Perspectives in Catalysis

Promotion in heterogeneous catalysis: a topic requiring a new approach?

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Received 2 May 2001; accepted 31 May 2001

Promoters, and their counterparts poisons, are two topics that have been studied extensively since heterogeneous catalysts have been used industrially. Commercial catalysts tend to involve multiple promoters to enhance the activity, selectivity, lifetime and structural integrity, in addition to guard beds or feedstock purification measures that are used to avoid the adsorption of poisons. Yet, at a fundamental level, there is still considerable debate as to how specific promoters function. Promoter effects tend to be specific to a particular catalyst formulation and generic effects are not common, yet this would be desirable. Generally, in acid catalysis and hydrogenation reactions, promoter effects can be dramatic and unexpected. However, in oxidation reactions of alkanes and alkenes, the promotion effects observed to date are somewhat limited. In this paper, the topic of promotion in heterogeneous catalysis is discussed. The complex interplay between structural and electronic effects of promoters is described using examples of both well defined metal surfaces (*e.g.*, the promoted iron catalyst for ammonia synthesis) and multicrystalline metal, metal oxide and metal phosphate catalysts (*e.g.*, Li-doped MgO for methane oxidation). Subsequently, a molecular approach for the promotion of heterogeneous catalysts is prepared and discussed. This is based on observations from well defined molecular catalysts for homogeneously catalysed processes of ligand accelerated reactions. Examples are described where the effects of ligand acceleration, increasing reaction rate by over two orders of magnitude, can be observed for heterogeneous catalysts for hydrogenation and acid catalysed reactions. The remaining challenge is to identify similar effects for partial oxidation reactions, and it is questioned whether a molecular approach can be developed to meet this challenge.

KEY WORDS: ammonia synthesis; hydrogenation of α,β-unsaturated aldehydes; alkane oxidation; asymmetric heterogeneous catalysts; ligand accelerated reactions

1. Introduction

The design of heterogeneous catalysts remains central to the efficient operation of the chemical industry. The identification of promoters, as well as poisons, is a topic that is factored in early in this design process. Promoter compounds are added to induce enhancement in activity, selectivity or lifetime, or to ensure the structural integrity of the catalyst surface. Indeed, some industrial catalyst formulations comprise many components, each of which is considered to have a specific function and often can seem very complex, *e.g.*, $Mo_{12}BiFe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ [1] which is used for isobutene oxidation to methacrolein. There appears to be a distinct difference between research carried out in industrial and academic laboratories concerning promotion. Although catalyst promotion is recognised as a crucial topic for academic research, most studies are carried out in industrial laboratories and reported in the patent literature. Most of the fundamental studies that are carried out by academic researchers concern non-promoted formulations and, consequently, our understanding of the origin of promotion effects is often less advanced than our understanding of the nature of the unpromoted active site. This is particularly true for oxidation catalysts and this dichotomy has been commented upon before [2]. In this paper, the topic of promotion of heterogeneous catalysts is considered. However, the article is not intended to be a definitive review. Such a project would involve several volumes of a book series to deal with the subject in sufficient depth. Rather, the topic is discussed from a personal viewpoint to determine if new approaches are now needed in our fundamental research to generate a new class of high activity catalysts.

2. Promotion effects on well-defined metal surfaces

The recognition of the importance of promoters and poisons in heterogeneous catalysis has been apparent since catalysts were first used in industrial processes. However, there have been few definitive reviews of this topic. In the publication series *The Chemical Physics of Solid Surfaces*, a single volume [3] was devoted to the complex topic of co-adsorption, promoters and poisons. Three reviews considered in detail the role of promoters in three synthesis gas reactions, namely ammonia synthesis [4], the Fischer–Tropsch synthesis [5] and the water–gas shift reaction [6]. These reviews usefully collected the level of understanding at that time for these metal catalysed reactions. Most importantly, well-defined surface science studies have played a valuable role and these have helped to underpin the understanding of the promoted industrial catalysts. Surface science methodology has been particularly well suited to the study of well-defined metal surfaces which can be doped to study the effects on the adsorption and co-adsorption of reactants/products.

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A fairly detailed understanding of the role of the additives in the promoted iron catalyst for ammonia synthesis has been developed [4]. The two main additives are Al_2O_3 and K_2O and it is known that there is an interplay between structural and electronic effects for these promoters. Al_2O_3 is known as a structural promoter and the main effect is to increase and stabilise the surface area of the catalyst [7]. Alumina, together with other oxidic materials, preferentially segregates to the grain boundaries of the iron crystallites. This forms a physical barrier preventing crystallite growth through sintering. In effect, alumina is acting as a promoter since the activity of the catalyst is enhanced due to the higher iron surface area achieved. The alumina also interacts with the potassium promoter and this reduces the loss of potassium from the surface. Hence, the optimum concentrations of alumina and potassium are linked and require careful optimisation for the industrial catalyst. The interplay between the promoter concentration, promoter coverage on the surface and catalyst activity has been explored theoretically by Bowker [9] (figure 1). This indicates that the promotion effect is highly concentration dependent and this has been observed for numerous promoted catalysts. Indeed, Bowker comments [4] on the striking similarity of the experimental results of Krabetz and Peters [10] for the effect of potassium promotion of an iron catalyst (figure 2) which indicates an optimum promotion effect for *ca.* 0.2 wt% K with his theoretical results (figure 1). Of course, it must be remembered that a large amount of this potassium will be phase segregated with the alumina at the grain boundaries, and so the real *effective* promoter concentration could well be considerably lower. This indicates a level of complexity in studying promoters in real catalysts due to the heterogeneous nature of the catalyst structure and surfaces. However, the detailed work on Fe single crystals by Somorjai and Ertl have proved to be extremely useful in understanding the role of potassium as a promoter. Ertl *et al.* [11,12] (figure 3) have shown that surface potassium acts as an electronic promoter increasing the low coverage N_2 sticking co-efficient significantly (*e.g.*, by a factor of 8 for Fe(111)). This effect is also observed when O atoms are co-adsorbed [12] but the magnitude of the effect is decreased. The detailed model that emerged from these studies is that N_2 dissociation occurs *via* a weakly adsorbed nitrogen species and the potassium increases the binding of the molecular state, reduces the barrier to dissociation and enhances the adsorption rate of N_2 [11].

