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Catalyst potential: a key for controlling alcohol oxidation in multiphase reactors

T. Mallat *, A. Baiker

Department of Chemical Engineering and Industrial Chemistry, ETH-Zentrum, CH-8092, Zürich, Switzerland

Abstract

The possibilities and advantages of measuring the catalyst potential during alcohol oxidation with molecular oxygen and supported platinum metal catalysts is discussed. The steady-state catalyst potential is a sensitive indicator of the balance between oxidation and reduction processes taking place on the active sites. In this short review we focus on the application of the potential measurements for adjusting the rate of oxygen supply to the rate of alcohol oxidation and avoiding catalyst deactivation. Other uses are the control of selectivity in the consecutive reaction sequence alcohol → aldehyde → acid and the elucidation of the nature of catalyst deactivation. The partial oxidation of cinnamyl alcohol in a multi-phase reactor has been chosen as an example.

1. Introduction

The platinum-metal catalyzed oxidation of alcohols to carbonyl-compounds or carboxylic acids is an environmentally friendly technology: molecular oxygen is used under mild conditions (1 bar, <90°C) in aqueous medium [1–3]. The most active catalysts are supported Pt and Pd, which are frequently promoted with heavy metals, such as Bi or Pb. The selectivity is usually high, above 90%. The reaction mechanism is an oxidative dehydrogenation, in which only the metallic surface sites (Pt^0 or Pd^0) are active. Consequently, the catalyst has to be pre-reduced before reaction and the reactor should be operated in a transport limited regime, i.e. the oxygen supply from the gas phase to the catalyst surface should be the rate determining step. If the rate of oxygen supply is set higher than the rate of oxygen consumption for alcohol oxidation, the surface metal atoms are successively oxidized and the catalyst deactivates. However, the choice of a too low rate of oxygen supply results in low and uneconomic reactor performance.

The advantage of using low oxygen partial pressure has already been described in the seventies [4,5]. Another possibility is to adjust the concentration of dissolved oxygen to a constant, low level (usually below 5% of the saturation value) to avoid over-oxidation [6]. The amount of oxygen can be controlled by using an oxygen sensor in the liquid phase. If the catalyst is over-oxidized, it can be reactivated by substituting oxygen to nitrogen for 10–15 min [7]. During this period the oxidized surface sites are reduced by the reactant alcohol.

An interesting solution, the use of Pt supported on a carbon extrudate, in which the outer zone of the carrier acted as a diffusion barrier for oxygen, was proposed later [8]. This technique suffers from the drawback that it necessitates the preceding optimization of the system. Besides, it oper-

* Corresponding author.

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ates with constant rate of oxygen supply while in a batch reactor — which is the general choice for this process — the reaction rate changes with time (conversion) due to declining concentration of reactants or to catalyst deactivation.

From an engineering point of view, the aim is to maximize the overall reaction rate (or minimize the catalyst loading necessary to achieve full conversion). For this purpose the oxygen concentration has to be adjusted to the actual rate of the surface reaction. The steady-state catalyst potential is a direct indication of the oxidation state of metallic active sites [9,10]. It provides real on-time information on the balance between reduction and oxidation processes and offers a good basis for controlling the rate of oxygen supply.

Catalyst potential measurements have been extensively used in studying hydrogenation reactions in slurry reactors [11–13]. The study of carbon suspension electrodes [14–17] revealed the characteristics of charge transfer between the collector electrode and the catalyst particles. During measuring the potential of a suspended catalyst, the collector electrode should indicate the mean potential of the catalyst particles. Important variables, influencing the measured potential and the rate of charge transfer, are the size (capacity) and material of the electrode, the catalyst concentration, the frequency and duration of collisions and the resistance of electrolyte and the electronic contact. The (electrochemical) reactions at the surface of the electrode should be small compared to the reactions at the catalyst surface. In contrast to earlier suggestions [18,19], a bright Pt wire electrode was found to be the most suitable in alcohol oxidation: its potential was within ± 10 mV of the reference value (not disguised by charge transfer problems) even in a dilute 0.15 g/l catalyst slurry [20]. This technique provides reliable values also when using metals over non-conductive supports, such as Pt/alumina.

