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Recognising the best catalyst for a reaction

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Abstract

Heterogeneous catalysis is immensely important, providing access to materials essential for the well-being of society and improved catalysts are continuously required. New catalysts are frequently tested under different conditions making it difficult to determine the best catalyst. Here we describe a general approach to identify the best catalyst using a data set based on all reactions under kinetic control to calculate a set of key performance indicators (KPIs). These KPIs are normalised to take into account the variation in reaction conditions. Plots of the normalised KPIs are then used to demonstrate the best catalyst using two case studies: (i) acetylene hydrochlorination, a reaction of current interest for vinyl chloride manufacture and (ii) the selective oxidation of methane to methanol using O₂ in water; a reaction that has attracted very recent attention in the academic literature.

[H1] Introduction

Catalysis is crucially important for the world economy and the well-being of society and is a core area of contemporary science that underpins the manufacture of ca 90% of chemicals necessary to produce essential materials, including medicines and fertilisers. Indeed, a single catalysed reaction, namely the fixation of nitrogen by the Haber–Bosch process, is responsible for ensuring that almost 50% of the global population can be fed¹. Consequently, catalysis contributes significantly to world GDP, and it is therefore not surprising that there is a continual requirement for the discovery of new catalysts or improvements to existing catalysed processes. Every year new catalysts are being discovered. Understandably, each research group tends to study their catalyst under conditions that are best for that particular catalyst. This often leads to multiple claims for being the best catalyst which clearly cannot be true in all cases. A key example of this behaviour was the discovery of the oxidative coupling of methane by Lunsford² which led to a flood of publications citing new catalysts all of which were considered to be the best^{2,3}. Lee and Oyama⁴, highlighted that these catalysts were evaluated with different reaction conditions (temperatures 550–800 °C, catalyst mass/flow rate ratios 0.1–7.2, different CH₄/O₂ ratios) making a genuine comparison difficult, although Lee and Oyama made a very good attempt at this. Ironically, it was later found that by raising the reaction pressure, the reaction proceeded far better with no catalyst at all⁵, though such discoveries are a very rare occurrence. There are other examples. In the field of platinum catalysts for enantioselective hydrogenation, it was realised that a standard fully characterised platinum catalyst was needed as a baseline to validate the catalyst performance, and this was done with use of the standard EuroPt-1 catalyst⁶. More recently, Lange has described a number of parameters such as waste/CO₂ production, selectivity, and productivity, which are important when developing sustainable methods for the production of fuels and chemicals⁷.

In this article we ask the question; how can the best catalyst for a reaction be easily recognised? We develop a general approach to answer this key question. We will address this question using heterogeneous catalysts as a general topic although the approach can be applied more generally for other types of catalysis. We then apply the approach to two specific examples; namely (i) acetylene hydrochlorination for the manufacture of vinyl chloride monomer (VCM). This is a reaction of current academic and industrial importance where there are many candidates each claiming to be the best. Here we untangle these claims in a logical manner; and (ii) the selective conversion of methane to methanol using zeolite catalysts in water. This reaction has recently attracted many studies and here we consider whether it is a genuinely viable approach to this

major catalysis challenge. The two reactions have been selected as they emphasise different key reaction parameters for consideration when comparing literature, as in case (i) selectivity is not important due to the majority of catalysts studied yielding only VCM as product, whereas for case (ii) selectivity is a crucial consideration for comparing catalyst performance. In addition, acetylene can be produced commercially from methane and as methane can be obtained from sustainable sources as biogas it is possible that identifying the best catalysts for these two reactions can have a role in de-fossilising the production of some chemicals.

[H1] The general approach

When evaluating the performance of a heterogeneous catalyst there are many variables to consider, all of which can be tailored to present a catalyst in a favourable way. For reactants in a fixed bed tubular reactor these include: (i) Catalyst mass/volume, (ii) Catalyst loading (metal wt.%), (iii) Contact time (iv) Gas hourly space velocity (GHSV) which is the volume of reactant flowed per unit volume of catalyst (reactant and total, if a diluent is used), (v) Temperature, (vi) Pressure, (vii) Reaction time, (viii) Reactant concentration, (ix) Reactant ratios. Consequently, there is immense scope to manipulate the reaction conditions to fine tune the catalyst performance.

Unfortunately, the comparison of catalysts under the same conditions is rarely performed. This is not a new problem for the field of heterogeneous catalysis, and has persisted for many years^{3,4}. When comparisons are made with literature data, it should be recognised that the use of differing reaction conditions can significantly influence catalytic activity, thus making a catalyst appear more or less active than under optimal reaction conditions. Conversely, it is also possible for two catalysts with vastly different intrinsic activities to be presented as having similar observed activities when factors such as mass transfer effects are not taken into consideration.