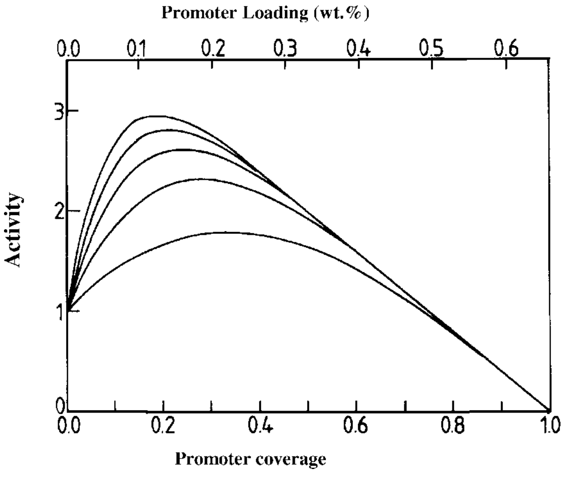


Figure 1. The effect of promoter loading and coverage on the activity of a catalyst based on theoretical calculations of Bowker for a catalyst with surface area 10 $m^2\,g^{-1}$ [9]. It is assumed that the promoted site has four times the turnover frequency of an unpromoted site. The curves of increasing activity correspond to increasing ensembles of 2, 4, 6, 8 and 10 affected sites around the promoter atom.

The complexity of studying the role of promoters at higher pressures can be noted from the studies of Somorjai and co-workers [8,13–15] and, from this work, two additional effects are apparent. First, potassium also acts to aid the desorption of ammonia. This is consistent with the observation that the promotional effect of potassium is only apparent at high pressures with high ammonia concentrations where the effect of ammonia desorption could be expected to be significant, as discussed by Spencer [16]. Second, in the high pressure studies, alumina was observed to reconstruct the less active iron crystal faces when water vapour was present [17]. This effect could enhance the activity of these surfaces by over two orders of magnitude. In addition, when potassium and alumina are combined, additional potassium is stabilised at the surface. Again, this indicates the complex relationship between the structural and electronic effects induced by promoters.

Studies of potassium-promoted iron Fischer–Tropsch synthesis catalysts demonstrate that a similar role for potassium can be described by enhancing the adsorption and dis-

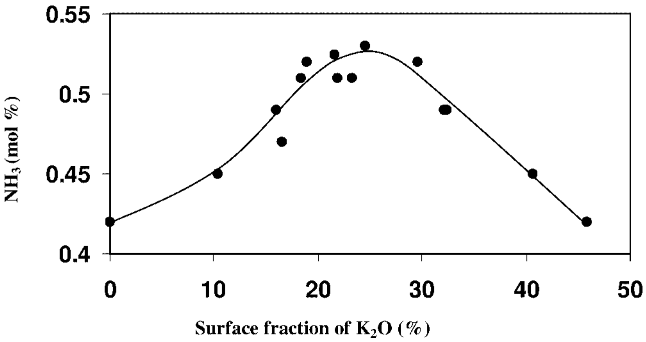


Figure 2. Experimental results for promotion of an iron catalyst [10].

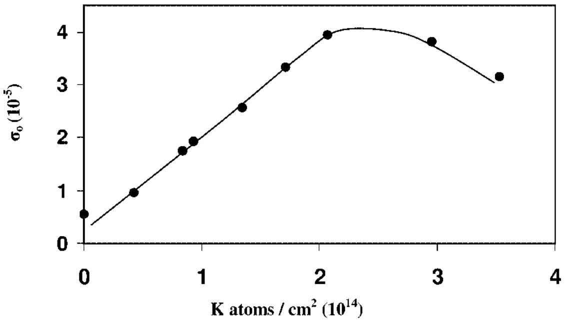


Figure 3. Relationship between dissociative sticking coefficient of N_2 on Fe(111) with increasing potassium concentration [11].

sociation of CO [5,18]. Again, the effect is concentration dependent. Similar promotion effects have been observed by Campbell and co-workers [6,19,20] for the water–gas shift reaction catalysed by cesium-promoted copper catalysts. The addition of cesium enhances the rate of the reaction with an optimal Cs/Cu ratio of *ca*. 0.04. Again, the experimental relationship observed between the activity of the catalyst and the concentration of the promoter is similar to that predicted in the theoretical study by Bowker [9] (figure 1).

Apart from the electronic effects which aid the adsorption/dissociation/desorption processes on a metal catalyst surface, there are two other ways in which promoters act to aid selectivity enhancement. The oxidation of ethene to ethene oxide using silver catalysts has been extensively studied and it is known that the addition of chlorine compounds or NO_x, together with the reactants, significantly enhances the ethene oxide selectivity [21]. In general, this is considered to result, at least in part, by the elimination of non-selective homogeneous gas phase oxidation reactions. Similar effects for the addition of chlorine containing compounds for the oxidation of methane have also been observed [22] and this is also due to the elimination of non-desired gas phase reactions. Another route by which additives enhance catalyst selectivity is by blocking surface sites. For example, the addition of bismuth to supported platinum catalysts has been shown to enhance the selectivity of oxidation reactions (*e.g.*, glycerol oxidation [23]) and this is considered to be due to bismuth atoms selectively blocking specific surface platinum sites.

From this initial discussion, it is clear that the study of metal surfaces has shown that promoters can act in a number of ways and that, in particular, there is a complex interaction between structural and electronic effects.

3. Interplay between structural and electronic effects

The general statement that promoters can induce enhancement in activity/selectivity through either structural and/or electronic effects can be described further using three examples.

3.1. Methane oxidation using Li-doped MgO

The oxidative coupling of methane has been extensively studied [24–27] as it was considered to be a potential route for the utilisation of remote natural gas. In the early work of Lunsford and other researchers [25–27], it was observed that the addition of Li^+ to MgO significantly enhanced the catalyst performance. In a detailed study of pure MgO and doped MgO catalysts [28], the regular cubic morphology of MgO, that can be prepared by burning Mg in air or the thermal decomposition of $Mg(OH)_2$, is found not to be particularly selective in forming the C_2 products, ethane and ethene. However, the addition of Li^+ enhanced the formation of C_2 products (table 1) when the results are compared at similar O_2 conversion (oxygen is the limiting reactant under the reaction conditions), whereas addition of Au decreased the conversion and enhanced the total oxidation products [29]. From a detailed microscopy study, we found that these differences in catalytic performance could be understood in terms of the structure of the catalysts (figure 4). The undoped MgO (figure 4(a)) exhibits distinct cubic morphology with crystallite sizes of *ca*. 20–40 nm. The addition of Li^+ to the MgO, by the impregnation of lithium carbonate using the incipient wetness technique, increases the crystallite size markedly to 200–400 nm. The MgO crystals lose their distinct cubic morphology (figure 4(b)) and the crystals now contain irregular grain boundary dislocations and dislocations in the bulk of the crystals. It is considered that the substitution of Li^+ for Mg^{2+} in the MgO lattice gives rise to these defects, and the enhanced catalytic performance is related to the presence of these defects. In this case, the Li^+ creates a new active centre (a defect site) that is not present on the surface of the unpromoted MgO. Since the surface area of the Li-doped MgO is much lower compared to the undoped MgO, the specific activity of the doped catalyst is significantly enhanced for the formation of C_2 hydrocarbons. The addition of Au to MgO, by the impregnation of $HAuCl_4$ by incipient wetness, also leads to an increase in the MgO crystallite size, but this is not marked and the crystallites are *ca*. 30–50 nm in size. In addition, dislocation defects are not a prominent feature of this system. Au films (figure 4(c)) are apparent and these are considered to be the sites associated with the total oxidation of methane. However, it should be noted that the effects on catalytic performance, although significant, are not in excess of an order of magnitude.

