Theoretical feasibility for catalytic property of certain ores

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With the continuous growth in catalysis research, it is always the intention of both the manufacturers and the users to minimize the cost of catalysts. Catalysts have a worldwide market of several billion dollars. Transition elements have a respectable position in catalysis as they can act as industrially important catalysts in various reactions such as hydrodesulphurization, polymerization, reformation, oxidation, etc. The study of crystal structure of certain transition metal oxide ores shows that they can act as a metal-support system. Higher temperature reduction will form active sites in Fe-Ti spinel ores in which Fe^{3+} occupies the tetrahedral sites. In such a case, strong metal–support interactions will play an important role in this kind of metal–support system. Ores will be certainly a cheaper version in catalysis.

ONE of the aims in catalysis research is to minimize the cost of catalysts and to increase their selectivity. Hence better methods for catalyst selection and preparation, novelty of reaction, ease of use, product purity (selectivity) and increasing environmental compliance, etc. are attempted.

High price of the raw material and complicated process of preparation are the reasons for the high cost of the conventional catalysts, which are prepared with the analytical grade or reagent grade chemicals with different procedures of catalyst preparation. The total catalyst system is not a single metal compound, but is a combination of several metal oxides, with the catalyst, support and promoter (if any) as the components. Any material, which is directly available from nature, will be cheaper than the synthetic variety. Can we think of ores as the natural alternative of these synthetic catalysts?

Ores and transition metals

Primarily, two kinds of ores may be considered: oxides and sulphides. What should be the parameters for selecting certain ores as catalysts? Among the first series of transition elements, Fe, Co, Ni, V, Mn and Cr are the most significant members to be used as catalysts. Most heterogeneous catalysts are supported, where the 'active material' is deposited on an 'inert' carrier, typically a refractory oxide. Although the support is termed 'inert', it affects the performance of the active material. A complete

distribution of metal-support interaction has come into play, namely weak, medium and strong[1]. Vishwanathan and Mary[2] distinguished different kinds of metal-support interactions and related them to the change of phase of the support materials at different temperatures. They concluded that TiO_2, Nb_2O_5, La_2O_3 and Sm_2O_3 show strong metal-support interaction (SMSI), whereas SiO_2, Al_2O_3 and ZrO_2 do not show SMSI. The transition metal–oxide interface is assumed to be a better catalyst than the transition metal alone[3]. The phase transition of different structures is also known to be catalysed by the metal loaded on the support[4].

There are certain transition metal ores in solid-solution with other refractory metal oxides. We are trying to find out whether these ores act as metal-support systems and hence act as catalysts. Some of these ores are titanomagnetite ($Fe_3Ti_2O_4$), ilmenite ($FeTiO_3$), bauxite $\{(FeAlTi)_2O_3 \cdot xH_2O\}$, magnetite ($Fe_3O_4$) and hematite ($Fe_2O_3$) to name a few of them. Let us examine how these ores can act as metal-support systems.

Metal-support system in ore

The concept of phase transformation as a cause for observation of SMSI effect[5,6] may have originated from the observation of Dickenson et al.[7] who reported that titanium cations of the hexagonal form of barium titanate formed direct chemical bonds with several transition metal ions by the overlap of their respective d-orbitals. The phase transition of the support will be observed only when the metal ions are dissolved in the support lattice and yield strong cation–cation interactions by suitable overlap of d-orbitals[8]. The high temperature reduction allows the

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dissolution of metals ions and produces the reduced cations of the support which act as donor cations and the reduced state of the metal ion functions as acceptor cations, which eventually results in a strong cation–cation interaction. Madhusudhan *et al.*[8] have shown that considerable amount of Fe is found in the subsurface layers of gel-supported Fe/TiO_2 catalyst and the extent of reduction for 9.2% Fe/TiO_2 catalyst in crystalline phase is 75%, whereas it is only 25% for gel-supported Fe/TiO_2 catalyst[8]. The ore equivalents of the earlier mentioned catalyst systems are titanomagnetite and ilmenite which contain much higher percentage of FeO in the system. Titanomagnetite has inverse spinel structure (Figure 1). In a magnetite structure, Ti^{4+} substitutes the tetrahedral Fe^{3+}. Several studies have been performed on the Zn/Cr spinel catalyst for higher alcohol synthesis[9–12]. Thus synthetic spinels are certainly used as catalysts. In spinel structures, however, the general concepts of radius ratio do not apply; indeed larger cations are in the smaller polyhedrons and vice versa. This is explained by the crystal field stabilization energy (CFSE) instead of geometric concepts, and larger cations may actually occupy tetrahedral sites[13]. The near-surface concentration of the tetrahedral sites of the spinel structure which are occupied by the Fe^{3+} and Ti^{4+}, creates active catalyst sites with a strong interaction between Fe^{3+} and Ti^{4+} ions. Electron beam scattering studies have also shown that low coordinated surface metal sites dissociate H_2 in a single collision at 300 K (ref. 14). On strongly interacting supports, high reduction temperatures (600–650°C) are required and they lead to extensive agglomeration and the formation of large metal particles[15]. However, these low coordinated metal sites will be the active centres for catalytic reactions.