To address this, a unified approach for the comparison of catalyst performance is required. The simple approach we propose is based on standard reaction engineering concepts, but we appreciate these may not be commonly known in the chemistry community and this is a central reason for this article which we hope will be thought provoking. In the article we are not seeking to make a scientific breakthrough but rather aid the community to do just that. For any reaction one needs to determine at the outset what the most important parameters for commercial operation are. These can be wide ranging and will not be the same for all catalysed

reactions, but it is crucial to recognise the key requirements for a commercial catalyst for a particular reaction. These parameters include productivity, selectivity, lifetime, stability/deactivation as well as toxicity of the catalyst. Furthermore, catalyst cost or more importantly, the catalyst lifecycle cost can be important factors. Some catalysts have very long lifetimes when operated commercially (e.g. iron catalysts for ammonia production); whereas others have short lifetimes (fluid catalytic cracking where the catalyst is deactivated by coke formation in seconds, but it can then be regenerated and reused multiple times). Such differences in catalyst lifetime can be handled by reactor engineering or through catalytic regeneration procedures (as is the case with zeolite catalysts). Often research into new catalysts for new processes allows reactors to be optimized for the best reaction conditions and this can involve a myriad conditions being explored and reported. However, if a drop-in replacement is being proposed to replace an existing commercial catalyst, then it is crucial that it can operate in the installed reactors with the same or better lifetime. This is the case of VCM manufacture where a catalyst is sought for such an existing process, which has many installed reactors only capable of a certain operating window. In such a case it is not always possible to tune a reactor to the conditions optimal for the new catalyst. Additionally, while it is appropriate to replace a toxic or environmentally hazardous catalyst with a safer material, the reverse is not the case.

It must be stressed that for the greater majority of catalysed reactions selectivity is the most important key parameter. This is particularly the case in redox reactions²⁻⁴ where there often exists a multiplicity of potential products. Selectivity is particularly important in methane oxidation, and this will be explored in the second example we have selected.

Once the key parameters for the selected commercial reaction have been determined, it is essential to collect a full data set from all the available published data, both in patents and in peer reviewed journal articles. The next step is to normalise the reaction rates as best one can. For example, if there are variations in the range of temperatures under which the catalysts have been evaluated, then an estimate of the activation energy to normalise the rates can be applied. The final step is to plot these normalised data so that constructive comparisons can be made. We demonstrate this approach with a specific case study; namely hydrochlorination of acetylene. This is a reaction that is commercially operated in China using a toxic and environmentally unfriendly mercury catalyst⁸. This has prompted a great deal of research in the quest for an alternative non-toxic catalyst. To date claims have been made that the best catalyst for this reaction comprises precious metals such as gold⁹ or platinum¹⁰, earth abundant metals such as copper¹¹ or metal-free catalysts based on carbon¹². Therefore, it would be

instructive if the relative performance of these catalysts can be compared directly and answer the key question as to which of these catalysts is preferred for operation under commercial reaction conditions.

[H1] Case studies

[H2] Acetylene hydrochlorination

Acetylene hydrochlorination for the manufacture of vinyl chloride monomer (VCM) is a reaction of immense renewed interest with VCM production of 18 Mtpa from coal-based acetylene in China¹⁰. There has been a rising number of research papers and patents since 1945 (Fig. 1) and notably the rise is most marked post-2013, an increase that far outstrips the natural increase in scientific publications (typically 4% per annum¹³). 2013 was the year when China signed the Minamata convention signalling that a non-mercury drop-in replacement catalyst was urgently required. It is clear that the number of patents on this reaction is now in excess of research publications confirming there is immense commercial interest in this reaction as well as academic interest. Liu et al.⁸ summarised much of the data available in the academic literature, where the catalysts are compared by acetylene conversion despite there being a wide range of operating conditions. On that basis, it was not possible to determine which catalyst is the best. This demonstrates that a new approach to comparing catalyst performance is now required. However, acetylene hydrochlorination is a good starting point to test the proposed methodology as the supported metal catalysts all exhibit very high selectivity to VCM regardless of their active metal component. Additionally, the reaction is operated at near ambient pressure, as carrying out reactions with pressurised acetylene can be extremely hazardous. Excess acetylene is known to rapidly deactivate the catalysts and so the study is limited to conditions employing a slight excess of HCl. As a result, the number of key reaction parameters is conveniently limited for this test case.