Table 1
Oxidative coupling of methane over doped MgO catalysts.[a]

Catalyst	Conversion (%)		Product selectivity (%)	
	CH_4	O_2	C_2	CO_x
MgO	15.8	99.4	29.9	70.1
0.56% Li/MgO	25.2	98.9	73.4	26.6
0.65% Au/MgO	7.4	67.8	8.0	92.0

[a] MgO prepared by thermal decomposition of $Mg(OH)_2$, reaction conditions: 750 °C, $CH_4/O_2 = 5.5$, $CH_4/He = 1.0$.

3.2. Butane oxidation using doped vanadium phosphate catalysts

Vanadium phosphate (VPO) catalysts probably represent one of the most extensively studied heterogeneous catalysts. In part, this is due to VPO catalysts being the only commercially used catalysts for the selective oxidation of an alkane. Commercial VPO formulations for the oxidation of n-butane to maleic anhydride contain a range of promoters including Fe, Mo, Zn, Co and the literature on promotion up to 1991 has been reviewed [30]. In this review, it was proposed that the promoters had a twofold role (a) to enable the formation of the required VPO compounds and (b) to form solid solutions which exhibit enhanced specific activity. Most industrial formulations utilise VPO catalysts with $P/V > 1.1$

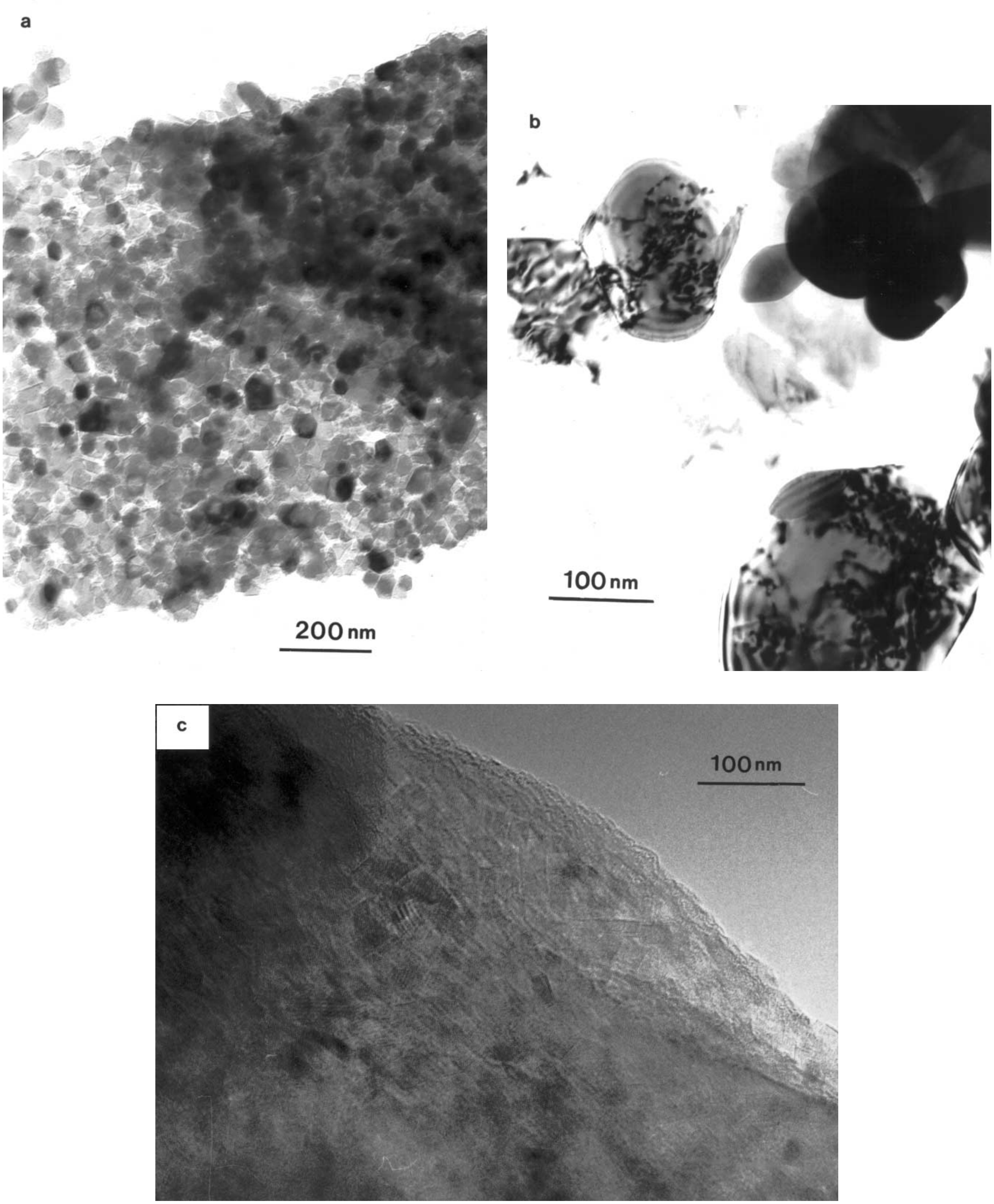


Figure 4. Bright field transmission electron micrographs of MgO catalysts. (a) MgO from magnesium hydroxide, composed of small cubes 20–40 nm, (b) Li-doped MgO showing dislocation arrays formed at grain boundaries, where adjacent crystallites have sintered and individual dislocations that traverse the bulk of the MgO crystallites, (c) Au-doped MgO showing thin surface films of Au, and (d) dark field transmission electron micrograph of Li-doped MgO showing dislocations.

