysts are less than those observed for catalysts obtained by conventional impregnation methods. Encapsulation of Pt crystallites by support, decoration of Pt by Sn and more favourable interaction of Sn with alumina could be the possible reasons for low dispersion values displayed by SG catalysts.
- TPR studies reveal that in SG catalysts Sn support interactions are more prominent than Pt-Sn interactions.
- BSG series of catalysts show better attenuation of acidity compared to ASG series but with relatively poor Pt-Sn interaction and higher Sn-support interaction compared to ASG.
- Controversy regarding the influence of SG preparation method, single step or two step on the metal dispersion remains unsolved.
- For comparison, Pt-Sn/Al_2O_3 catalysts of similar chemical composition (mono and bifunctional) have been prepared using OD alumina and conventional co-impregnation technique and characterized.
- XRD studies on conventional catalysts reveal the presence of only gamma alumina phase, with Pt and Sn well dispersed with better crystallinity compared to SG catalysts.
- Pt-Sn/Al_2O_3 catalysts prepared by conventional methods are typically mesoporous, with a surface area of 160-170 m^2/g and pore volume of 0.6-0.7 ml NTP/g, mean pore radius 80-90 Å and typically broad pore size distribution.

- Total acidity expressed as millimoles of ammonia/g, of the conventional catalysts are closer to those observed for sol-gel catalysts and shows parabolic trend with respect to Sn/Pt atomic ratio.
- TPR studies have shown that Pt-Sn interactions are strong for conventional bifunctional catalysts, while it is a shade less with monofunctional ones. Presence of residual chloride plays a critical role in Pt-Sn interactions.
- Conventional catalysts display better platinum dispersion that increases with Sn loading while in SG catalysts effect of Sn loading on dispersion is less pronounced due to the interaction of Sn with support.
- Pt metal dispersion emerges as the sole factor responsible for activity of the catalysts, conventional or sol-gel.
- IMP series of catalysts with better dispersion display higher activity compared to SG catalysts that have relatively poor dispersion.
- SG catalysts display higher TOF values compared to IMP catalysts indicating that the nature of active sites is different in SG catalysts.
- Selectivity for mono olefins formation follows regular trend with respect to Sn/Pt ratio in the case of IMP catalysts while no trend is observed for SG catalysts.
- Coke contents in spent SG catalysts are higher than those on IMP catalysts indicating higher level of deactivation in SG catalysts.
- Deactivation rates observed for monofunctional IMP series is less compared to those observed for bifunctional IMP catalysts. Residual chloride in bifunctional catalysts is responsible for deactivation by coking.
- Deactivation rates for SG catalysts are higher than those for IMP catalysts, possibly due to weak Pt-Sn interactions strong Sn-support interactions.
- Coke formation in SG catalysts is related to acidity as well as the fraction of unalloyed platinum.
- The unique relationship between unalloyed Pt and coke content reveals the importance of Pt-Sn interaction (ligand effect).
- Platinum dispersion, Pt-Sn interaction and acidity are the major factors that influence the overall performance of conventional as well as sol-gel type catalysts.

- Higher TOF values observed for SG catalysts points towards immense potential that the technique offers for catalyst preparation. The short-comings observed with SG technique, like, loss of active metals, strong interaction with the support, poor dispersion and encapsulation of active elements could be overcome with suitable modifications in the preparation procedure. Attempts in these directions have already been reported by Sault and co-workers **(1)**.
- The positive aspects of SG technique, ie tailoring of textural properties, compositional homogeneity, molecular level interactions between active elements and availability of wide ranging preparation parameters for tailor- made products are worth exploring further. Preparation of Pt-Sn/Al_2O_3 catalysts by single step SG technique has tremendous relevance with respect to large scale catalyst production provided the aspects on loss of metals is taken care of.

References

1. Sault, A.G., Martino, A., Kawola, J.S. and Boespflug, E., *J. Catal.*, **191**, 474, (2000)