[H3] Selection of key reaction parameters

When designing a heterogeneous catalyst for acetylene hydrochlorination it is important to consider that it is highly likely to be a drop-in replacement for the mercury catalyst. This is because an extensive infrastructure of reactors for VCM production already exists using the mercury catalyst and this has to be utilised rather than replaced. Hence, the reactor

configuration — in this case a fixed bed multi tubular reactor — is fixed as is the catalyst volume. This determines that the catalyst productivity ($\text{mol}_{\text{VCM}} \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$) is the first key parameter as this must match or exceed that of the currently operating process. This representation of activity as productivity, known as space time yield (STY) is an important measure for the commercial operation of a catalyst for this reaction as it demonstrates how much product can be produced in a reactor per unit time per measure of catalyst. STY is a concept which is largely considered to be a convenient means of comparing catalytic activity. The second key parameter is the catalyst lifetime that coupled with STY gives the overall amount of product that a particular catalyst can make. Once again, it is important that this should exceed that observed with the standard mercury catalyst⁹. The mercury catalyst has a lifetime in commercial operation of 6–12 months so it is not unreasonable for a drop-in catalyst replacement to have an improved lifetime. Obtaining data on catalyst lifetime could require that the reaction be investigated over several months. However, the rate of catalyst deactivation during the initial period of time-on-stream can be readily obtained from published data and we propose to use this as being indicative of the overall deactivation profile.

As noted earlier, for many heterogeneously catalysed reactions the selectivity to the desired product is typically a key parameter. This is not the case in this reaction since supported metal catalysts that are active typically have selectivities to vinyl chloride > 99% with selectivities of 99.9% often observed (Supplementary information Table S1). Hence, for this reaction selectivity is not considered a key parameter on which to base a comparison of catalyst performance. However, it should be noted that due to the high cost of acetylene, the difference in selectivity between 99.0% and 100% can make a significant impact on the process economics for the use of a catalyst in commercial operations, hence selectivity is still an important secondary parameter for this reaction. However, it should be noted that the high VCM selectivity experienced in this reaction, and therefore absence of significant by-products, allows evaluation of product distributions and competing reactions to be unnecessary.

Therefore, we consider that the two key parameters for the design of catalysts for acetylene hydrochlorination are catalyst productivity and deactivation rate, thus it is these two parameters that should be plotted against each other to determine the best catalyst for the reaction. It should be noted that the key parameters are dependent on the catalysed reaction in question and for many reactions other key parameters will be important, with different plots required to effectively assess catalyst performance. For reactions with more complex product

distributions, selectivity may be a more important parameter than productivity, particularly if product purification and separation from by-products is challenging. An additional point is that academic literature is often based on very high purity feedstocks, while catalysts might react different to real-life feedstocks and in that case by-products can form that differentiate two catalysts.

[H3] Selection and normalisation of the data set

The data for catalyst performance needs to be collected from all available patents and research publications. For acetylene hydrochlorination the data set is large (Supplementary information Table S1). The data in these publications is often obtained under very different conditions of reactant ratios, flow rates, catalyst mass, catalyst active component concentration and temperature. It is important that any attempt to compare catalyst performance takes all of these diverse range of conditions into account but also that the data to be considered are obtained under kinetic rather than diffusion limited control if this is possible. The data must therefore be collected at low conversions (typically <30%) when doubling the catalyst mass will lead to a doubling in rate. However, in the open literature such data can be rare. Indeed, when used commercially, acetylene hydrochlorination catalysts are typically operated at very high acetylene conversions. For this reason, it is desirable to select data sets that are far from complete conversion to ensure the data are those under kinetic control¹⁴. The use of data at low conversions also helps avoid data collected under non-isothermal conditions as the reaction is exothermic. Nevertheless, owing to the industrial relevance of this reaction, the majority of studies have been performed at high acetylene conversions, therefore it was not possible to limit the data to those at low conversions (< 30%), although data that were clearly obtained under mass transfer limitations were excluded.

As the data set is obtained at different reaction conditions it is important that it is normalised. First the productivity ($\text{mol}_{\text{VCM}} \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$) needs to be calculated from the data available in terms of reactant ratios, flow rates, and catalyst mass together with acetylene conversion and VCM selectivity. It should be noted that numerous reports exist where insufficient experimental details are provided to be able to calculate productivity and assess catalytic performance. In some cases, claims of superior catalytic activity are made without sufficient

details of reaction conditions to allow for literature-based comparisons, hence these reports are not included within our comparisons.