Chemisorption study of reduced ore catalysts shows metal crystallite size to be expressed in terms of dispersion, which is expressed as:

$$\text{Dispersion} = (\text{gram atoms of } H_2 \text{ adsorbed})/(\text{total gram atoms of metal present}).$$

In such a case, dispersion of metal atoms has to be studied to evaluate and predict their performance as catalysts.

The other iron–titanium ore, ilmenite, is a titanate of ferrous iron ($Fe^{2+}Ti^{4+}O_3$) rather than a double oxide of ferric iron and titanium. It crystallizes in the hexagonal system. In ilmenite, iron is in + 2 state, which is desirable, as reduction of the Fe^{2+} is easier from energetics and hydrogen consumption point of view. So, in Fischer-Tropsch synthesis (FTS) for hydrocarbons, titanomagnetite and ilmenite may be good alternatives for titania-supported iron catalysts.

SMSI of TiO_x support increases the rate of hydrogenation and also controls the product distribution upon certain transition metal catalysts[16,17]. TiO_2 being a strong Lewis acid, forms Lewis acid–base complex with adsorbed CO or H_2CO at the metal-support interface, facilitating the breaking of C=O bond. There is a recent trend of studying the CO hydrogenation, mostly on TiO_2-supported metal catalysts.

A comparative study has been performed on hematite and magnetite ores in FTS for hydrocarbons[18]. The study has shown that though hematite ores have higher effective surface area, the activity of magnetite ore is higher (Table 1). The difference in the crystal structure of magnetite and hematite may be the reason for this difference in activity. In hematite structure (hexagonal) Fe^{3+} is in six-fold co-
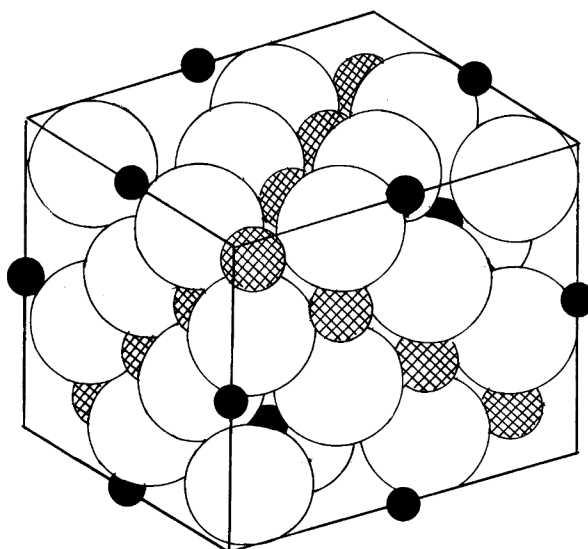
Figure 1. Perspective view of the structure of spinel. Large spheres, oxygen; Small black spheres, tetrahedral positions; Cross-hatched spheres, octahedral positions (ref. 20).

Table 1. Yield of hydrocarbons for magnetite and hematite ore
catalysts at different temperatures (ref. 18)

Ore catalyst	Temperature (°C)	C_1-C_4 Paraffins	C_2-C_4 Olelins	C^{5+}	Total yield g/m^3
Magnetite	220	2.2	1.8	143.1	147.1
	240	2.2	1.8	143.6	147.6
Hematite	220	11.4	6.2	113.4	131.0
	240	5.3	2.8	139.0	147.1

ordination, but Fe^{3+} is at tetrahedral position in magnetite which has a spinel structure. Two-thirds of the cations (Fe^{3+}) in magnetite are in alternate layers with four-fold coordination. The near-surface position of the tetrahedral sites and low coordination of Fe^{3+} increase the activity of magnetite as catalyst.

The domestic price (including the cost of processing) of highly purified ilmenite (52% TiO_2) ore is Rs 25 per kg (Source, *Indian Minerals Year Book, 1998–1999*, Indian Bureau of Mines), whereas the calculated cost for catalyst (ore equivalent) prepared from commercial grade chemicals is almost Rs 700 per kg. The advantages of this study in considering ores as catalysts are that certain low-grade ores, which are rejected for their lower-order metal content, can be tested as raw materials for catalyst preparation. So, the low-grade ores which are dumped as wastes will find a new kind of applicability in catalysis. All ores have to be processed before using them as catalysts.

Conclusions

The progress in catalysis would have been fast if there would have been a detailed theoretical understanding of the process, than an empirical understanding as at present. Wienberg *et al.*[19] devised the bond-energy bond-order (BEBO) model which predicts bond strength and allows prediction of activation energies of surface reactions. The bond energy of the surface adsorbate bond varies with bond distance and bond order. Still, understanding of catalytic property of certain materials depends on the experimental output rather than on the theoretical predictions. But certain selected ores/low-grade ores may act as catalysts for hydrocarbon synthesis in FT process, NO_x reduction or desulphurization of coal.

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