Here we will discuss the application of the method in alcohol oxidation with molecular oxygen in aqueous alkaline solutions. The selective oxidation of cinnamyl alcohol to cinnamaldehyde over Pt/alumina and Bi–Pt/alumina has been chosen as an example:

$$\text{Ph–CH–CH=CH}_2\text{OH} + \tfrac{1}{2}\text{O}_2 \rightarrow \text{Ph–CH=CH–CHO} + \text{H}_2\text{O} \quad (1)$$

The applicability of the aqueous medium has been shown for the oxidation of water-insoluble alcohols in the presence of a detergent [3,10,20–23]. It was found that arylsulfonic acid sodium salt type detergents are stable during the oxidation reaction and has no detrimental effect on the catalytic activity or the reliability of the catalyst potential measurement.

2. Experimental

The Bi-promoted catalysts were prepared by consecutive reduction of Bi^{3+} with hydrogen onto a 5 wt.-% Pt/alumina catalyst (Engelhard E 7004, Pt dispersion 0.30, determined by TEM) [10]. Details of the preparation technique and the characterization of these type of catalysts can be found elsewhere [10]. Preferential deposition of Bi onto Pt particles has been confirmed by combined TEM-EDX analysis. The Bi content was determined by inductive coupled plasma atomic emission spectroscopy.

Oxidation of cinnamyl alcohol to cinnamaldehyde was performed at 40°C in a 200 cm^3 thermostated glass batch reactor, equipped with magnetic mixing, reflux condenser, thermometer and electrodes. Generally, the reactor worked in a mass transfer limited regime, controlled by the oxygen partial pressure (1 bar total pressure, diluent: nitrogen), gas flow rate (10 $cm^3\ min^{-1}$) and mixing rate (1500 min^{-1}). Before reaction, 0.14 g catalyst was pre-reduced in nitrogen with cinnamyl alcohol (3.5 g) in 30 cm^3 60 μM aqueous Li_2CO_3 solution containing dodecylbenzenesulfonic acid sodium salt (DBS, 13 μM). Before the oxidation of cinnamaldehyde, the catalyst was pre-reduced by hydrogen and the reaction was carried out at pH of 11 adjusted by 0.4 M Na_2CO_3. The hydrogenation of cinnamyl alcohol was per-

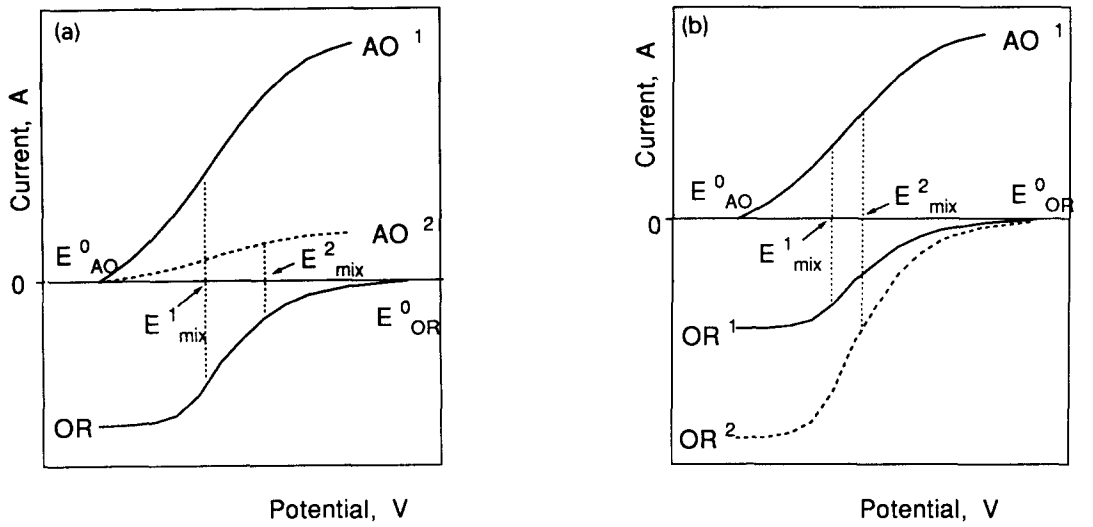

Fig. 1. Schematic representation of the development of steady-state catalyst potential, considered as a mixed potential (E_{mix}). (a) Influence of catalyst deactivation; (b) influence of higher rate of oxygen transport.

formed at 1 bar, in the same solution and under the same conditions as those of the oxidation reaction. Yield and conversion were determined by GC analysis (after extraction with i-propyl acetate) [10]. The total amount of detectable by-products (besides cinnamic acid) was less than 0.1%.