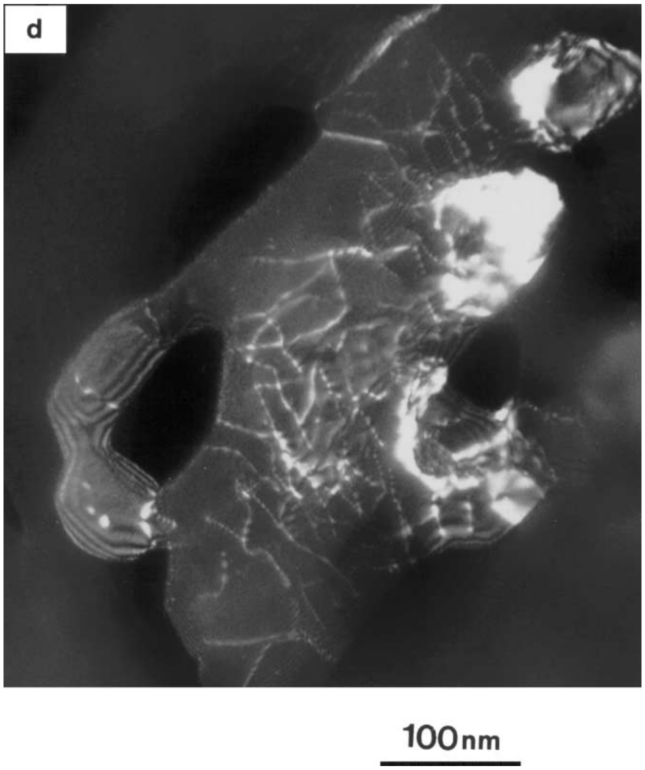


Figure 4. (Continued.)

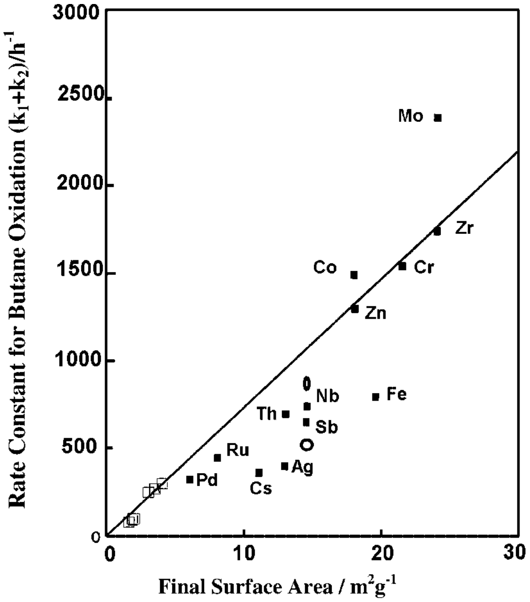
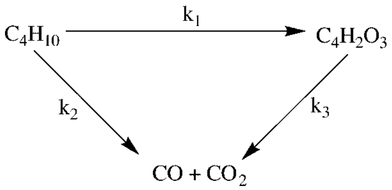


Figure 5. Dependence of rate constants for butane oxidation on final catalyst surface area: (□) unpromoted aqueous HCl preparation method, (○) unpromoted non-aqueous HCl method evaporated to dryness, (◇) unpromoted non-aqueous HCl method collected by filtration and (■) promoted catalysts (for full details see [36]).

(atomic ratio) and, in addition, phosphorus compounds are often added during use, since catalyst deactivation is considered to be related to phosphorus loss from the catalyst surface. However, excess phosphorus in the catalyst preparation can lead to the formation of $VO(H_2PO_4)_2$ which has been shown to give poor selectivity to maleic anhydride [30,31]. VPO catalysts have been found to be promoted by the addition of Co, Cd, Ni [32], Zn, Bi, Cu, Li [33], U [34] and Zr [35]. The amount of promoter added is typically similar to the amount of excess phosphorus, *i.e.*, P/promoter $\approx$ 1. Although the activity per unit mass of catalyst is increased by the addition of the promoter, a factor that is clearly important for the industrial operation of these catalysts, when the surface area is taken into account, the specific activity either remains unchanged or is decreased. For this reaction, it is known [36] that the reaction data can be modelled by a simplified kinetic scheme involving series and consecutive pseudo-first-order reactions:



The rate constant for butane conversion ($k_1 + k_2$) can be viewed as a measure of catalyst activity and, for most promoted catalysts, this shows a linear dependency on surface area (figure 5). This demonstrates that, for most additives, their function is to increase the surface area of the active catalyst (*cf.* the role of Al_2O_3 in the Fe ammonia synthesis catalyst), but the activity per unit surface area is unaffected. In view of this, it is important to consider the intrinsic activity of a catalyst (activity per unit surface area per unit time) when determining if a true promotional effect is apparent. Unfortunately, this is not the case in many reported studies and, indeed, in many cases the “promoter” decreases the intrinsic activity of the catalyst (*e.g.*, Fe, Cs and Ag in figure 5). In these VPO catalysts, the promoter is often present as a phosphate and the role of these promoters has been determined [30] as hindering the formation of $VO(H_2PO_4)_2$ since this material, if present, decreases both the selectivity and the surface area of the catalyst.

However, there are reports where significant increases in the intrinsic activity of the catalyst are observed. These typically involve very low levels of promoters and this has been observed with Cr, Fe, Hf, Zr and Ce [37] and Otake [38] also reported this effect for Fe. Optimum V/Fe atomic ratios were typically 0.03–0.06, and this was considered [38] to be due to the formation of solid solutions of the promoter into the pyrophosphate active phase, *i.e.*, $(V_{0.95}Fe_{0.05}O)_2P_2O_7$. The promotional effect is highly dependent upon the concentration of the promoter and this is shown for Co-doped VPO catalysts in figure 6, but similar effects can be expected for the promoters with $(VO)_2P_2O_7$ or with other vanadium phosphate compounds [30]. However, it should be noted that the increase in intrinsic activity is typically less than an order of magnitude.

It is interesting to consider the origin of this promotional effect when low concentrations of a promoter (*e.g.*, Ce, Co, Cr, Cu, Fe, Hf, La, Mo, Nb, Ni, Ti and Zr) are introduced into the $(VO)_2P_2O_7$ as a substituent for V^{4+}. A number of recent studies have shown that the catalytic performance is

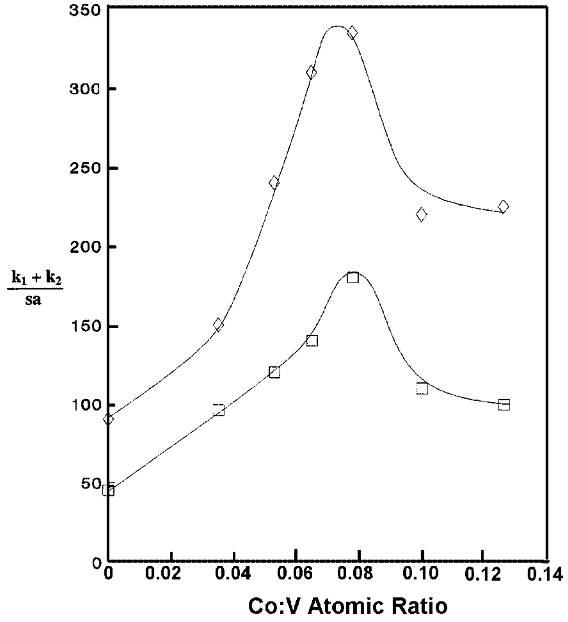
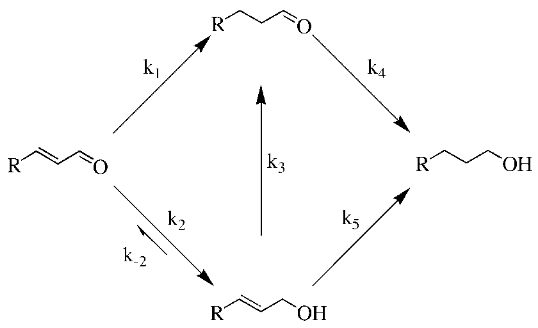


