CARBIDE CATALYSTS

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Platinum group catalysts find multitudinous applications in various industrial processes such as hydrogenolysis, isomerisation, dehydrocyclisation, dehydrogenation, etc. They are also involved in manufacturing everyday items such as polymers, drugs and fuels. Unfortunately, the resources of platinum group catalysts are limited. In particular ruthenium, rhodium, iridium, palladium and platinum are extremely rare and expensive. Some scientists and space agencies have proposed mining meteors, which often contain relatively high levels of platinum group metals. But it would be too expensive. Hence their future is uncertain.

The transition metal carbides have attracted the attention of many scientists, due to their unique physical properties like high m.p, metal-like high thermal and electrical conductivity, super conductivity, inertness at room temperature. It has been found that, by combining molybdenum and tungsten, both readily available metals, with carbon, the resultant metal carbides have catalytic properties quite similar to platinum group metals. Also, Mo and W are less expensive than platinum group metals.

Early researches also showed the similarities between platinum and molybdenum or tungsten carbide. In 1961, a paper in a Russian journal described the dehydrogenation of cyclohexane to benzene over a metal carbide. In 1970, the French research team of Jean-Marie Muller and Francois Gault isomerised 1,1,3-trimethylcyclopentane to xylene on tungsten metal, a reaction typically catalyzed by platinum. A year later John Sinfelt at Exxon in New Jersey, US, showed that the rate of hydrogenolysis of ethane over molybdenum increases 60 fold as the catalyst's surface is converted into molybdenum carbide. Researches at AEG-Telefunken, in Frankfurt, Germany, found that tungsten carbide could be used instead of platinum as an electrode for hydrogen oxidation. Levy and Boudart recognized the catalytic, and possibly electronic, similarities between tungsten carbide and platinum when they isomerised 2, 2-dimethylpropane to 2-methylbutane and oxidized hydrogen to water over tungsten carbide.

Several studies have been attempted to explain the reasons for similarities between platinum's behaviour as a catalyst and molybdenum and tungsten carbide. Some of the reasons may be as follows-

i) Carbon in the carbide donates electrons to 'd' band of the metal. Adding four electrons to Mo or W shifts their electronic properties along the periodic table to coincide with platinum. The same effect also shifts Mo more to right of the periodic table.

ii) By dissolving a nonmetallic element like carbon in a metal group of VIB (Mo,W) which strongly chemisorbs molecules, the surface reactivity of host metal increases. It may be due to structural differences in the active sites between the metal carbide and pure metal catalyst. In metal carbide the positive charge on the metal atom results from the electron transfer between the metal and carbon. This positive charge causes the formation of multiple adsorption sites on metal atom.

Nowadays, a range of methods is available for synthesizing carbides suitable for catalysis. Some of the methods are:

1) Reactions of metals, metal hydrides or metal oxides with appropriate amounts of carbon in protective or reductive atmosphere. The reaction temperature are generally very high e.g. greater than 1500K.for Mo_2C.
2) Reactions of metals or their oxides with carburising gases such as light hydrocarbons or CO.
3) MoO_3 is heated at slowly increasing temperature in a stream of CH_4 / H_2 to produce Mo_2C.

Industrial Applications

(1) Hydrodesulfurisation of thiophene (HDS): HDS is of prime importance in processing crude oil. This reaction converts sulfur compounds to H_2S and desulphurised organic compound in presence of H_2. Following graph shows the activity of Mo_2C and presulphided Mo/Al_2O_3 catalyst.

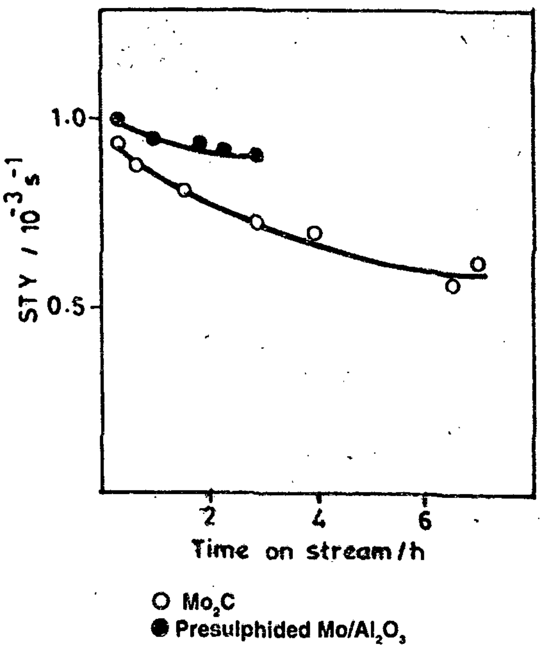

Fig.1 : Comparison of activities of Mo_2C and presulphided Mo/Al_2O_3 catalysts for HDS process.