The potential of the catalyst was measured with a Pt wire collector electrode against a Ag/AgCl/$KCl_{(sat)}$ reference electrode ($E = 197$ mV) during the oxidation reaction. The latter was separated from the reaction medium by two diaphragms in order to minimize the pollution by Cl^- ions. The influence of reaction conditions and the non-conductive support on the reliability of the measured value has been tested and reported elsewhere [20]. All potentials in the text and figures are referred to reversible hydrogen electrode.

3. Results and discussion

3.1. Interpretation of steady-state catalyst potential

The interpretation of the steady state catalyst potential measured during alcohol oxidation is based on the mixed potential theory [9,24–26]. The overall reaction (1) can be decomposed into the alcohol oxidation (AO) and oxygen reduction (OR) reactions:

$$Ph\text{–}CH{=}CH\text{–}CH_2OH + 2OH^- \rightarrow Ph\text{–}CH{=}CH\text{–}CHO + 2H_2O + 2e^- \quad (2)$$

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (3)$$

A schematic representation of the development of mixed potential is shown in Fig. 1a. The AO^1 and OR lines represent the current–potential curves for reactions (2) and (3), respectively. There is a limiting current in the oxygen reduction process due to transport limitations in the three-phase system. Each Pt particle functions as a 'short-circuited' electrochemical cell, where both the anodic (alcohol oxidation) and cathodic (oxygen reduction) half-reactions take place at the same rate and the same potential (mixed potential, E_{mix}). At the mixed potential the anodic and cathodic currents ('mixture' currents) are equal, i.e. no net current flows through the catalyst.

The steady state catalyst potential is a function of all reaction parameters, which influence the rate of any of the component reactions. An example is the decrease of the rate of alcohol oxidation (e.g. due to catalyst deactivation). By Faraday's law, the lower reaction rate corresponds to lower cur-

Table 1
Catalyst reuse in the oxidation of α-tetralol to α-tetralone with air over a 0.75 wt.-% Bi–5 wt.-% Pt/alumina catalyst[a] [20]

Run	Rate[b] (mmol·min^{-1})	Conversion (%)	E^{c}_{cat} (V)
1	0.13	99	0.10
2	0.09	67	0.47
3	0.04	28	0.58

[a]Aqueous Li_2CO_3 + DBS, catalyst:reactant weight ratio = 0.10, 85°C, 1 bar.
[b]Reaction rate at 10% conversion.
[c]Catalyst potential at 10% conversion.

Table 2
The influence of oxygen partial pressure on the rate of oxidation of diphenyl carbinol to benzophenone over a 0.75 wt.-% Bi–5 wt.-% Pt/alumina catalyst[a] [20]

Pressure bar	Rate[b] (mmol·min^{-1})	Time[c] (h)	E^{d}_{cat} (V)
0.05	0.05	5.5	0.07
0.21	0.14	2.5	0.24
1.00	0.86	8.0[e]	0.60

[a]Aqueous Li_2CO_3 + DBS, catalyst:reactant weight ratio = 0.03, 75°C, 1 bar.
[b]Reaction rate at 10% conversion.
[c]Reaction time necessary to achieve 98–99% conversion.
[d]Catalyst potential at 10% conversion.
[e]Catalyst deactivation after about 10 min.

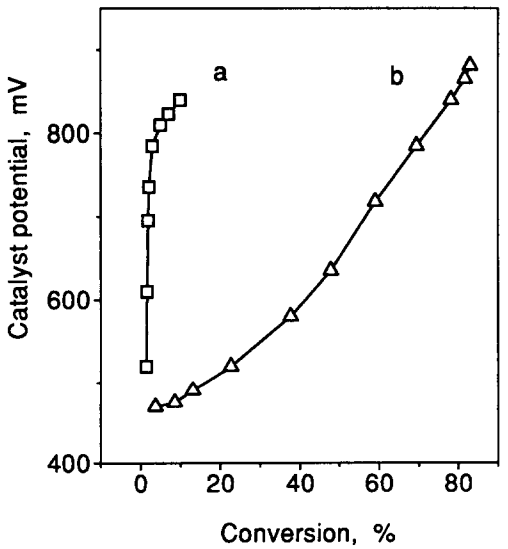

Fig. 2. Catalyst potential during the oxidation of cinnamyl alcohol over (a) 5 wt.-% Pt/alumina and (b) 0.9 wt.-% Bi–5 wt.-% Pt/alumina (aqueous Li_2CO_3 + DBS, 40°C, air).

rent density (Fig. 1a, dashed line of AO^2). As a result, the catalyst potential is shifted to the positive direction (E^2_{mix}), which corresponds to a more oxidized state of the platinum metal active sites. An example to this case is shown in Table 1. The formation of irreversibly adsorbed by-products decreased both the reaction rate and the final conversion under identical conditions during repeated reuse of the catalyst.

