# Some experiences in industrial catalysis

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## A R T I C L E   I N F O

## A B S T R A C T

Some case histories are presented to illustrate aspects of industrial applied catalysis research. The examples include the investigation of potential new feedstocks for the production of commodity chemicals (para-xylene, phenol), the development of highly selective catalysts for ethylene oxide, and some problems of catalyst selection for reductive amination of carbonyl compounds. For new processes, the importance of realistic target setting and the interrelation of scientific and commercial factors in techno-commercial evaluation are considered. In new and existing processes, a step-change improvement to a catalyst system or an entirely new catalyst system may be desirable and worth pursuing even if rather difficult. For specialty chemicals, it may not be easy to provide convincing scientific reasons why the ranking of catalyst performance can change for reactions that are otherwise quite similar.

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## 1. Introduction

The discovery of any new catalyst or catalytic reaction is always a welcome addition to the general body of scientific knowledge. The extent and nature of the research into the properties of catalytic reactions will depend on the objectives. Academic catalysis research is usually concerned with developing the scientific framework for the composition and the behaviour of well-defined catalysts under laboratory conditions. Such work helps to underpin and guide applied catalysis. The main aims of applied catalysis – to do something useful with the catalyst and to do it well – are economic as well as scientific. The number of combinations of catalysts and catalytic reactions is vast, and the resources for research are always limited, and so it is important that most effort in applied catalysis is directed at catalytic systems that have a realistic potential for beneficial application.

Although Eric Derouane was certainly a very active luminary in academic research during the past 30 years, he was also always interested in industrial applied catalysis, including the factors, which influence the commercial viability of new catalysts and new processes. As well as spending several sabbatical periods in industry, he actively sought industrial sponsorship for research projects and provided expert consultancy to many companies. He successfully combined his dual interest in academic research and applied research after he was appointed head of the Leverhulme Centre for Innovative Catalysis (LCIC) at Liverpool, and there was extensive interaction between academic and industrial scientists at the LCIC during this period. Accordingly, this paper is concerned with some past case histories of industrial applied catalysis carried out in ICI. The intention is to illustrate the overlap between the fundamental and the applied disciplines as well as some of the commercial constraints, which determine process viability.

## 2. Exploratory research: new feedstocks for commodity chemicals

### 2.1. Isobutane to para-xylene

The growth in North Sea oil production during the 1970s led to the availability of natural gas liquids as a feedstock for the chemical industry. One potential application was the 3-stage conversion of isobutane to para-xylene, described in Fig. 1. All three stages require suitable catalysts. Chromia-alumina was the preferred candidate for stages (i) and (iii), and bismuth oxide for stage (ii), the oxidative coupling of isobutene.

The analogous reaction of propylene using bismuth phosphate or bismuth oxide as oxidant [1,2] or as catalyst [2] had previously been reported, the kinetics in both cases following 1st order dependence on propylene. The mechanism for this reaction was thought to involve coupling of allyl radicals, formed by abstraction of H atoms by the oxide surface [1,2]. For isobutene, the reaction would involve the coupling of methallyl radicals.

Exploratory research was carried out mainly on stage (ii). Tests were carried out in a laboratory microreactor. The primary selectivity to the C8-dimer product (2,5-dimethyl-1,5-hexadiene) over fully oxidised $Bi_2O_3$ at 550 °C in the absence of oxygen was estimated to be close to 100% from experiments at very short contact time (i.e., isobutene conversion extrapolated down to zero). However, selectivity to the C8-dimer decreased with increasing conversion. The C8-dimer contains allylic H atoms, and so further H atom

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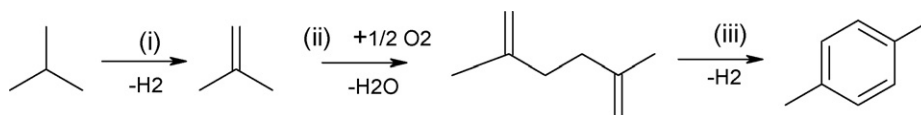  E-mail address: john.birtill@ntlworld.com.