It can be noted that both Mo_2C and presulphided *Mo/Al_2O_3 have comparable selectivity and reactivity.* Hence Mo_2C catalyst can be effectively used for HDS process. HDS process may become more important as in future the sulphur restrictions in petrol will be tightened.

(2) Fischer-Tropsch synthesis: In the Fischer-Tropsch synthesis of hydrocarbon, ruthenium is a very active catalyst for hydrogenation of CO. But at low temperature and high pressure it produces large amount of very high molecular mass waxes. As a solution the powdered TiC, TaC & Mo_2C catalyst can be used which exhibits high catalytic activity for the production of various hydrocarbon-including ethylene from CO and H_2 mixture Above process yields CH_4, H_2O, CO_2, C_2H_6. The Mo_2C catalyst favors the production of C_2 and C_3 hydrocarbon.

An important fact about these metal carbide catalysts is that they can produce hydrocarbons higher than ethane under conditions of high temperature and high H_2/CO ratio, which is in contrast with Ru or Ni catalyts where the major hydrocarbon product is methane.

(3) Synthesis of methyl formate from methanol: The dehydrogenation of methanol to produce methyl formate is currently an important problem in heterogeneous catalysis. However the Cu is always used for higher selectivity (>~70).

Dehydrogenation of methanol can be effectively carried out on carbides such as TiC, Mo_2C and WC. The metal carbide catalysts ensure high selectivity and productivity.

(4) Syngas production: Molybdenum oxide supported on silica gives the highest yield of syngas. Due to carburisation at the initial stages of the reaction, molybdenum oxide converts to molybdenum carbide which in turn is active for syngas formation from methane. The processes available for syngas production are steam reforming, dry reforming with carbon dioxide and partial oxidation with oxygen or air. Mo and W carbides are active for all the three processes and their activity is comparable to best of the platinum group catalysts. These catalysts push the reaction to thermodynamic equilibrium i.e. very high conversion of methane. Selectivity is more than 90%. Carbides are active at elevated pressure and no carbon is observed on catalyst after reaction.

(5) Isomerisation and hydrogenolysis: Carbide catalysts are active in isomerisation of 1,1,3-trimethylcyclopentane, 2- and 3- methylpentane, of 1-hexene to *cis-* and *trans-* 2-hexene and 2-butene to 1-butane. In the isomerisation of n-hexane, the carbide catalysts are 25 times more active than conventional platinum group catalysts in terms of specific rate and selectivity. Only 10% of hydrocracked molecules are formed. Carbide catalysts are also active in hydrogenolysis of ethane, 1,1,3- trimethylcyclopentane, cyclopentane, cyclohexane and methylcyclopentane.

In the above reactions one may achieve conversion approaching thermodynamic equilibrium where cracking is expected in case of conventional platinum group catalysts. Selectivity is also high. Carbide catalysts are more resistant to catalytic poisons such as sulphur typically found in crude oil.

Figure 2 shows applications of early transition metal carbides and nitrides for catalysis.

Future Potentials

Carbides can be effectively used as microthrusters in satellites. Microthrusters are used to change the orbit of a satellite. Current technology uses the supported iridium catalyst to decompose hydrazine. Scientists have found that the performance of tungsten carbide compares favourably with iridium catalyst and provides a higher thrust to the microthruster. Due to high mechanical resistance and hardness the tungsten carbide wears more slowly than iridium i.e. the catalyst has a longer life.