Fig. 1b shows the influence of a change in the oxygen reduction process. The dashed line of OR^2 corresponds to higher rate of oxygen supply (e.g. due to higher oxygen pressure or more efficient mixing). As a result, the mixed potential (E^2_{mix}) is shifted to the positive direction. Besides, the mixture currents are also higher, which indicates higher overall reaction rate at higher rate of oxygen supply. The influence of oxygen partial pressure on the rate of oxidation of diphenyl carbinol as an example is shown in Table 2. At low oxygen pressures the reactor worked in a transport limited regime, which was indicated by the constant rate of overall reaction until 80–85% conversion. When oxygen was used as oxidant at 1 bar, the reactor was operated in the kinetic regime and — as expected — the surface active sites were gradually oxidized and the catalyst deactivated after about 10 min.

3.2. Control of oxygen supply

In Fig. 2 the catalyst potential is plotted during the oxidation of cinnamyl alcohol over Pt/alumina and Bi-promoted Pt/alumina catalysts under identical conditions. The rapid increase of the potential of Pt/alumina with conversion at the very beginning of the reaction indicates that the rate of oxygen supply is too high compared to the rate of alcohol oxidation. Fig. 3, curve a shows that the reaction rate over Bi–Pt/alumina is high and almost constant during the first part of the reaction (transport limited regime). On the contrary, Pt/alumina (Fig. 3, curve b) has low activity almost from the beginning of the reaction. The conversion after about 5 h was only 10% with Pt/alumina and 83% with Bi–Pt/alumina.

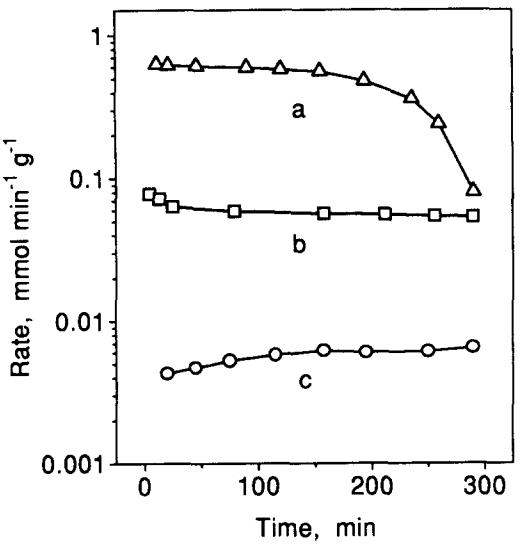

Fig. 3. Rate of oxidation of cinnamyl alcohol at constant air flow rate and mixing rate over (a) 0.9 wt.-% Bi–5 wt.-% Pt/alumina and (b) Pt/alumina, and (c) at constant potential (450±20 mV) of Pt/alumina (aqueous Li_2CO_3 + DBS, 40°C, air).

Based on the cyclic voltametric measurements of Pt and Pd in neutral and moderately alkaline solutions, the limit between hydrogen and oxygen sorption is around 0.5 V [20–23,27]. Below this value the active sites are in a reduced state (partially covered by H_{ad}), and above 0.5 V they are partially oxidized (covered by OH_{ad} [28]). This 'borderline' is only slightly influenced by the nature of anions or the presence of Bi or Pb promoters. The standard potentials for simple alcohol → carbonyl compound transformations, calculated from thermochemical data, are around 0.1 V [29]. Accordingly, if there is no deactivation and the oxygen supply is properly adjusted, the catalyst potential is low (0.1–0.3 V) and the active sites are in a reduced state during alcohol oxidation, in agreement with the dehydrogenation mechanism. The oxidation of several primary and secondary alcohols revealed that over-oxidation and catalyst deactivation occurs only above 0.8 V [10,20–23,30]. Note that the relatively high potential of Bi–Pt/alumina even at low conversions (Fig. 2, curve b) indicates some by-product formation during reaction. The strong adsorption of these by-products on the active sites ('chemical poisoning', [3,10,23]) slows down the reaction and shifts the mixed potential in the positive direction.