**Fig. 1.** Schematic process for conversion of isobutane to para-xylene (i) dehydrogenation; (ii) oxidative dimerisation; (iii) cyclisation and dehydrogenation.

abstraction can take place, leading to intramolecular dehydrogenation/cyclisation or further intermolecular coupling reactions. The potential influence on selectivity of consecutive intermolecular coupling reactions via the methyl groups is examined by a simple kinetic model in Table 1.

In the presence of oxygen the selectivity to C8-dimer was reduced. At low $O_2$ concentration and near total $O_2$ conversion, dimer selectivity was ~90% at 5% isobutene conversion (with some surface catalyst reduction in the rear section of the bed). The degree of oxidation to methacrolein and $CO_2$ increased with higher $O_2$ concentration and also at lower temperature (475 °C). Evidence from pulsing experiments supported the view that the reaction was catalytic in the presence of oxygen, i.e., solid re-oxidation was faster than solid reduction.

Due to the decline in selectivity to the C8 dimer with isobutene conversion, it was desirable to encourage consecutive dehydrogenation/cyclisation of the C8 dimer. However, attempts to incorporate cyclisation into stage (ii) by incorporating other metal oxides into the catalyst were not very successful. Additional p-xylene was observed with $Bi_2O_3/Ga_2O_3$, but unidentified by-products or, at higher $O_2$ concentration, additional $CO_2$ were also produced.

The overall cost of production per tonne of product includes contributions from raw material usages, energy requirements, and fixed costs, especially capital depreciation. In general, operation at low conversion will drive up both energy and capital costs; low selectivity will drive up raw material costs; process complexity will drive up capital costs. The estimated raw material and energy costs for a new process can be compared to an existing process in preliminary evaluation. Extraordinary equipment costs should also be identified. In order to justify proceeding beyond exploratory research, a more detailed evaluation is required, including the cost of building the plant. This can be done very approximately on a comparative basis, using published data, or by more sophisticated methods. In this case, the estimated capital cost for a 3-stage process was too expensive, and so the process was restricted to two stages with no intermediate separations. For a process with stages (ii) and (iii) combined into a single stage, the overall target was 30% isobutene conversion with 90% selectivity to p-xylene. The reactivity of p-xylene over $Bi_2O_3$ was confirmed to be low compared to isobutene. However, the target still seemed too difficult on account of the tendency in stage (ii) for consecutive isobutene-dimer coupling reactions and oxygen incorporation. Basically, radical chemistry is rather difficult to control. It was concluded that the research targets were too difficult for a process that would be commercially viable compared to existing technology.

The oxidative coupling reaction over $Bi_2O_3/SnO_2$ catalysts (single oxides, mixtures and mixed oxides) was investigated more recently by Mazumder and Védrine at the LCIC [3,4]. At ~7%

isobutene conversion over $Bi_2O_3$ catalyst at 500 °C in the presence of excess oxygen, the selectivity was ~55% to the dimer and ~40% to $CO_2$ [3]. The results for mixed $Bi_2O_3–SnO_2$ catalysts suggested that the dimer and p-xylene are formed by different pathways over these mixed oxide catalysts [4]. This would not satisfy the techno-commercial objective of a selective pathway to p-xylene.

### 2.2. Toluene to phenol

Most phenol is produced globally from benzene via cumene hydroperoxide. During the 1980s (and periodically ever since) the demand for phenol was predicted to grow faster than that of the co-product acetone, and so there was industrial interest in decoupling phenol and acetone production. The feedstock vision was that the methyl group in toluene was 'cost-free' compared to the benzene price, and so it could be sacrificed in the production of phenol. Dow had previously developed a 2-stage liquid phase process via benzoic acid [5], and several plants were constructed worldwide, based on this process, although it was only ever a minor source of phenol production. The two stages are based on reactions (iv) and (v).

