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THE CHARACTER OF CATALYSIS

Catalysis had and still has an enormous impact on human society,

having transformed its life and lifestyle during the years.

By any measure, catalysis is a remarkable phenomenon. There is an almost magical quality about the ability of small amounts of a substance to change - to increase or decrease - the rate of a chemical reaction by many orders of magnitude, transforming millions of times their own weight of chemicals, without itself being consumed in the process. Equally significant is the ability to control selectivity, usually thought of as a catalysts accelerating one of a number of competing reactions, but which can also be achieved by the catalyst selecting one reagent out of a complex mixture. The catalyst can change only the rate at which equilibrium is attained; it cannot change the position of equilibrium, so the possibilities that are open to catalysis are completely constrained by the thermodynamics of the system.

However, the practical outcomes can be manipulated by clever control of transport. Even by the barest scientific criteria, catalysis is a uniquely fascinating subject.

The application of catalysis is also unique in having transformed the life and lifestyle of human society. During the last two centuries, innovative catalytic technologies have played a pivotal role in the production and use of the inorganic and organic chemicals, polymers, and the petroleum derivatives that so dominate our industrial society, to the extent that a 1998 estimate proposed that 30-40% of the GDP of the developed world depended on them [1]. These figures ignored the importance of the technologies in food manufacture, and predate the rapid growth of the technologies for DNA manipulation that ultimately rest on the catalytic ability of RNA to cleave DNA strands in a controllable reproducible fashion.

In analysing the application of catalysis we can consider and relate events and dimensions that range over orders of magnitude, from the fundamental atomic and molecular phenomena that configure catalytic phenomena - such as the stretching and breaking of chemical bonds, or collision of molecules with a solid surface - to the lifetime of catalytic plants and the distances travelled by the molecules that are converted within them (Fig. 1).

Considerations of application also encourage us to examine the economic impact of catalysis, on a scale that stretches from the value of an individual product of catalysis, such as a used polythene bag, to the annual value of the chemical, pharmaceutical, and energy industries, about 10 trillion Euros.

The impact of catalysis on human society can be appreciated only by a more qualitative examination.

The earliest conscious applications of catalysis were in food preparation techniques; archaeological evidence gives brewing a history of at least 10,000 years, with baking and dairy applications coming soon after. But it was with the blossoming of inorganic chemistry around the end of the eighteenth century that catalysis in a recognizably modern form entered the scientific literature. When concentrated mineral acids became available, acid catalysis was quickly discovered in reactions like the dehydration of ethanol and the hydrolysis of starch. A few years later experiments by Davy, Döbereiner and others with the new metal platinum revealed its power to catalyse the combustion of hydrocarbons and of hydrogen. Catalytically active enzymatic ferments were isolated later in the 19th century (Fig. 2).

During the 20th century the science and technology of catalysis split into three distinct disciplines. Heterogeneous catalysis nucleated around the technology of porous inorganic solids, and the reactions that can be induced on their surfaces, in contact with either a gas phase or a liquid phase. Homogeneous catalysis is almost entirely a liquid phase phenomenon, and is identified closely with reactions utilising the flexible coordination chemistry of transition metal complexes. Biocatalysis rests on enzymatic reactions, but may utilise whole organisms as reaction vessels.