Where the data are obtained at different reaction temperatures, the productivity values need to be normalised to account for these variations in reaction temperature. Most of the data has been obtained at 180 °C and the activation energy for acetylene hydrochlorination has been approximated at 30 kJ mol⁻¹¹⁵, as there are reported activation energies for this reaction in this range (Table S2). We therefore propose that the productivity between 160–200 °C can be normalised using equation (1).

$$\text{Mol}_{\text{VCM}}\text{kg}^{-1}\text{h}^{-1}_{\text{cat}} \text{ at } 180 \text{ }^{\circ}\text{C} = \exp \left((-E_a/R) \left(\frac{1}{T_{180}} - \frac{1}{T_R} \right) \right) \times \text{mol}_{\text{VCM}}\text{kg}^{-1}\text{h}^{-1}_{\text{cat}} \text{ at } T_R \quad (1)$$

$$\text{mol}_{\text{VCM}} \text{ kg}^{-1}\text{h}_{\text{cat}}^{-1} \text{ at } 180 \text{ }^{\circ}\text{C} = e^{\left(\frac{E_a}{R} \left(\frac{1}{T_{180}} - \frac{1}{T_R} \right) \right)} \cdot \text{mol}_{\text{VCM}} \text{ kg}^{-1}\text{h}_{\text{cat}}^{-1} \text{ at } T_R \quad (1)$$

Where E_a is the activation energy for the process (kJ mol⁻¹), R is the molar gas constant (J·K⁻¹·mol⁻¹), T_R is the reaction temperature in Kelvin at which the data was obtained and, T_{180} is 453.15 K

The second key parameter, the rate of catalyst deactivation, can be determined from the time at which the maximum conversion is reached to a time when a lower conversion is recorded (Supplementary information Table S1). This is represented as a function of decreasing acetylene conversion as a function of time (% h⁻¹), given by equation (2).

$$\text{Deactivation rate } (\% \text{ h}^{-1}) = X_{\text{Residual}} (\%) - X_{\text{Max}} (\%) / \Delta t \text{ (h)} \quad (2)$$

Where X_{RESIDUAL} = C₂H₂ conversion at steady state determined after the initial induction period⁹, X_{MAX} = maximum C₂H₂ conversion, Δt = time taken for conversion to decrease from maximum to residual levels

There are several reports wherein only the initial activity of a catalyst is discussed with no data about the performance of that catalyst as a function of time, thus these data have also been excluded from the plot. Whilst we appreciate that it is not always possible to study catalytic performance for sufficient timescales to obtain full deactivation data, it is important to monitor the activity of a catalyst over a period of time to allow for deactivation to be estimated.

Data has been reported within the temperature range 100-320 °C, although only data between 160-200 °C was normalised and plotted. It should be noted that whilst productivity was normalised to 180 °C, the deactivation rate is based on the decrease in activity at the original testing temperature. Whereas productivity is related to temperature, as shown in the Arrhenius-

based equation (1), no such relationship exists between deactivation and temperature. For Au catalysts, the deactivation mechanism has been shown to vary depending on reaction temperature. At low reaction temperatures, deactivation predominantly occurred by the deposition of carbonaceous deposits whereas at higher reaction temperatures deactivation was ascribed to the reduction to Au⁰ and subsequent sintering¹⁶. For this reason, it was not considered appropriate to plot normalised productivity and deactivation rate for data obtained outside 160-200 °C due to the required assumptions about deactivation rates outside of this range. Additionally, at the extremes of temperature (i.e. diverging further from 180 °C), large normalisation constants are generated leading to uncertainty in the calculated values of normalised productivity.

[H3] Comparison of supported metal catalysts

Recently, a number of supported metal catalysts have been proposed as candidates to replace the mercury catalyst used in VCM production – all claim to have potential as a ‘drop-in’ catalyst. The support of choice is activated carbon, with the catalysts often prepared by the impregnation of a metal salt onto carbon. The plot of normalised productivity versus deactivation rate (Figure 2a,b) clearly demonstrates that Au catalysts show the highest activity together with the lowest deactivation rates by a significant margin. The next best catalysts comprise Ru, Cu, Pd or Pt but Ru, Cu and Pt show productivities approximately one third that of Au when compared in this way. Whilst the plot shows a Pd catalyst with high (*ca.* 100 mol_{VCM} kg_{cat} h⁻¹) productivity, the deactivation rate for this catalyst was significantly higher than for several Au catalysts and this higher deactivation rate would preclude the use of this Pd catalyst commercially.