Figure 6. Relationship between specific activity of Co-promoted vanadium phosphate catalyst and Co/V atomic ratio: (□) 385 °C and (◇) 420 °C (for full details see [36]).

related to the V^{5+}/V^{4+} surface ratio [39,40] and that defect sites may be important on the surface of $(VO)_2P_2O_7$. In addition, it has been observed that $(VO)_2P_2O_7$ can be oxidised to $(VO)^{2+}_{2-x}(VO)^{3+}_x(P_2O_7)^{4-}_{1-x/2}(PO_3)^{3-}_x$, *i.e.*, V^{4+} is oxidised to V^{5+} [41]. The replacement of V^{4+} by the promoter cation can be expected to introduce defects into the structure as well as influencing the oxidation state of the surface. Both of these effects may be important with respect to the promotion of VPO catalysts. Hence, again it is an interplay of structural and electronic factors that is important.

3.3. Hydrogenation of α,β-unsaturated aldehydes using sulfur-promoted Cu and Au catalysts

The selective hydrogenation of α,β-unsaturated aldehydes is often used as a model reaction to explore the factors affecting regioselective hydrogenation. In particular, the formation of the unsaturated alcohol due to the selective hydrogenation of the carbon–carbon double bond is of most interest, since this is an important synthetic step in the fine chemicals sector. The overall reaction can be represented by the following scheme:



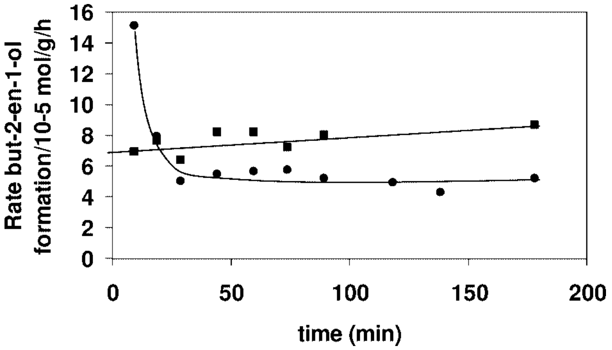


Figure 7. Effect of thiophene addition on the rate of hydrogenation of but-2-enal to but-2-en-1-ol (mol h^{-1} × 10^5) over Au/ZnO: (□) unmodified and (■) thiophene modified (for full details see [48]).

One approach to this synthetic problem was to block specific sites on the surface of active hydrogenation catalysts. For example, Pt/TiO_2 [42] were considered to give enhanced selectivity to the unsaturated alcohol due to the decoration of the surface of the platinum crystallites by TiO_2. In addition, Ponec [43] found that modification of supported Pt catalysts by Ge, Ga and Sn also enhanced the selectivity to the unsaturated alcohol. In view of this, we also investigated this reaction [44–46] using supported Cu catalysts modified by sulfur compounds. Sulfur is known to be a poison for Cu catalysts [47] and our approach was to attempt to poison the hydrogenation of the carbon–oxygen double bond relative to the hydrogenation of the carbon–carbon double bond. We demonstrated that very low levels of sulfur (1.8–2.7×10^{-3} S atoms/surface Cu atom) could significantly enhance the selectivity for the formation of the unsaturated alcohols. On the basis of a detailed kinetic analysis [44], we were surprised to find that sulfur was acting as a promoter for the hydrogenation of the carbon–oxygen double bond (*i.e.*, rate constant k_2 enhanced by *ca.* 50%), while sulfur did, indeed, act as a poison for the hydrogenation of the carbon–carbon double bond (*i.e.*, rate constant k_1 decreased by an order of magnitude). The combined effect increases the selectivity to the unsaturated alcohol. This was the first example of sulfur acting as a promoter for a Cu hydrogenation catalyst. The effect underlines the complex relationship between promotion and poisoning of catalytic reactions since, in this case, sulfur is acting in both capacities. In addition, the enhancement in selectivity was dependent upon the concentration of sulfur added, but could be generally observed for a range of supports and a range of sulfur compounds. In view of the low surface loading of sulfur required to achieve this effect, it was considered that the effect was not due to a steric effect alone (*i.e.*, blocking of surface sites). Based on a detailed IR spectroscopy study, using CO as a probe molecule, it was concluded that the main promotional effect of sulfur was electronic in nature. New Cu^+–S sites are formed on the addition of low levels of sulfur to the Cu catalysts, and these act as the selective hydrogenation sites. It is interesting to note that we have recently shown [48] that supported Au catalysts are also promoted by sulfur for the same reaction. The effect (figure 7) is similar in magnitude to that observed for Cu catalysts, and again is considered to be due to sulfur acting as an electronic promoter. This is based on detailed transmission electron microscopy studies and infrared spectroscopy studies that have shown that sulfur modification does not affect the morphology or size of the supported Au crystallites [49].

4. Molecular approach to promotion: ligand accelerated reaction

The preceding section has described relatively complex heterogeneous catalysts. The catalysts are prepared by precipitation and impregnation techniques and comprise surfaces with an inhomogeneous distribution of active sites and surface structures. These examples of metal, metal oxide and metal phosphate catalysts for oxidation and hydrogenation reactions all demonstrate clear and significant promotional effects on catalyst performance. However, in real terms, the enhancement in the intrinsic activity of the catalyst is typically less than an order of magnitude. Such an enhancement in activity is of great value for the use of heterogeneous catalysts in industrial applications. Indeed, these enhancement effects ensure the catalysts can be used. The question that these observations stimulate is, can promotional effects considerably larger than an order of magnitude be achieved for these complex heterogeneous catalysts? To answer this question, it is necessary to consider examples from homogeneous catalysis using well-defined molecular catalysts.

Sharpless and co-workers [50] have developed an approach for the design of homogeneous catalysts based on *ligand accelerated reactions*. For example, in the Sharpless epoxidation reaction, a chiral titanium tartrate dimer acts as a highly enantioselective catalyst for allylic alcohol epoxidation with alkyl hydroperoxides as oxygen donor [51]. In the absence of the tartrate ligand, no reaction is observed. Another example is the Jacobsen manganese-salen catalyst [52] which is an enantioselective epoxidation catalyst for aromatic substituted alkenes using hypochlorite as oxidant. Again, in the absence of the chiral salen ligand, no reaction is observed. It is clear that, in these examples of molecular catalysis, the Ti^{4+} and Mn^{3+} cations are being activated/promoted by the bonded ligands and, in this case, the rate acceleration is clearly many orders of magnitude. This effect can also be observed in heterogeneous catalysts and two examples can be discussed (a) enantioselective hydrogenation using cinchona-modified platinum catalysts and (b) the modification of zeolites with chiral dithiane 1-oxides.