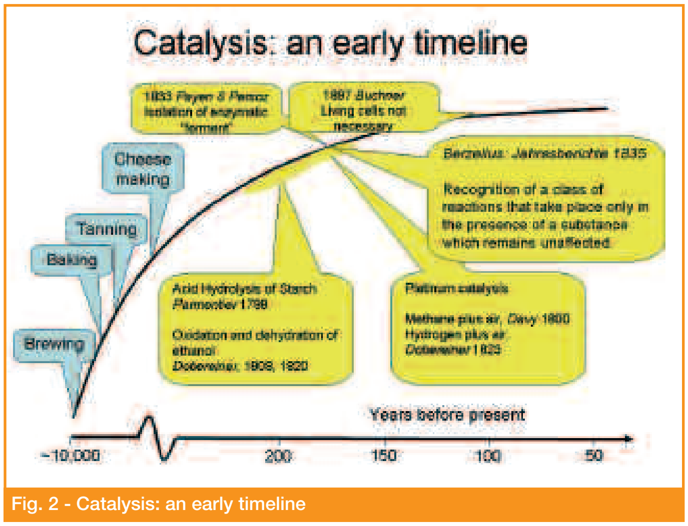


Fig. 2 - Catalysis: an early timeline

Döbereiner's invention of the Feuerzug, a portable and reliable device for creating a flame, led to the first recognizably modern catalytic innovation. It happened with a speed and a marketing flair that astonish even today. Within just six years of his independent observation that platinum gauze ignited a jet of hydrogen in air, sales of the Feuerzug were booming, both in the plain industrial version, and in the very attractive pottery designs intended for the sitting-rooms of genteel society. Millions were sold. It would be inconceivable now that we would introduce into our homes the hazardous ability to make hydrogen by dipping zinc into sulphuric acid, let alone setting fire to it, but at the time - well before safety matches - it was a vast improvement over the available methods: it filled a real need (Fig. 3).

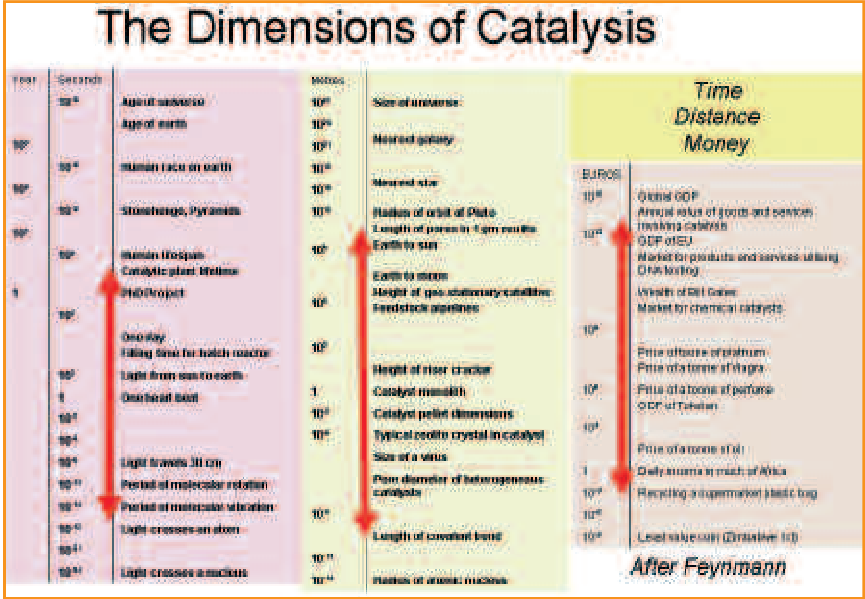


Fig. 1 - The Dimensions of catalysis

It was a different human need that inspired the next illustrative example we consider. In 1900 the western world feared a shortage of nitrate, an essential ingredient for making explosives and munitions that came mainly from animal excrement, especially the droppings of seabirds around the Pacific Ocean. How could the next war be fought without nitrates? Fritz Haber, in Germany, initiated an empirical experimental search for a catalytic process to make ammonia by combining nitrogen from the air with hydrogen, potentially available in large quantities by the steam reforming of coal and hydrocarbons; the ammonia could then be oxidized to nitric acid.