This analysis is in agreement with the original prediction that Au would be the best catalyst for this reaction¹⁷. This was confirmed recently using an *in situ* XAFS study which confirmed that the active site for the reaction was well dispersed Au⁺ cations with a correlation demonstrated between catalytic activity and the ratio of Au⁺:Au³⁺ present. Computational modelling showed that a low energy pathway for the formation of VCM existed for the subsequent addition of first acetylene and then HCl to Au⁺¹⁸. The original prediction was based on a plot of catalyst activity versus the standard electrode potential for over thirty supported metal chloride catalysts. This initial prediction did not include data for precious metals such as Au, Pt and Ru but the correlation was confirmed in subsequent studies¹⁹. In view of this we have plotted the best-in-class data for the normalised productivity for different supported metal catalysts against

the standard electrode potentials of the cations (Figure 1c). While the productivity of many metal catalysts is in agreement with the correlation, some do not align and their productivities fall well below the correlation line. This could imply that there is scope for significant improvement for these metals, although the trend would suggest that they will not be able to compete with Au even after optimisation. Most importantly for this set is Pt; in previous studies Pt has been found to much less active than expected for this correlation²⁰, as highlighted in figure S1. However, in more recent work by our group, Pt was shown to fit the correlation well when catalysts were made by a similar facile preparation method and tested under conditions identical to Au, Pd and Ru²¹, as illustrated in figure S2. This further highlights the importance of using similar conditions to make useful comparisons. The significantly lower number of papers in the academic literature regarding Pt catalysts is also a possible factor for the low correlation to the best-in-class catalysts for the metals shown. There are far more literature reports discussing the use of Au, Cu, Ru and Pd catalysts than Pt catalysts for acetylene hydrochlorination, thus it may be possible to further optimise Pt catalysts and improve their productivity.

We consider that the broad range of activities observed for supported Au catalysts is likely due to the inclusion of both nanoparticulate Au and cationic Au species. Lower activities can be associated with nano-particulate Au catalysts owing to the reduced formation of the active complex and decreased active site density. In addition to catalyst productivity (which relates to the total amount of catalyst present), another important measure of catalytic activity is turnover frequency (TOF), which relates the number of reactant molecules converted per unit of time to the number of catalytically active sites. A benefit of TOF, in contrast to productivity, is the intrinsic normalisation of catalytic activity to the number of catalytically active sites, although determining the quantity of active sites in a given catalytic system is often far from trivial. As discussed, *in-situ* XAS experiments have been used to confirm the active species as Au⁺ and correlate activity with the relative ratios of cationic Au species. Notably, it was not possible to effectively use XPS as a characterisation technique due to beam induced photoreduction of Au³⁺ leading to an overestimate of Au⁰; the higher photon incident energy of XAS techniques results in a lower absorption cross section compared with XPS, with no photoreduction occurring¹⁸. Unfortunately, the TOF of Au catalysts and other metal catalysts is often not reported for acetylene hydrochlorination due to insufficient information on the number of catalytically active species present. Furthermore, the nature of the active site or species in other catalytic systems is less well-defined than with Au catalysts. Additionally, due

to the required drop-in nature of a replacement for a mercury catalyst, STY is considered a more convenient measure of activity than TOF, due to the varying amounts of metal (or active non-metal) depending on catalytic system and the fixed volume and configuration of existing reactors.

[H3] Metal-free catalysts

Most recently there has been an intense interest in metal-free catalysts for this reaction, with many claiming to be a suitable drop-in replacement for the mercury catalyst. In early studies it was noted that there is low activity that can be ascribed to the carbon support when blank reactions are considered, and this had been thought to be related to impurities in the carbon⁹. One of the driving forces for designing metal-free catalysts is economic. However, given that the most active catalysts comprise of *ca.* 0.1% metal⁹, the carbon support is often the most expensive part of the catalyst, particularly as the metal can be recycled. In addition to this, the preparation of non-metal catalysts often relies on complex synthetic methods which may preclude larger scale preparations.

A further consideration is that a metal-free catalyst can exhibit a lower rate of deactivation. Deactivation in supported metal catalysts is often ascribed to the reduction of the metal cation to metal and subsequent sintering¹⁶. This is clearly not a possibility in metal-free catalysts, thus removing one possible deactivation mechanism. However, deactivation in metal-free catalysts can occur through coke formation, although the design of new materials with heteroatom doping can improve the electronic properties of the catalyst by inhibiting coke formation caused by acetylene polymerisation⁸. Heteroatom doping can increase the electron density of the catalyst, strengthening the chemisorption of HCl and C₂H₂ and decreasing the re-adsorption of the product, vinyl chloride.

The identification of the active sites in N-doped materials is a subject of debate, with catalysts often containing pyridinic, pyrrolic and graphitic N functionalities, with no consensus at present. However, the data is available so that the normalised productivity at 180 °C can be determined for catalysts tested between 180-220 °C. Data for catalysts tested at higher temperatures have been excluded as it is unlikely that these catalysts which operate at such elevated temperatures could be used as a drop-in replacement in existing reactors. It is clear (Table 1) that all metal-free catalysts exhibit a very low normalised productivity, typically two

to three orders of magnitude lower than supported metal catalysts. Hence, none can be considered as a potential drop-in catalyst for the replacement of the mercury catalyst.