$$C_6H_5CH_3 + (3/2)O_2 \rightarrow C_6H_5COOH + H_2O$$

$$\text{stage 1 air, soluble Co catalyst, } \sim 140\,°C. \qquad (iv)$$

$$C_6H_5COOH + (1/2)O_2 \rightarrow C_6H_5OH + CO_2$$

$$\text{stage 2 air/steam, Cu(II)/Mg benzoate catalyst, } \sim 230\,°C. \quad (v)$$
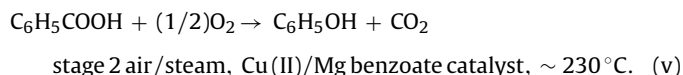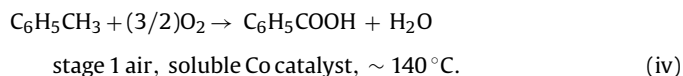
The proposed mechanism for reaction (v) involved nucleophilic attack by benzoate at the ortho position of an adjacent benzoate group, followed by decarboxylation and hydrolysis of phenyl benzoate. The mechanistic history has recently been reviewed by Buijs [6], who proposed an alternative mechanism, involving electrophilic aromatic substitution by benzoyloxy cation on benzoic acid or benzoate ion.

The Dow process had several economic and environmental disadvantages, especially stage 2. The by-product tars required incineration or disposal as waste, and made the recovery of catalyst and product more difficult. Hence, there was industrial interest in a heterogeneous, gas phase version of the Dow process, which also had the potential for higher space–time yields and longer catalyst life. Several patents were published for stage 2, covering solid Cu- or Ni-based catalysts [7]. Accordingly, some exploratory research was carried out to assist techno-commercial evaluation of this approach.

Reaction (v) was found to work moderately well in practice, using supported alkalised copper oxide catalysts at ~300 °C. The product was a mixture of phenol, diphenylether, phenylbenzoate, benzene and $CO_2$. Steam co-feed suppressed the ether and ester products and the overall rate. The best selectivity to phenol (disregarding stoichiometric co-product $CO_2$) was only ~75% at modest feedstock conversion. Some by-product tars were collected in a catchpot. The results for supported CuO/LiOH/KOH catalyst are compared to those in the patent literature in Table 2.

The catalysts quickly deactivated at realistic benzoic acid conversion. In the above example, the half-life was ~16 h, but activity was restored by oxidation in air at 350 °C, during which organic deposits (included in the selectivity calculation) were oxidised to $CO_2$. It was confirmed that this catalyst would tolerate a crude benzoic

**Table 1**
Potential influence of consecutive coupling reactions.

| Isobutene conversion % | Selectivity % C8-dimer | Model selectivity % |
| --- | --- | --- |
| 0 | 100 (extrapolated) | 100 |
| 10 | 90 | 93.5 |
| 25 | | 82 |

Model assumes 1st order conversion of isobutene and C8-dimer to methallyl radicals followed by coupling; $k_{C4} = k_{C8}$. No intramolecular reactions considered.

**Table 2**
Observed and published results for oxidative decarboxylation of benzoic acid.

| Ref. | Catalyst | Temperature (°C) | Pressure (bar) | Feed mol ratio[a] BA:O2:H2O | GHSV STP (h$^{-1}$) | Conversion (%) | Selectivity (%) | | | | | |
| --- | --- | --- | --- | --- | --- | --- | PhOH | DPO | PB | PhH | CO$_2$ XS[a] | Coke/tar[a] |
| This work | 5%CuO/2.6%LiOH/0.6%KOH/α-Al$_2$O$_3$ | 300 | 1 | 3:5:55 | 2750 | ~50 | 60 | 6 | 7 | 7 | 9 | 12 |
| [7] | 4%CuO/3%ZrO$_2$/4%KOH/α-Al$_2$O$_3$ | ~300 | 8 | 1:1.5:74 | 2200 | 64 | 69 | 2 | | 3 | | |
| [7] | 35%CuO/2%V$_2$O$_5$/5%LiOH/SiO$_2$ | 300 | 1 | 1:0.2:10 | | 35 | ~80 | 6 | | 1.7 | ~12 | |
| [8,9] | 48%NiO/51%Fe$_2$O$_3$/0.7%NaOH | 400 | 1 | 1:0.8:10 | 7700 | 95 | 90 | | | 8 | 2 | |