Fig. 3 - Döbereiner's Feuerzug

What emerged from thousands of experiments was a catalyst made by reduction of magnetite. The process conditions needed for an effective transformation had to balance the requirements of the thermodynamics (favouring high pressure and low temperature) with the high temperature needed to provide the energy to break the strong N-N and H-H bonds. The reaction did not go to completion, reaching an equilibrium at 35% conversion to ammonia, introducing the extra requirement that the ammonia be separated by cooling, and the permanent gases returned to the reactor. So novel were these new process requirements that they could be implemented only by inventing a new discipline, chemical engineering.

The technology for manufacturing ammonia in large fixed bed plants has remained essentially unchanged through to present plant. Ammonia production now exceeds 100 million tones per annum, and is largely used for the fertilizer that has raised yields of cereal cops, and made possible the frightening and dangerous growth of the human population to over 6 billions.

Improvements have been made in the catalysts, particularly to reduce the energy required (Fig. 4). These went hand-in-hand with a development in the understanding of the process mechanism, something that took over 80 years to complete [2]. It is a complex system, requiring several different phases of iron to be present, each of which has a role in dissociating the diatomic reactants and in stepwise recombination of the N and H atoms. The action of promoters and poisons is well understood, though there is still a slow and irreversible decline in catalyst activity, perhaps 5-10% per year. Probably it is not in the interests of catalysts manufacturers to market everlasting catalysts.

Interestingly, the energy consumed in combining nitrogen and hydrogen in a plant making 250,000 tonnes per annum is proportionately smaller than the energy used in natural systems that fix nitrogen, for example in the bacterial nodules that symbiotically infest with the roots of leguminous plants, though the comparison does not include the energy of industrial hydrogen production.

Over the last hundred years many different metals, oxides, polymers and other materials have found application as heterogeneous catalysts. Beginning in the 1980s, the desire for new catalysts inspired the development of the whole science and technology of microporous materials. Equally varied are the physical forms in which the catalyst is manufactured, each design tailored to particular applications. Pellets for use in fixed bed reactors are shaped to give optimum transport properties. Porous monoliths are coated with catalytic oxides for automobile exhaust catalysts, and other high throughput situations. There are flexible catalysts made from fibres. Mechanical strength is always an issue for heterogeneous catalysts.

Catalyst and reactor design have frequently evolved together. The most dramatic example is catalytic cracking of gasoil. Very active faujasite zeolite catalysts were introduced in the 1960s to raise gasoline yields, but required very short contact times to take full advantage of the selectivity. The conventional fluid bed reactor was replaced by a vertical riser, over a hundred meters tall, the catalyst spheres being transported upwards in a few seconds by the vapourising and expanding flux of gasoil and cracked product, before being separated in a cyclone and regenerated by burning off the deposited coke. The rate of catalyst circulation is controlled so that the exothermic carbon combustion provides just enough heat to drive the endothermic cracking reaction.

Homogeneous catalysis using transition metal complexes is a science from the second half of the 20th century. Its great triumph has been to expand by orders of magnitude the range of methodologies for making carbon-carbon bonds, and it is used in poly-

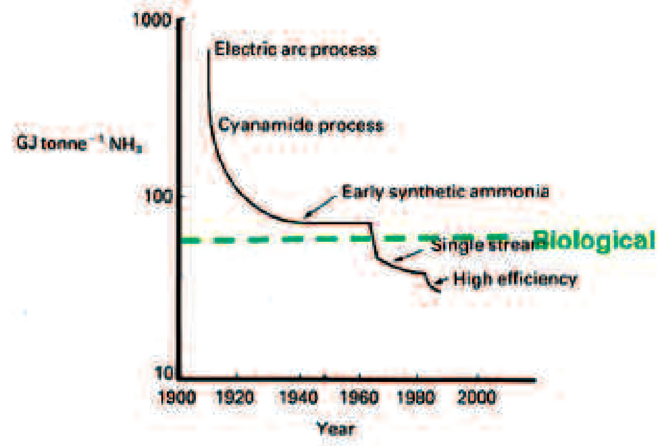


Fig. 4 - Energy use in ammonia manufacture

mer manufacture, in bulk and speciality chemicals, and in pharmaceuticals, and very widely as a laboratory synthetic tool. The labile nature of the coordination spheres of the complexes, and the accompanying subtle shifts in their electronic structures, have led to some highly selective and productive chemistries, and to the seductive promise - so far fulfilled in only a few cases - of controllable enantioselectivity.