[H2] Methane oxidation to oxygenates over zeolites

The oxidation of alkanes is a topic that has attracted much research attention. Key among target reactions is the oxidation of methane to oxygenated products, in particular methanol. This is a reaction that has been viewed as one of the grand challenges of catalysis. To date tens of thousands of papers and patents have been devoted to the selective oxidation of methane. As yet there have been no commercialised processes despite the intense research effort. As noted earlier Lunsford and Ito's seminal publication² on methane coupling provided the initial impetus for much of the following research and some catalysts have been taken to very large demonstration scale units but commercialisation remains elusive. Recent interest has switched from methane coupling, which makes hydrocarbon products, to selective oxidation to oxygenated products (methanol and acetic acid).

It should be recognised that the chemical industry has developed a range of processes to efficiently use methane for the production of fuels and chemicals using indirect processes. For many decades methane has been converted into synthesis gas ($\text{CO} + \text{H}_2$) which can then be converted to methanol using a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst or to hydrocarbons using the Fischer–Tropsch synthesis. These processes are operated at very large scales with very expensive infrastructure with current plants planned to be in operation for decades to come. It is thus unlikely that a new direct process based on methane oxidation to methanol would replace these indirect processes unless the process economics were to be extremely favourable. However, 4% of global natural gas production is flared annually as it is uneconomic for recovery and use; representing a major resource ($1.45 \times 10^{11} \text{ m}^3$ natural gas/annum)⁴⁷. The use of this resource would be a viable target for any new methane conversion process that could directly convert this flared natural gas to valuable liquid products that can be readily transported. There is therefore a real and pressing need to identify new catalysis for the direct conversion of methane to methanol.

There have been several phases in the research into the discovery of new catalysts for methane conversion to methanol. Initially, high temperatures (ca. 400 °C) were utilised with oxides and control of the oxygen partial pressure was important; limiting the oxygen partial pressure led

to very high selectivities to oxygenated products but methane conversion was far too low to be of commercial interest⁴⁸. Subsequently, research has focussed on using lower temperatures to enable improved selectivity to oxygenated products, but often these involve reaction cycles that are not closed. A key example was reported by Periana and co-workers using electrophilic Hg and Pt-complexes to oxidise methane in oleum^{49,50}, forming methyl hydrogen sulfate which has to be hydrolyzed separately to release methanol and SO₂. As the hydrolysis step leads to a dilution of the acid the catalytic process can only be closed by re-concentrating the acid, and the energy costs involved in this have precluded commercialisation of what is in effect a novel solution to retaining selectivity. However, the trend set by using lower temperatures has been retained in recent years⁵¹.

[H3] Selection of the key reaction parameters and selection of the data set

Selective hydrocarbon oxidation is an important commercialised reaction. The oxidation of butane to maleic anhydride⁵² and the oxidation of propene to acrylic acid⁵³ are two examples of this type of process being carried out on a large scale. In general, for oxidation reactions two parameters are considered important if the design of a drop-in catalyst is being considered for these reactions. These are selectivity to the desired product and the conversion of the hydrocarbon. Often data for these reactions are plotted as selectivity versus conversion curves at constant temperature, and small gains in selectivity at high conversion are sought.⁵² This is well demonstrated for butane oxidation to maleic anhydride in a comprehensive review of all the patent and academic literature showed that this approach could identify the best catalysts⁵². With respect to the selective oxidation of methane to oxygenates this reaction is far from commercialisation and so a different approach is suggested. In this case the first key reaction parameter is the selectivity to the oxygenated products since any product other than CO and CO₂ is more valuable than methane and therefore the combined selectivity is a convenient way of representing this. The second key parameter is the overall productivity in terms of product made per unit mass of catalyst per unit time. On this basis the activity of respective catalysts can be usefully compared.

The selective oxidation of methane in water using metal cations or metal nanoparticles supported on zeolites is a current topic of intense interest.⁵¹ It should be noted that only small amounts of products are being reported and so these reactions are really only of academic

interest at present. However, the purpose of this exercise is to try to identify which catalysts are worth researching further.