[a] Feed for this work in vol%, balance N$_2$, GHSV at STP. DPO = diphenyloxide (ether); PB = phenylbenzoate. CO$_2$ is excess over co-product. Average coke from oxidation. Average tar from catchpot. Coke/tar ~3/1.

acid stream from the first stage (i.e., containing toluene, benzaldehyde, benzyl alcohol), and so a 2-stage process could be operated without intermediate product separation. However, separation of benzaldehyde and phenol would be difficult on account of their similar boiling points.

The approximate economic appraisal once again included raw material, energy (including steam) and capital costs. The observed overall selectivity of ~70% to phenolic products was poor compared to the cumene-hydroperoxide route, for which 95% of theoretical yield can be achieved, 98% if dimethylbenzyl alcohol is recycled [10]. The price differential for toluene over benzene is constrained by other process options for toluene conversion (e.g., hydrodealkylation, disproportionation). Allowing a generous 12% discount for the molar price of toluene relative to benzene, the target selectivity to phenolic products would still need to be in the range 83–87%, although some credit for by-product benzene might be possible. In terms of relative importance as cost factors, the ranking was selectivity > capital > steam. Assuming that the selectivity could be improved, the overall evaluation indicated the potential for a modest cost advantage compared to the cumene-hydroperoxide route, but this was insufficient incentive to continue research.

The economics of the original Dow liquid phase process were also sensitive to the toluene/benzene price ratio and acetone demand. Some, possibly all, of these plants have closed down in recent years. However, interest in the gas phase process has continued. Better results have been reported more recently over alkalised iron–nickel oxide catalysts (see Table 2) at 400 °C [8,9]. No tars were reported, although the phenol selectivity declined significantly with increasing mole ratio O$_2$: benzoic acid. The stability of the catalyst was improved by addition of vanadium oxide in order to assist re-oxidation of Ni(0) [11]. The reported results indicate a step-change improvement on Cu-based catalysts, and would appear to justify re-evaluation of the process economics. The Fe–Ni catalyst system was investigated following observations of phenol formation in an empty stainless steel reactor [12], an example of fortuitous discovery. More recently, the oxidative decarboxylation of benzoic acid in very dilute solution in high temperature water has been studied using various solid metal oxide catalysts [13]. However, such conditions are unlikely to be of industrial interest due to the high costs of operation and equipment (for reaction and separation) arising from high dilution, high pressure, and a corrosive medium.
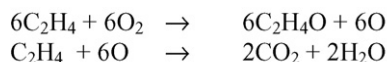
## 3. Simple models may be misleading: improved catalysts for ethylene oxide

The development of highly selective catalysts for production of ethylene oxide was certainly commercially attractive. During the 1980s, commercial catalysts for this reaction were based on alkali-promoted silver, supported on α-alumina, and moderated by traces of organo-chlorides in the feed.

It is one of the wonders of catalysis that ethylene can be oxidised at >80% selectivity to ethylene oxide, a substance that is so reactive in other conditions. The general reaction scheme is shown in Fig. 2. However, precise mechanism by which this transformation takes place has been a matter of scientific debate for almost 40 years.
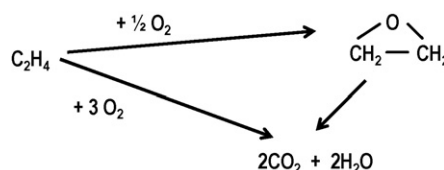


**Fig. 2.** Ethylene epoxidation.

One explanation involved the selective reaction of a molecule of adsorbed $O_2$ with a molecule of ethylene to produce one molecule of ethylene oxide and one adsorbed atom of oxygen. The oxygen atoms then reacted unselectively to produce $CO_2$. The overall stoichiometry of this simple scheme led to a popular belief that the maximum possible catalyst selectivity was 85.7%, i.e., 'the 6/7 rule' [14].