While the coordination chemistry around the transition metal has attracted the most research attention, the design of processes using homogeneous catalysts has utilised advanced *in situ* spectroscopy to define and monitor the various species in the catalytic cycle (Fig. 5). This was used to very good effect by BP in their development of the CATIVA process for making acetic acid, where the introduction of an iridium catalyst increased selectivity, productivity, and the robustness of the catalyst [3].

Biocatalysis as mentioned above is the oldest catalytic technology, and is increasingly viewed as a "green" alternative to chemical catalytic methods. Successful application of enzymes to chemical manufacturing often depends on finding or modifying enzymes for work in concentrated media, not a hard task as many enzymes are lypophilic. Without these adaptations, biocatalysis often requires dilute aqueous conditions that bring large energy penalties when the product has to be extracted. Nevertheless, the promise of complex biocatalytic systems is immense, as the recent multi-enzyme system for conversion of starch to hydrogen and carbon dioxide vividly demonstrates [4].

Perhaps the most striking 20th century application of biocatalysis, however, is found in nearly every home, and is used by perhaps half the world's population. Enzymes are incorporated in most products for cleaning clothes. They catalyse the hydrolysis of soils such as proteins, fats, or starches, and by allowing clothes to be cleaned at lower temperatures potentially contribute to energy conservation. They also play a role in keeping clothes in good condition, especially cheap knitted cotton garments: cellulase enzymes, like the ones found in the fungi that attack wood, snip off the small pills that grow due to abrasion during wear and give the impression of fading colour. The wonder is that the enzymes have to be adsorbed onto the fabric in order to carry out their cleaning and conditioning activities, but are present in the wash liquor only in micro-molar concentrations. Truly exceptional molecular design (Fig. 6).

Biocatalysis is rapidly spawning applications outside manufacturing and consumer goods. In medical diagnostics, enzymes combine with analytical chemistry to provide fast and reliable assays of metabolites: the glucose monitors used by diabetics are mostly based on oxidising glucose to glucolactone, which can be measured in several ways. A rapidly growing category of treatments work by switching off enzymes, including common prescriptions for hypertension and for erectile dysfunction. And of course the whole raft of new technologies based on splitting DNA depend on the ability of RNA to split the nucleic acid chain.

Catalytic technologies are ubiquitous, but their value is largely unrecognised by the public. By contrast, the concept of a "catalyst" as an "agent of change", has escaped from the confines of the scientific literature to inhabit the world of advertising cliché. In 1835 Berzelius recognised that "catalytic power actually means that substances are able, *by their mere presence*, to waken affinities which are asleep at this temperature".