Most recent interest has centred on metal-exchanged zeolite catalysts. Here activated forms of oxygen (e.g. H_2O_2 , N_2O)^{51,54-56} or co-reductants (e.g. H_2 , CO)^{57,58} are used to enable the activation of methane with a closed catalytic cycle. However, these catalysts show no activity when O_2 is used as the terminal oxidant. For large scale processes it is essential that catalysts are designed that use O_2 rather than the more expensive oxidants (e.g. H_2O_2 , N_2O) and furthermore that co-reductants also need to be avoided. In consideration of the data set we therefore have excluded these studies as the selective oxidation of methane using O_2 is the grand challenge in catalysis that needs to be addressed. Recently, the focus has switched to using O_2 or H_2O as the oxygen source for the oxygenated products from methane oxidation. The catalysts are Cu or Au zeolites, and these will be the focus for this case study. The data set for these catalysts is given in Table S3.

[H3] Comparison of zeolite catalysts

The study of methane oxidation with zeolite catalysts using $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$ mixtures has focussed on the use of Cu which is ion-exchanged into the zeolitic framework. These catalysts, on activation with a heat treatment in O_2 , lead to the formation of Cu_2O which is considered the active species. To date there have been relatively few studies⁵⁹⁻⁶⁴ but all are exceptionally well cited indicating this is a research field of current interest. The Cu zeolite catalysts are operated in two modes. The initial studies used a non-closed catalyst cycle in which the catalyst is first activated in O_2 at high temperature, then this activated catalyst is reacted with CH_4 often at a lower temperature and the product methanol is then extracted with water at a lower temperature. As the CH_4 and O_2 are not in contact the methanol selectivity is reported as 100%. A second set of reaction conditions involves the continuous feeding of $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$ mixtures over the pre-activated catalyst. These give lower selectivities. There is a recent report⁶⁵ of Au ZSM-5 as a catalyst for this reaction. This catalyst is also reacted with $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$ mixtures but in this case in a stirred autoclave reactor. It is clear that in all these studies water is an important component and with the Cu catalysts the latest report has concluded that H_2O was in fact the source of the oxygen in the methanol product⁶⁴. In this case normalisation of the reaction data was not considered feasible as the entire data set is both small and collected using

very different reaction conditions; namely, (i) non-closed catalyst cycle⁵⁹⁻⁶¹, (ii) closed catalytic cycle in a flow reactor⁶²⁻⁶⁴ and (iii) closed catalytic cycle in a stirred tank autoclave reactor⁶⁵. In this case we have used the total oxygenate productivity as indicative of relative activity and the comparison of the productivity and oxygenate selectivity is shown in Figure 3. From this it is clear that the non-closed catalytic cycle experiments always give 100% selectivity by virtue of the way experiments are conducted as the methane and oxygen are kept apart. When the CH₄/O₂/H₂O mixtures are co-fed the selectivity is markedly lower and in this regime the Cu ZSM-5 and Au ZSM-5 catalysts behave similarly especially when compared as initial rates or in pulse feed experiments. In the co-feed regime, the Au catalysts might show slightly improved selectivity to oxygenated products. However, Au ZSM-5 catalysts produce acetic acid as well as methanol. The Cu and Au catalysts clearly operate by different mechanisms and active sites. For the Cu catalyst the Cu²⁺ is ion exchanged into the porous zeolitic structure whereas the Au is present in nanoparticles on the exterior zeolitic surface. However, although the two catalysts operate in different experimental conditions the method of comparing the performances of the two catalysts as shown in Figure 3 can be instructive.

[H1] Conclusion

We have tried to show how a very important question; namely “How can the best catalyst for a reaction be easily recognised?” can be answered in a logical manner. To do so, we selected two case studies. The first is based on acetylene hydrochlorination requires the design of a drop-in catalyst for existing reactors and this therefore places a number of constraints on the catalyst design. The second is based on the dream reaction of the direct conversion of methane to methanol with O₂ as the terminal oxidant. For this catalyst there are no existing commercial units and so there are no particular constraints on catalyst design. In the future, the desire to de-fossilise the production of key chemicals will potentially lead to the use of sustainable sources of carbon such as methane from biogas or as a by-product of CO₂ hydrogenation. As acetylene could be produced from methane using sustainable energy sources the two reactions selected as case studies could be very relevant for the future.⁶⁶

For the case study concerning acetylene hydrochlorination, applying our simple generalised method, supported metal catalysts are far superior to metal-free catalysts when compared on a rational basis. Furthermore, it is clear that the best metals are Au, Pt, Pd, Ru and Cu. Not only was Au shown to be significantly more active than the other metals, but the deactivation rate was also often lower. With the exception of Pd, the activity of Au was shown to be

approximately three times that of the next best metals, but the most active Pd catalyst had a significantly higher deactivation rate than many Au catalysts. Of course, there are several other factors that need to be considered when operating a commercial catalyst. These include safety (e.g. Are potentially hazardous reaction intermediates formed?), the catalyst cost, the possibility of catalyst regeneration or recycling, the scalability of a proposed preparation method and the overall feasibility of the catalyst synthesis including waste generation. Nevertheless, a general method of comparing catalyst performance should be undertaken when considering a drop-in replacement for a currently operated commercial catalyst.