4.1. Enantioselective hydrogenation using cinchona-modified platinum

The hydrogenation of α-ketoesters using heterogeneous catalysts has been extensively studied, particularly for the reaction of ethyl pyruvate using modified Pt catalysts [53–55], although recent studies have begun to generalise this system to a broader range of substrates and metals [56]. The reaction was originally described by Orito *et al.* [57–60] and has become the most intensively studied heterogeneous enantioselective catalytic reaction. The reason for this interest is that it is viewed by many workers as a model reaction on which to base other enantioselective studies. The approach adopted, *i.e.*, the creation of a chiral active site by the adsorption of pure enantiomers onto a metal surface, has also proved successful in the related studies by Izumi [61] for the hydrogenation of β-ketoesters with tartrate-modified nickel catalysts.

Extensive studies have revealed that hydrogenation of α-ketoesters in the presence of cinchona alkaloids as modifiers is best carried out using Pt catalysts (figure 8) [62]. The Pt can be supported on a diverse range of materials, Al_2O_3, SiO_2, TiO_2, C, and the best results have been obtained with methyl pyruvate using 5% cinchonidine-modified polyvinyl pyrrolidone-stabilised platinum clusters [63]. The optimum Pt particle size is considered to be >2 nm, and catalysts with smaller Pt particle sizes have been shown to be less selective.

Most research effort for this reaction has concentrated on the optimisation of the enantioselection and, specifically, on the design of the chiral modifier for the supported Pt catalyst with ethyl pyruvate as the substrate, and a selection of the results is summarised in table 2.

Early work focused on the method of modification by cinchona alkaloids and it was recognised that the choice

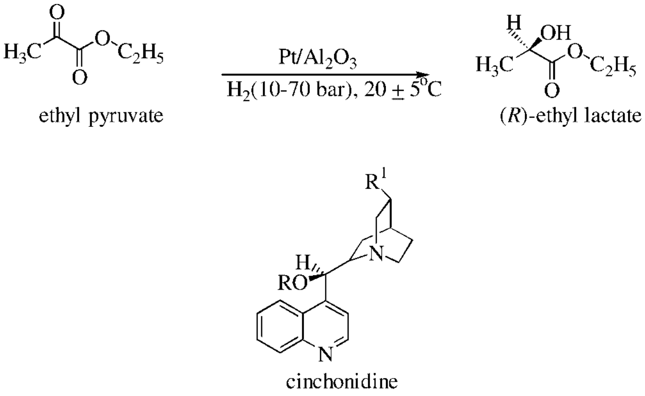


Figure 8. Hydrogenation of ethyl pyruvate using Pt/Al_2O_3 catalysts modified with cinchonidine.

Table 2
Hydrogenation of ethyl pyruvate with Pt/Al_2O_3 using cinchona related modifiers.[a]

Modifier[b]		Solvent	ee[c]
R	R^1		(%)
H	Et	Acetic acid	90
Me	Et	Acetic acid	95
H	CH_2OH	Acetic acid	91
(*R*)-lactate	Et	Acetic acid	44
(*S*)-lactate	Et	Acetic acid	46
(*R*)-benzyllactate	Et	Ethanol	20
(*S*)-benzyllactate	Et	Ethanol	25

[a] Source [64]. Reaction conditions: 50–100 mg Pt/Al_2O_3, 10 ml ethyl pyruvate, 20 ml solvent, ambient temperature, 100 bar.

[b] R and R^1 as in figure 8.

[c] Best ee reported for (*R*)-enantiomer.

of solvent was important for the attainment of high enantiomeric excess (ee). The highest ee is obtained when acetic acid is used as solvent and the ee was found to increase in the order: ethanol < toluene < acetic acid, when either 10,11-dihydrocinchonidine or 10,11-dihydro-*O*-methylcinchonidine were used as modifiers and ethyl pyruvate or ethyl-4-phenyl-2-oxobutyrate were used as substrates. From this early work, it was concluded [64] that the minimal requirements for an efficient modifier for the hydrogenation of α-ketoesters is the presence of a basic nitrogen centre in close proximity to one or more chiral centres and an aromatic ring system, with best results being obtained with planar ring systems, *e.g.*, quinolyl or naphthyl. To date, it is generally agreed that 10,11-dihydrocinchonidine is the most effective modifier for high pressure hydrogenation of ethyl pyruvate. However, recent extensive studies by Baiker [65] have indicated the efficacy of mechanistic studies for the design of new chiral modifiers in enantioselective hydrogenation that can be used to replace the cinchona alkaloids.

One of the most important observations for the Pt/cinchona catalyst system is the observation that the rate of hydrogenation of the α-diketone is significantly enhanced on the addition of the cinchona modifier (table 3). A rate enhancement is observed with both cinchonidine and 10,11-dihydrocinchonidine.

The same effect is observed when Pt colloids are used as catalysts (table 4), and this indicates that the nature of the support may not be of great significance for this effect.

To date, the origin of the rate enhancement has not been determined, partly due to the fact that most studies have concentrated on the optimisation of enantioselection. It is tempting to link the observation of the rate enhancement effect with the enantioselection that is achieved with this catalyst system. However, the rate enhancement is observed for racemic hydrogenation. For example, Blaser *et al.* [63] have shown that aniline, triethylamine and quinuclidine all enhanced the rate of racemic hydrogenation of ethyl pyruvate when added to the Pt/Al_2O_3 catalyst and that there was a relationship between the pK_a of the nitrogen base and the degree of rate enhancement. The rate enhancement observed with cinchonidine is much higher than that predicted by pK_a considerations alone, indicating that other factors are important. Interestingly, Rylander [66] had previously noted that racemic amines could enhance the rate of hydrogenation of ketones. It can be expected that the Pt/cinchona system is a catalyst where the nature of the active site will be identified at the molecular level in the near future using a combination of experimental and theoretical studies. Central to this understanding, it is hoped, will be the identification of the origin of the rate enhancement effect. The relative rate enhancement with colloidal Pt particles is not particularly significant (table 4), since the effect is less than an order of magnitude. However, the effect of cinchonidine modification on Pt/Al_2O_3, where *ca.* 2 nm Pt particles are present, is fairly dramatic and is between one and two orders of magnitude. The origin of this effect probably comes from a specific interaction of the substrate and modifier on the Pt surface. It is clear that this effect deserves further investigation, especially to see if it can be further enhanced.