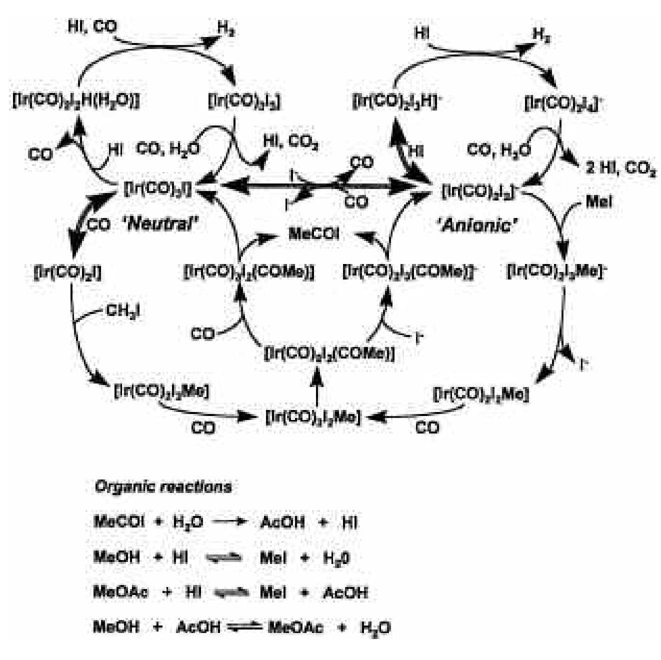


Fig. 5 - CATIVA process mechanism

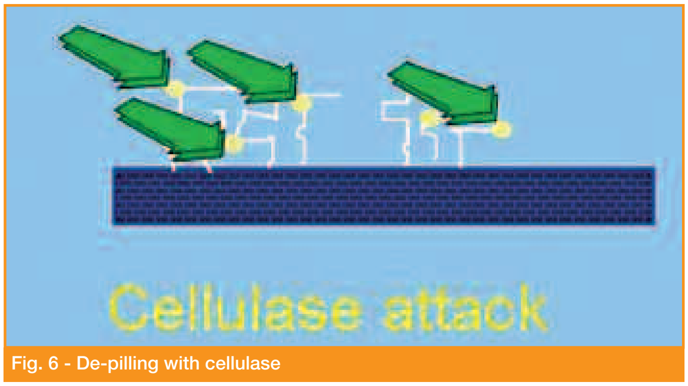


Fig. 6 - De-pilling with cellulase

Fig. 7 – Catalysts as agents of change (by permission of Dark Horse Comics)

Before 1900, papers in *Nature* used the term “catalyst”. By 1950 (according to the Oxford English Dictionary) the word was being used in literary circles to describe a cause of sudden change of view or mood. Google “catalyst” and you will find the name applied to a host of products and organisations that have adopted the name to persuade potential customers of their ability to induce positive changes. Lots of management consultancies and training companies, replete with logos; bars, especially in college towns; a perfume; a rather good blended red wine from California; and a company selling sailing holidays in the Caribbean. No-one, at least to the author’s knowledge, has yet suggested that a catalyst can cause a sea-change.

Other cultural allusion to the catalytic phenomenon, however, stand out as most apt metaphors for the development of catalysis in the 21st century. The first is the role of super-hero, as in the Dark Horse comic illustrated in Fig. 7. The transformation of the world energy, transport, and manufacturing systems from dependence on fossils to a sustainable basis cannot be accomplished without the help of new and clever catalytic technologies. The list of goals has been rehearsed frequently, and is given without comment.

The generic technology challenges are fearsome, and only a few are mentioned here. Not only is there a need for 100% selectivity, catalysts will need to be more specific, to select preferred reactants from complex mixtures. resistance to poisoning and deactivation will be at a premium. There will be a demand for reliable miniature devices capable of working reproducibly for long periods. And many of the metals used in catalysis may well be in short supply, not least platinum.

Fortunately catalytic technologists will have an impressive range of research tools for their work. *In situ* measurement is more or less possible on distances from atoms in a lattice to a large reactor in a chemical plant: the gaps can be filled in by computation, increasingly used to verify experimental results. Process modelling also covers similar scales. The development of nanotechnology provides new ways for assembling catalytic bodies, and of microreactors new ways of engineering reactions.

There will also be new paradigms for how catalysis research is done. It is at present hypothesis driven: the researcher uses experience to envisage candidate catalysts, which are then tested, investigated, and optimised, including the use of high throughput and library technologies. However, during the next few years sufficient understanding will be gained and collated about key parts of the catalytic operation that design from first principles may become possible. Such a rational approach to design of catalytic technologies is at present only feasible in a few isolated cases (Fig. 8).