$$6C_2H_4 + 6O_2 \rightarrow 6C_2H_4O + 6O$$
$$C_2H_4 + 6O \rightarrow 2CO_2 + 2H_2O$$
$$\text{-----------------------------------------------}$$
$$7\,C_2H_4 + 6O_2 \rightarrow 6C_2H_4O + 2CO_2 + 2H_2O$$

The observation of selectivity >86% was eventually reported in patent examples for certain alkali-promoted catalyst formulations for which the performance was improved by addition of nitrate- or nitrite-forming substances (e.g., $NO_x$, nitromethane, etc.) to the reaction feedstock [15]. Some examples are shown in Table 3. However, the reported high selectivity was either ignored or dismissed as not credible for many years. The additional promoter for such highly selective catalysts was generalised as "an efficiency-enhancing salt of a member of a redox-half reaction pair", preferably $KNO_3$ [16]. ICI eventually sold its ethylene oxide business to Union Carbide. Alternative, highly selective catalyst formulations have also been patented, e.g., with rhenium [17], and manganese [18] among other additives.

It was concluded from a recent study of a conventional Cs-promoted catalyst that EO and $CO_2$ are formed from a common intermediate, following reaction of ethylene with adsorbed O atoms, that Cl is a sub-surface modifier, which reduces the activation energy for the epoxidation pathway relative to $CO_2$, and that the role of Cs is to block relatively unselective, stepped or defect surfaces of Ag [19,20]. On the latter point, it would be interesting to check if under-alkalised catalysts (i.e., insufficient Cs to block stepped/defect surfaces) become intrinsically more selective as the relative proportion of stepped/defect surfaces decreases with catalyst age (parallel life-tests, fixed temperature, increasing residence time to maintain constant conversion; catalysts discharged at different times for surface characterization).

Enhanced selectivity for triply promoted (K + NO + Cl) catalyst over two-promoter combinations was confirmed in an electrochemical study, although the highest observed selectivity was only 83% [21]. The minimum requirements for enhanced promotion were sub-monolayer quantities of alkali on the metal surface and ppm levels of gaseous $NO_x$. It was suggested that the oxygen for epoxidation might be provided by reduction of nitrate ion to nitrite, which is then cyclically re-oxidised.

Hence, there is to date no published unified mechanistic theory, which covers all known formulations of silver catalyst. The simplicity of the original '6/7' rule was attractive but misleading.

## 4. New and improved processes: some general lessons

Improved catalyst performance (selectivity, activity and life) is important for both new and existing processes. In general, for a new process to replace an existing process on commercial grounds, there must be a significant commercial advantage. Although potential processes may appear attractive on paper, they will fail if the overall process economics is unattractive. Techno-commercial evaluation is desirable at an early stage in order to avoid wasted effort on unrealistic objectives. Briefly, the methodology should include an exploratory investigation of the reaction, an outline process design, initial assessment of the cost of production compared to existing processes, setting of targets for the new process, and technical assessment of the prospects for meeting the targets, for which simple kinetic models may be required. Is there a reasonable expectation that the technical targets can be met with the catalyst