Table 3
Effect of cinchona modifier on the rate of hydrogenation of ethyl pyruvate with Pt/Al_2O_3 catalyst.[a]

Modification			Rate
Modifier	Time (h)	Solvent	$(\mathrm{mmol}^{-1}\ \mathrm{g}^{-1})$
None	–	None	50
None	–	Ethanol	35
C	1	Ethanol	1100–1300
DHC	1	Ethanol	1100–1300
DHC	18	Ethanol	1490

[a] H_2 pressure 10 bar, 10 °C.
[b] C = cinchonidine, DHC = 10,11-dihydrocinchonidine.

Table 4
Enantioselective hydrogenation of ethyl pyruvate with Pt colloids using 10,11-dihydrocinchonidine as modifier.[a]

Solvent	ee (%)	Relative rate[b]
Ethanol[c]	0	1
Ethanol	45	6
Toluene	15	2
Isopropanol	50	4

[a] Data taken from [64].
[b] Rates relative to hydrogenation rate in absence of modifier.
[c] No modifier present.

4.2. Dehydration of butan-2-ol using dithiane 1-oxide modified zeolite Y

A second example of a heterogeneous catalysed reaction, for which a dramatic promotion in catalytic activity is observed, is given by the modification of zeolite Y by dithiane 1-oxides (**I**) [67,68]. We presented this study as a *proof of concept* stage concerning our approach to the design of enantioselective heterogeneous catalysts using modified zeolites. We have demonstrated that cations present within the micropores of zeolites, or the mesopores of MCM-41 type materials, can be modified by chiral ligands and can function as enantioselective catalysts. Our initial study concentrated on the modification of the proton in zeolite H-Y using chiral dithiane 1-oxides (**I**), which we demonstrated functioned as a chiral acid catalyst [67,68]. Subsequently, we demonstrated that Cu^{2+}-exchanged zeolite Y or Al-MCM-41 modified by chiral bis(oxazoline)s are heterogeneous enantioselective catalysts for the aziridination of alkenes [69,70]. Although it has been the enantioselectivity that has been the focus of our research attention, the modification of zeolite Y by dithiane 1-oxides gave rise to a dramatic increase in the rate of dehydration of butan-2-ol. This effect was also noted for the racemic dehydration reaction. Our initial experiments were carried out using zeolite Y modified with racemic 1,3-dithiane 1-oxide. We found that the dithiane oxide modified zeolite Y is considerably more active than unmodified zeolite Y by several orders of magnitude, and that this activity was maintained without significant loss over several days.

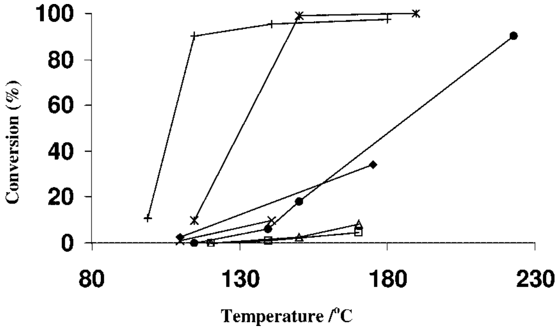
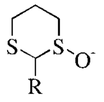


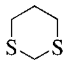
Figure 9. Effect of temperature on the conversion of butan-2-ol over zeolite Y: (●) zeolite H-Y (LZY 82, Union Carbide), (+) zeolite H-Y (LZY 82) after modification with 1,3-dithiane 1-oxide, (∗) zeolite H-Y (LZY 82) after modification with 2-methyl-1,3-dithiane 1-oxide, (□) zeolite H-Y (Crossfield), (×) zeolite H-Y (Crossfield) with 1,3-dithiane 1-oxide, (△) zeolite H-Y (Crossfield) after modification with 2-phenyl-1,3-dithiane 1-oxide and (♦) H-Y (LZY 82) after modification with 1,3-dithiane. Reaction conditions: catalyst (0.3 g) reacted with butan-2-ol (3.2 × 10^{-3} mol h^{-1}) prevaporised in nitrogen (4.3 × 10^{-2} mol h^{-1}).

Under our reaction conditions, unmodified zeolite Y only became active at temperatures above 150 °C and required a reaction temperature of 225 °C to achieve 90% conversion, whereas the modified zeolite gave 90% conversion at 115 °C. We have now observed this effect with a number of other dithiane oxides (figure 9). These results show that modification of zeolite Y with the dithiane 1-oxide creates a new high activity acid site. We consider this observation of rate enhancement to be of crucial importance in the design of novel enantioselective catalysts.

Modification of zeolite H-Y with dithiane oxide (**I**) leads to the creation of a catalyst that has enhanced activity for the acid catalysed dehydration of butan-2-ol when compared with the unmodified zeolite or when modified with the corresponding dithiane (**II**). This effect is observed both for samples prepared by addition of the modifier to the synthesis gel and for the post synthesis modification of two different commercial samples of zeolite Y (Crossfield and Union Carbide). When the modifier is added to the synthesis gel, the resulting zeolite contains only a small quantity of the modifier, but the effect is still apparent [68].



I



II

The interaction of alcohols with the acid forms of zeolites has been well studied in recent years and, for butanols, it is generally considered that the adsorbed species that is formed initially is a butoxide species adsorbed at the active site that is formed from the dehydration of butan-2-ol. *In situ* FTIR spectroscopy confirmed that, in our study, a butoxide species was formed on reaction of the butan-2-ol with both the unmodified zeolite and the dithiane oxide modified zeolite [68]. Consistent with the enhanced reactivity observed with the flow reactor studies, the *in situ* FTIR spectroscopy experiments reveal that the alkoxide species is formed at a significantly lower temperature for the dithiane oxide modified zeolite than for the unmodified zeolite.

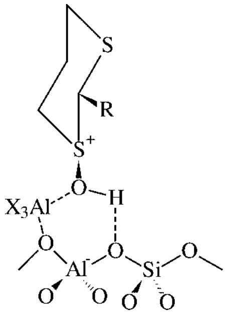


Figure 10. Schematic representation of the structure of the high activity site formed on addition of 1,3-dithiane 1-oxide to zeolite H-Y (A1X$_3$ denotes extra-framework aluminium species).