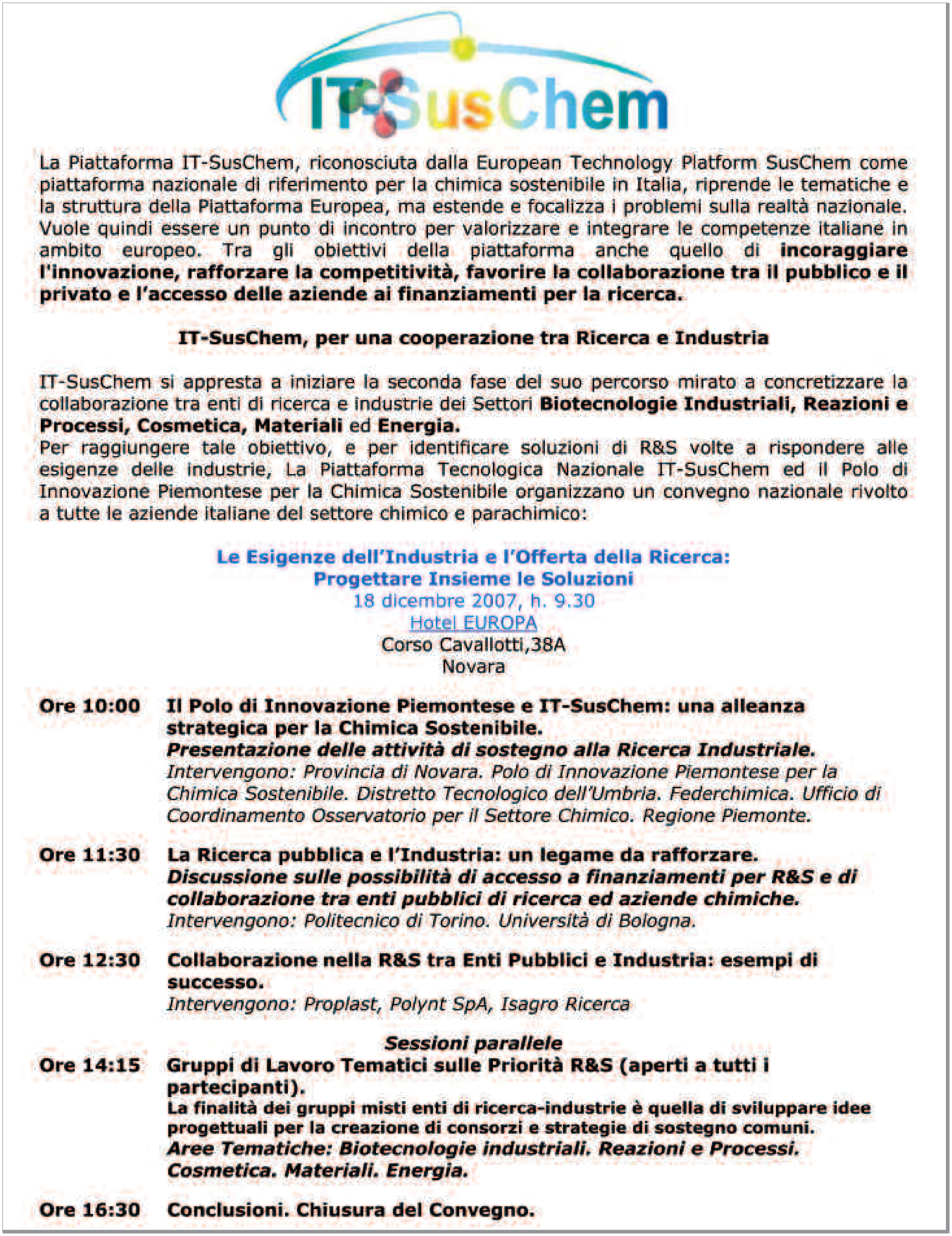
Success in catalysis research requires an interdisciplinary approach. It is necessary to secure collaboration between the makers and users of catalysts, and the various scientific and engineering disciplines that contribute to the creation of successful technology. Catalysis research will of necessity become more international, as cooperation increases between the world’s leading scientific nations, for example through the ACENET ERAnet [5]. In this we see exemplified that last cultural allusion of “catalyst”, the Chinese characters for which also mean “marriage broke”, emphasising the role of a catalyst in bringing together different partners to create a fruitful union.