The second example we selected is representative of an aspirational reaction for which there is no existing commercialised process. For this reason, methane selective oxidation continues to attract immense research activity in the catalysis community. The most recent trend has been the use of zeolite catalysts which incorporate metals, and here Cu and Au appear to offer the most promise. However, the reactions are carried out in excess water and the amounts of products are vanishingly small. As such, from an industrial perspective these results do not appear to be commercially attractive; but the research does offer scope for future improvement.

We should highlight that the advantage of the method we set out in this paper is that it provides a way in which it is quick to compare published information for a specific reaction. We emphasise the approach should be considered a precursor to experiments based on like-for-like tests and full kinetic studies. However, it should be noted that it would be preferable if the comparisons could be made on the basis of useful performance data that can readily be compared to others e.g. kinetic data (rate constants, TOF) and it would be preferable for future studies that these data are routinely reported in any catalysis study.

Author contributions

AL, LRS and GJH performed the literature search and collated all the data. All authors contributed substantially to the writing, reviewing and editing of the manuscript prior to submission.

Competing interests

Peter Johnston and Joost Smit are employees of Johnson Matthey, a company that commercially supplies a gold catalyst for acetylene hydrochlorination for use in China. Graham

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Figure 1. Acetylene hydrochlorination publications A search of papers and patents relating to “acetylene hydrochlorination” between 1945 and 2020, Key: red = patent applications, blue = research publications (Source: data compiled from Scopus & Google Patents)

Figure 2 Acetylene hydrochlorination reaction data based on KPIs **a)** Normalised VCM productivity vs deactivation rate for a range of catalysts. The active component of the catalysts is shown in the legend; with the exception of the non-metal catalysts, all the catalysts are supported metal catalysts. Normalised productivity and deactivation rate were calculated in accordance with equations (1) and (2), respectively. See table S1 for details of the data contained within the figure; **b)** Normalised VCM productivity vs deactivation rate for a range of catalysts, highlighting those with low deactivation rates; **c)** Correlation between normalised maximum productivity and standard electrode potential for the reaction $M^{2+} + 2e^- \rightarrow M$ or $M^{3+} + 2e^- \rightarrow M^+$. Data taken from references specified by the data point^{10,11,20,22-27}

Figure 3. Selective methane oxidation reaction data based on KPI Total oxygenate selectivity and total oxygenate productivity for a variety of catalytic systems for methane oxidation to oxygenates over zeolite catalysts. Closed symbols represent a closed catalytic system whereas open symbols represent a non-closed cycle. Data taken from references specified by the data point.⁵⁹⁻⁶⁵

Table 1. Normalised productivity for metal-free catalysts for acetylene conversion determined with equation 1.

Metal-free catalyst system	GSHV_{C₂H₂} /h⁻¹	HCl/C₂H₂ molar ratio	Temperature /°C	Normalised productivity /mol_{VCM} kg_{cat}⁻¹ h⁻¹	Reference
PANI-AC-900	36	1.10	180	1.90	28
NS-C-NH ₃	35	1.20	220	4.36	29
Activated Carbon marked as CBC	180	1.10	180	1.28	30
N-doped Carbon	36	1.08	220	2.66	31
SBMC-600	30	1.15	200	1.70	32
Activated Carbon marked as PBC	145	1.10	180	0.93	30
AC-n-U500	100	1.21	180	0.79	33
Activated Carbon marked as CCN	150	1.10	180	0.57	30
Activated Carbon marked as WBC	90	1.10	180	0.15	30
g-C ₃ N ₄ /AC	72	1.15	180	2.27	34
N-doped carbon	50	1.15	180	2.36	35
N-Carbon - Z4M1	50	1.14	180	1.05	36
N-OMC-O _x	300	1.20	180	1.47	37
g-C ₃ N ₄ : MF-600	30	1.20	220	1.46	38
N-MC-W	30	1.20	220	1.21	39
1H-imidazole	30	1.20	220	0.59	40
25% HMT/AC	30	1.20	220	0.59	41
3%S/BSAC-800	90	1.10	180	1.67	42
N@CBCFE	180	1.10	220	3.22	43
NC-800	30	1.15	220	1.25	44
PAN-400-air	30	1.20	220	0.87	45
NR-CAC	30	1.20	220	1.51	46