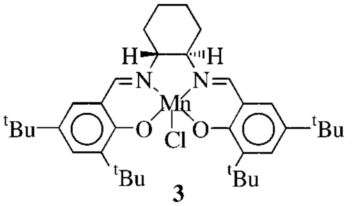
All these data indicate that, when the dithiane 1-oxide is added to the zeolite, a new high activity site is formed, and it was concluded that the degree of rate enhancement observed can be related to the presence of extra-framework aluminium. This must, however, act in combination with the Brønsted acid site of the bridging hydroxy group associated with the zeolite framework aluminium, since the dehydration reaction investigated is catalysed by Brønsted acidity. A number of studies have indicated that a combination of extra-framework (Lewis acid sites) and framework (Brønsted acid sites) aluminium can give enhanced acidity in zeolite catalysts. Haag and Lago [71] showed that steaming zeolites at 500 °C with low levels of water vapour can lead to an increase in the activity of the zeolite for acid catalysed reactions. Mirodatos and Bartemeuf [72] showed that superacid sites could be created in mordenite by a steaming procedure. These effects were subsequently explained by Fritz and Lunsford [73] in terms of the initial dealumination of the zeolite to form non-framework aluminium that imparts, presumably through an electrostatic effect, strong acidity of the remaining framework Brønsted acid sites. This leads to an increase in acidity of the zeolite and, for simple acid catalysed reactions such as cracking, an enhanced activity is observed. In our study, the high activity site is considered to be formed by the specific interaction of the dithiane 1-oxide with both the extra-framework aluminium and the Brønsted acid site associated with the framework aluminium (figure 10). Supporting evidence for this proposed model comes from detailed ^{27}Al MAS NMR spectroscopy studies and molecular simulations [74,75] that have shown that the dithiane 1-oxide interacts strongly with the extra-framework aluminium atoms.

The formation of high activity acid sites enables these modified zeolites to be used as enantioselective catalysts since, although only one active site per supercage is modified, it is many orders of magnitude more active than the remaining unmodified sites. When the dithiane oxide is used in the enantiomerically enriched form, the active sites are able to discriminate between the enantiomers of butan-2-ol. This important effect is achieved by enantioselective rate enhancement, *i.e.*, both enantiomers react faster in the chiral environment than in the absence of the chiral modifier, but one reacts faster than the other.

In both the previous examples, the dramatic increase in rate caused by the specific interaction of a modifier with a catalyst active site can be considered to be unexpected, but is crucial to their use as enantioselective catalysts. Clearly, this type of activity enhancement requires much more detailed attention at this time.

4.3. Selective oxidation catalysis: can a molecular approach help?

The two homogeneous examples cited earlier as examples of *ligand accelerated reactions*, *i.e.*, the Ti-tartrate Sharpless epoxidation catalyst [51] and the Mn-salen Jacobsen epoxidation catalyst [52], both demonstrate that selective oxidation reactions can be promoted using this molecular approach. Indeed, both have prompted a considerable effort into the design of heterogeneous enantioselective catalysts. To date, there is no reported heterogeneous analogue of the homogeneous Sharpless Ti-tartrate complex. Numerous attempts have been made to modify the Ti active sites of the titanium silicalite TS-1 and the titanium zeolite-β, but all have proved unsuccessful to date. Considerable success has been achieved in the immobilisation of the chiral manganese(III)-salen complexes and the subject has recently been reviewed by Canali and Sherrington [76]. A number of approaches have been attempted and, in particular, considerable attention has been given to the immobilisation using polymers [77–79] and inorganic supports such as zeolites and mesoporous materials [80–83]. Our approach has been to ion-exchange the chiral manganese(III)-salen complex onto Al-MCM-41 and we have shown that this provides an effective heterogeneous enantioselective oxidation catalyst for the epoxidation of *cis*-stilbene using iodosyl benzene as oxidant [84–86]. The main disadvantage with the manganese(III)-salen catalysts is that they rapidly degrade under reaction conditions. Consequently, turnover numbers of <50 are commonly observed. Unfortunately, none of the immobilisation methods that have been tried to date have improved this stability and, consequently, these catalysts cannot be used for commercial syntheses at present. However, the rate enhancement due to the interaction of the salen ligand with the manganese cation is still observed in the immobilised complex (**3**) (table 5).



3

(R,R)-(−)-N,N′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diaminomanganese(III) chloride (Jacobsen complex)

Table 5
Manganese catalysed epoxidation of *cis*-stilbene.

Catalyst[a]	Time (h)	Epoxide yield (%) Total	*Cis*	*Trans*	ee *trans* (%)
None	2	–	–	–	–
Mn acetate	24	1.5	0	100	–
Mn-salen complex (**3**)	1	86	29	71	77.5
Al-MCM-41	24	0	–	–	–
Mn–Al-MCM-41	2	3	0	100	–
Mn–Al-MCM-41 + salen	2	78	62	38	69

[a] *Cis*-stilbene/iodosylbenzene/catalyst = 7/1/0.13, 25 °C (full details see [85]).

The enhancement in rate observed is between two orders of magnitude for this oxidation reaction at 25 °C. Returning to the oxidation examples cited earlier in this paper, it is apparent that, for VPO catalysts, even with the optimum promoter identified to date, the promotional effect is considerably lower than an order of magnitude. Perhaps it is now time that modification of oxide and phosphate surfaces needs to be examined using a ligand enhanced reaction approach with modifiers that are stable under the reaction conditions. In this respect, some recent studies concerning VPO catalysts may indicate this is feasible. First, we have previously observed [87], using *in situ* laser Raman spectrometry of VPO catalysts, that during the formation of the active catalyst surface when the catalyst is pre-treated in an n-butane/air mixture, the surface of the catalyst becomes totally disordered. Furthermore, we showed that co-fed maleic anhydride affected this transformation and suggested that the maleic anhydride could be acting as a template for the formation of the active site. This would represent a form of *self-assembly* of the catalyst surface in which the product, in this case a very stable molecule, helps assemble the active surface. Second, we have very recently shown [88] that a totally amorphous vanadium phosphate catalyst, prepared using precipitation with supercritical CO_2 as an antisolvent, is considerably more active than the previously well studied crystalline vanadium phosphate catalysts. Perhaps the disorder in this system permits a higher density of the V^{5+}/V^{4+} active sites or, conversely, oxygen activation is enhanced. However, further studies are needed to determine the origin of the enhanced activity for the novel catalyst.

Of course, a key aim must be to design catalysts for the selective activation of hydrocarbons that operate at *ca*. 25 °C, since enzyme systems are readily capable of this. Low temperature heterogeneous oxidation is well known for two catalyst systems, namely supported Au catalysts [89] and $CuMnO_x$ catalysts [90], both of which can oxidise CO to CO_2 at 25 °C. Unfortunately, both catalysts are deactivated by water which would preclude their use for selective hydrocarbon oxidation, since water is a by-product of the selective oxidation. However, these catalysts could form the basis of new water resistant formulations capable of oxidation at ambient temperature. It is now necessary to identify oxidation resistant modifiers that can be introduced to these catalyst types to determine if the ligand accelerated reactions identified for asymmetric catalysts can be transferred to oxidation catalysis. Indeed, if this approach proves to be successful, then heterogeneous catalyst promotion by one or two orders of magnitude will be achievable and this will represent a significant improvement in the levels of activity and selectivity promotion above the levels that are often achievable to date.

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