Treating molybdenum carbide with oxygen creates new phase called molybdenum oxycarbide. This catalyst can be used in isomerisation of much longer *hydrocarbon-hexadecane and isodehydrogenated* butane to methyl propane - an important reactant for

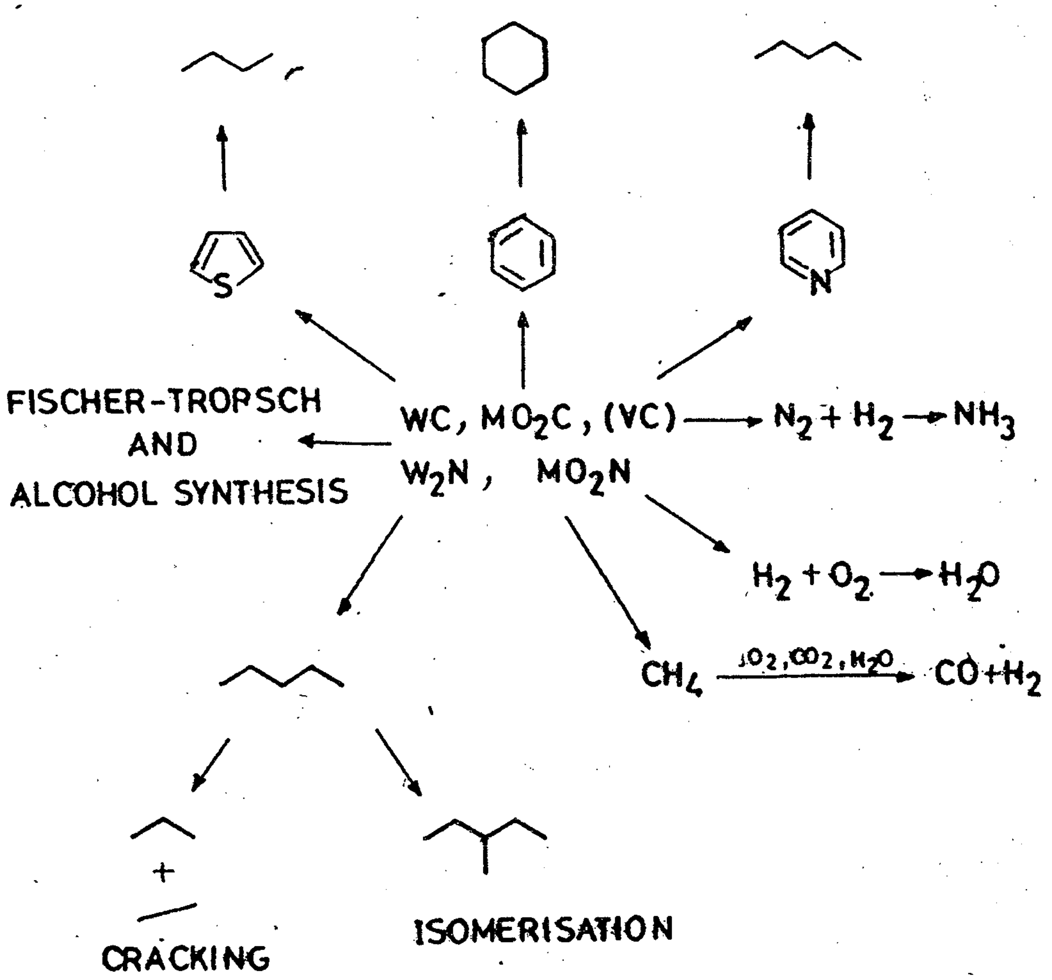

Fig 2 : Applications of early transition metal carbides and nitrides for catalysis.

producing MTBE (methyl tertiary butyl ether) fuel additives. In addition, these new catalysts may provide a way of upgrading diesel fractions and lubricant fractions, which is currently impossible. There is a good chance that molybdenum oxycarbide will be the future industrial catalyst for isomerisation.

Conclusion

Molybdenum and tungsten carbide catalysts are well on their way towards replacing noble metals as the mainstay of the chemical industry. They promise to provide better selectivity and productivity at a fraction of the cost exacted by noble metal catalysts as initial investment and maintenance. It is possible to design processes employing these catalysts that utilize raw material better, resulting in lower effluent loads and hence are kinder to the environment. Research is still required to understand the implications of their use more completely and to design ancillary equipment that will exploit their potential to the full.

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