**Table 3**
Highly selective Ag/α-Al2O3 catalysts for EO.

| Ref. | Ex. | Catalyst (alkali metal/salt) | Additive (other) | Temperature (°C) | Pressure (bar) | GHSV (h⁻¹) | Feed C2H4 (vol%) | O2 (vol%) | CO2 (vol%) | Cl (ppm) | NO (ppm) | Conversion O2% | Selectivity EO% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [15] | 10–24 | K/RbNO3 | | 220 | 16.5 | 6700 | 30 | 8 | 0 | 4 VC | 1.5 | 16 | 92 |
| [15] | 18 | KNO3 | | 240 | 16.5 | 5300 | 30 | 8 | 0 | 7.5 VC | 1.5 | 25 | 91 |
| [16] | 7 | KNO3 | | 240 | 20 | 8000 | 30 | 8 | 0 | 5 EC | 5 | 12 | 91 |
| [16] | 12 | KNO3 | | 270 | 20 | 8000 | 30 | 8 | ~6 | 20 EC | 15 | 20 | 88 |
| [17] | CL1 | Cs + Li | Re | 252 | 15 | 3300 | 30 | 8.5 | ~6 | 0.5–5 EC | 0 | 40 | 87.3 |
| [18] | 1–C4 | Cs2SO4 | Re, Mn | 225 | 10 | ~6000 | 30 | 8 | 6.5 | 3.6 EC | 0 | 13 | 87.2 |

Feed for [18] also contained 0.72% ethane. Otherwise, feed balance = N2 in all cases. Process recycle gas normally contains some CO2. VC: vinyl chloride. EC: ethyl chloride. Some data have been converted to a common basis. Refs. [16–18] also specify requirements for support composition.
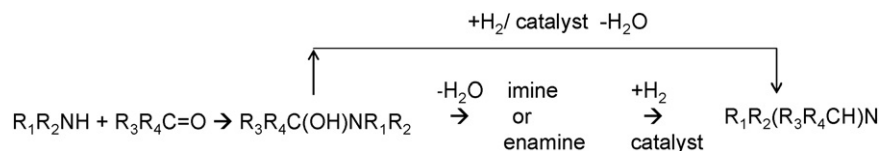
Fig. 3. Reaction steps in reductive amination.

system under consideration, or is it necessary to discover a new catalyst system with a step-change improvement in performance? However, it is important not to over-interpret poorly understood mechanistic theories (as in the EO example). If the target is worthwhile, then the technical difficulty should be treated as a challenge to be overcome. However, the catalytic mechanism needs to minimise or avoid any tendency of a product to undergo consecutive reactions.

## 5. Specialty chemicals: off-the-shelf catalyst selection

Reductive amination of aldehydes and ketones with ammonia or amines is used industrially to produce many specialty amines, including key intermediates for the manufacture of agrochemicals and pharmaceuticals. In single stage batch reductive amination, secondary or tertiary amine products can be produced without isolation of any intermediates by reacting carbonyl compounds with amines and hydrogen in the presence of a powder hydrogenation catalyst. The reaction chemistry may seem easy, but the industrial challenge is usually to achieve near total carbonyl conversion and $\geq$99% selectivity to the target product. In ICI, multi-batch production campaigns were typically carried out in multi-product reductive amination plants. Reaction pressure was constrained to 21 or 23 bar by the capability of the available equipment. The plant fixed and variable costs were known, and so it was relatively easy to work out the process economics based on feedstock and catalyst costs, experimental batch time, and distillation requirements. The exact catalyst cost required a plant study of catalyst recycle and also accounting for precious metal losses after catalyst recovery. The ICI batch plants were eventually shut down due to withdrawal of some key products for which feedstock was no longer available due to closure of another plant. The other reductive amination processes could not carry the entire fixed costs of the plant, and so they too were ended. Some of these processes and some of the problems which arose during their development and operation have been described elsewhere [22,23]. In this section, the interest is in some of the factors, which influenced the choice of catalyst.

The reaction intermediate in reductive amination is often assumed to be an imine or enamine, in line with the obvious sequential organic reaction mechanism in Fig. 3. Hydrogenolysis of the hemi-aminal (carbinolamine) intermediate is invoked when an imine or enamine is not possible, for instance, in the reactions of dimethylamine with cyclohexanone or benzaldehyde. However, if the reaction can take place more directly by hydrogenolysis of the hemi-aminal in some cases, then why not in all cases? The production of N-ethyl-3-methyl-2-butanamine or ethyldimethylpropylamine (EDMPA) from methylisopropylketone (MIPK) is shown in Fig. 4 (a). Fig. 5 shows that with Pt/C catalyst the selectivity ratio for the target amine and the alcohol by-product was invariant with degree of conversion of MIPK [23]. This suggested that both products are formed from a common intermediate, probably the adsorbed 'hemi-aminal' Ia in Fig. 4(b). The obvious sequential organic reaction mechanism is not necessarily relevant when reactants can adsorb on a catalyst surface.