觸媒

Fig. 8 - Catalyst as “Marriage Broker” in Chinese characters

Reference

[1] OECD Workshop on Sustainable Chemistry, 1998.
[2] G. Ertl *et al.* (Eds.), Handbook of Heterogeneous Catalysis, Wiley VCH, 1997.
[3] G.J. Sunley, D.J. Watson, *Catalysis Today,* 2000, **58,** 293.
[4] Y.-H.P. Zhang, *et al.,* PLoS1, 2007, e456.
[5] www.acenet.net



La Piattaforma IT-SusChem, riconosciuta dalla European Technology Platform SusChem come piattaforma nazionale di riferimento per la chimica sostenibile in Italia, riprende le tematiche e la struttura della Piattaforma Europea, ma estende e focalizza i problemi sulla realtà nazionale. Vuole quindi essere un punto di incontro per valorizzare e integrare le competenze italiane in ambito europeo. Tra gli obiettivi della piattaforma anche quello di **incoraggiare l'innovazione, rafforzare la competitività, favorire la collaborazione tra il pubblico e il privato e l'accesso delle aziende ai finanziamenti per la ricerca.**

IT-SusChem, per una cooperazione tra Ricerca e Industria

IT-SusChem si appresta a iniziare la seconda fase del suo percorso mirato a concretizzare la collaborazione tra enti di ricerca e industrie dei Settori **Biotecnologie Industriali, Reazioni e Processi, Cosmetica, Materiali** ed **Energia.**
Per raggiungere tale obiettivo, e per identificare soluzioni di R&S volte a rispondere alle esigenze delle industrie, La Piattaforma Tecnologica Nazionale IT-SusChem ed il Polo di Innovazione Piemontese per la Chimica Sostenibile organizzano un convegno nazionale rivolto a tutte le aziende italiane del settore chimico e parachimico:

Le Esigenze dell'Industria e l'Offerta della Ricerca:
Progettare Insieme le Soluzioni
18 dicembre 2007, h. 9.30
Hotel EUROPA
Corso Cavallotti,38A
Novara

Ore 10:00 **Il Polo di Innovazione Piemontese e IT-SusChem: una alleanza strategica per la Chimica Sostenibile.**
Presentazione delle attività di sostegno alla Ricerca Industriale.
Intervengono: Provincia di Novara. Polo di Innovazione Piemontese per la Chimica Sostenibile. Distretto Tecnologico dell'Umbria. Federchimica. Ufficio di Coordinamento Osservatorio per il Settore Chimico. Regione Piemonte.

Ore 11:30 **La Ricerca pubblica e l'Industria: un legame da rafforzare.**
Discussione sulle possibilità di accesso a finanziamenti per R&S e di collaborazione tra enti pubblici di ricerca ed aziende chimiche.
Intervengono: Politecnico di Torino. Università di Bologna.

Ore 12:30 **Collaborazione nella R&S tra Enti Pubblici e Industria: esempi di successo.**
Intervengono: Proplast, Polynt SpA, Isagro Ricerca

Sessioni parallele

Ore 14:15 **Gruppi di Lavoro Tematici sulle Priorità R&S (aperti a tutti i partecipanti).**
La finalità dei gruppi misti enti di ricerca-industrie è quella di sviluppare idee progettuali per la creazione di consorzi e strategie di sostegno comuni.
Aree Tematiche: Biotecnologie industriali. Reazioni e Processi. Cosmetica. Materiali. Energia.

Ore 16:30 **Conclusioni. Chiusura del Convegno.**