The choice of catalyst for the reductive amination reactions varied according to the process. Pd/C was the preferred choice for some products on grounds of selectivity and cost. Ni and Pt/C tended to
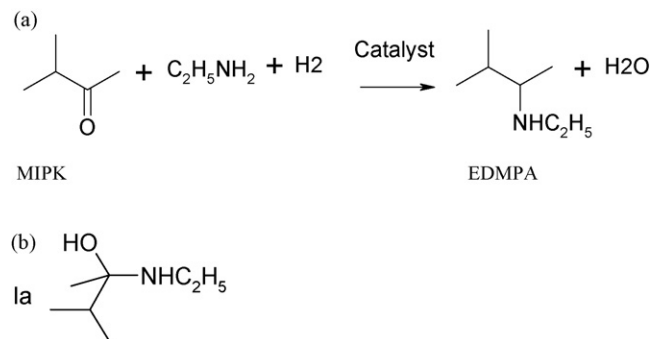


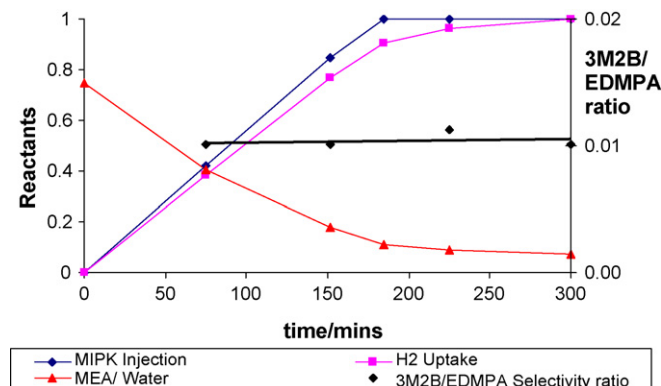Fig. 4. (a) Reaction scheme for EDMPA and (b) hemi-aminal intermediate.



Fig. 5. Ratio for alcohol and amine products during course of reaction.

produce too much by-product alcohol. Pd/C catalyst was found to have poor activity for production of EDMPA under mild conditions (100 °C, 20 bar $H_2$), although it showed good activity for similar reactions such as the preparation of ethylcyclohexylamine [22]. One possible reason for poor activity was surface stereo-hindrance for adsorption of the reaction intermediate due to the 2-methyl branch on the ketone. This idea was supported by the results with 2-methylcyclohexanone in Table 4.

**Table 4**
Effect of 2-methyl group on carbonyl reactivity.

| | | | Catalytic activity | |
|---|---|---|---|---|
| | | 2-Methyl branch | 5% Pd/C | 5% Pt/C |
| I | Methylisopropylketone | Yes | Low | High |
| II | Cyclohexanone | No | High | High |
| III | 2-Methyl-cyclohexanone | Yes | Very low | High |

**Table 5**
Cone angles for projections of atoms.

| | | Cone angle (°) | | |
|---|---|---|---|---|
| | | $-\overset{\mid}{\underset{\mid}{*\mathbf{C}}}-OH$ \\ $NHC_2H_5$ | $-\overset{\mid}{\underset{\mid}{C}}-OH$ \\ $*\mathbf{N}HC_2H_5$ | $-\overset{\mid}{\underset{\mid}{C}}-*\mathbf{O}H$ \\ $NHC_2H_5$ |
| Ia | HO  —NHC_2H_5 | 38.1 | 93.2 | 141.5 |
| IIa | OH  NHC_2H_5 | 39.5 | 103.9 | 138.7 |
| IIIa | OH  NHC_2H_5 | 33.2 | 101.3 | 135.1 |

In order to test this theory, molecular modeling studies were carried out on the adsorption of the three intermediate hemi-aminals (Ia, IIa, IIIa in Table 5) on the close-packed Pd (1 1 1) surface using the Cerius2 programme from Accelrys [24]. Calculation of repulsion between the metal surface and the adsorbing molecule was performed using the Universal force field (Van der Waal's repulsion). Energy expression included molecule–molecule and molecule–surface but not metal–metal interactions. Surface bonding was not investigated. The results suggested that, for O–Pd distance or N–Pd distance or C–Pd distance, there is no effect of additional steric repulsion between Pd (1 1 1) and structure Ia compared to IIa, but structure IIIa showed repulsion as the C–Pd distance was narrowed.

The availability of the adsorbing atom was another possibility. The adsorbing molecule was treated as a sphere, with a surface containing the projections of the nearest atoms (Fig. 6). The visibility of the atom of interest to the catalyst surface was defined in terms of its cone angle from the surface of the sphere. The results in Table 5 suggested that steric hindrance for Ia could be associated with less accessibility of the N atom for adsorption during the molecular approach to the surface, i.e., conformation on impact, but the magnitude of the variation for the three structures was modest.

Hence, no single explanation for possible steric hindrance was evident from this limited study. It is possible that the decisive factor might differ from case to case, or that there is some alternative explanation, possibly the formation of a stable adsorbed species,

which limits activity in some cases. If the greater effectiveness of Pt compared to Pd as catalyst is due to steric hindrance, then this would imply that active sites on Pt are more accessible. In conclusion, it is often not easy to provide convincing scientific reasons why different catalysts are sometimes preferred for apparently similar reductive amination reactions. The mechanistic evidence for reductive amination reactions in general has recently been reviewed by Gomez et al. [25].

## 6. Concluding remarks

Industrial catalysis research and development presents a wide variety of scientific problems and challenges. The underlying aim is to devise a catalytic process, which works sufficiently well for commercial operation. Techno-commercial appraisal, based on experimental results, kinetic models, and estimated cost factors, is desirable even from an early stage in order to avoid wasted effort. However, simple kinetic and mechanistic models may be misleading, and so should be treated with caution. Much more effort is usually devoted to development than new discovery, but if the research targets appear unrealistic, then the search for a step-change in catalytic technology may be the best option. Sometimes, new discoveries do arise from chance observations (e.g., activity of an empty reactor, transient phenomena during start-up), and so unusual results should not be ignored. Nowadays, the challenge of finding new catalyst formulations can be approached systematically by automated screening of 'libraries' of materials, but transient effects and the potential impact of trace gaseous additives may add more complexity to the process of discovery. Scientific understanding of fundamental mechanisms, ranking of catalyst preference, etc., may follow rather than lead discovery, but it provides inspiration and valuable experience for the scientist, and may point the way to further developments.

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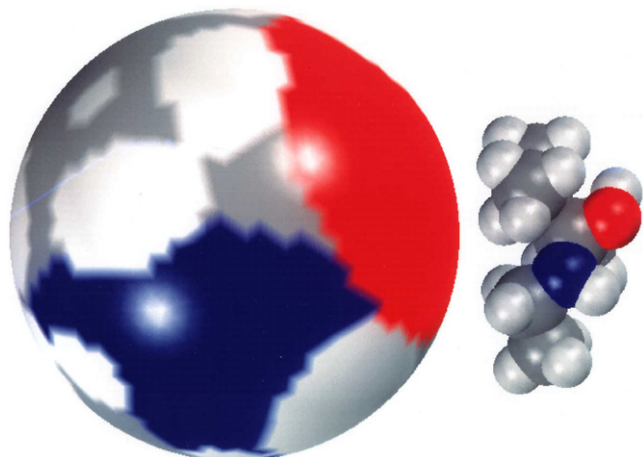[16] US patent 4,994,587, T.M. Notermann, E.M. Thorsteinson (Union Carbide Corporation), February 19, 1991.

**Fig. 6.** Projection of hemi-aminal intermediate as the surface of a sphere.

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