The rate of oxygen supply can be controlled based on the change of catalyst potential. In an ideal case (negligible side reactions) the increase of catalyst potential during reaction is minor, due to the logarithmic correlation between electrochemical potential and conversion (alcohol/aldehyde ratio). At the beginning of the reaction a rather high rate of oxygen supply can be used (high initial rate of alcohol oxidation), on condition that the catalyst potential is below 0.8 V. With increasing conversion either the oxygen partial pressure or the mixing rate should be reduced in order to maintain the balance between the oxidation and reduction processes and to avoid the increase of steady state catalyst potential to 0.8 V or above. By this way the amount of catalyst, necessary to achieve full conversion in the same time period, could be reduced considerably and 95% cinnamaldehyde yield was obtained in 5 h with a catalyst/reactant weight ratio of 0.04. In the oxidation of some secondary alcohols to ketones (e.g. diphenyl carbinol to benzophenone or 1-phenylethanol to acetophenone) this weight ratio was reduced as low as 0.01–0.02 [20].

3.3. Catalyst deactivation

The steady-state catalyst potential can be used as a general surface sensitive information on the working catalyst. Besides controlling reaction rates, it can help in elucidating the nature of catalyst deactivation. In the absence of considerable catalyst poisoning, e.g. in the air-oxidation of 1-phenylethanol or diphenyl carbinol [20–22], the potential of Bi–Pt/alumina was below 0.2 V up to 90% conversion. The reduced state and partial hydrogen coverage of Pt during the oxidation of (secondary) alcohols is in agreement with the dehydrogenation mechanism of the reaction. It was mentioned above that the relatively high catalyst potential of Bi–Pt/alumina at medium conversions (Fig. 2, curve b) can be attributed to some by-product formation and chemical deactivation of the catalyst during the oxidation of cin-

namyl alcohol. An even more serious chemical poisoning was observed in the oxidation of L-sorbose, which prevented any reaction below 0.7 V, independent of catalyst composition, pH or oxygen partial pressure [30]. This higher catalyst potential corresponds to a partial oxygen (OH_{ad}) coverage of Pt which is necessary for the oxidative removal of the irreversibly adsorbed impurities and reactivation of the catalyst. The destructive adsorption of alcohols (including polyols) and carbonyl compounds on Pt and Pd in aqueous acidic or alkaline solutions, and the reductive or oxidative removal of the irreversibly adsorbed species have been thoroughly investigated in the past years [31–36]. These data, obtained in electrochemical cells with single crystal and polycrystalline metals, support our observations in slurry reactor using supported noble metal catalysts.

An example on the poisoning and self-cleaning of Pt is shown in Fig. 3. The oxidation of cinnamyl alcohol over Pt/alumina (curve b) was repeated while keeping the catalyst potential at around 450 mV (curve c). At this potential the OH_{ad} coverage of Pt is negligible and the surface impurities cannot be removed by oxidation. The much lower average reaction rate (by a factor of about 10), compared to reaction b at constant rate of oxygen supply, demonstrate the efficiency of this self-cleaning process at higher catalyst potentials. There are several other examples in the literature [10,20,30,37], in which the partially oxidized state of the catalyst during alcohol oxidation in a slurry reactor has been proved. In these instances the careful control of the rate of oxygen supply is particularly important, as the reaction takes place only in a narrow potential (OH_{ad} coverage) region. Below this range the active sites are covered by impurities which hinders the alcohol oxidation, and above this 'active' range of OH_{ad} coverage the number of metallic active sites (Pt^0 or Pd^0) is too low, which slows down the reaction.

The technique discussed above and shown in Fig. 3c can be generally applied for the separation of the two phenomena: (i) the catalyst over-oxidation due to the too high rate of oxygen supply compared to the rate of the surface oxidation reaction and (ii) the partial oxygen coverage of the noble metal which facilitates the removal of irreversibly adsorbed species from the active sites. In the former case the prevention of 'over-oxidation' eliminates catalyst deactivation and increases the reaction rate (the number of M^0 active sites). In the latter case the absence of OH_{ad} results in low reaction rate ('chemical poisoning' [3,38]).

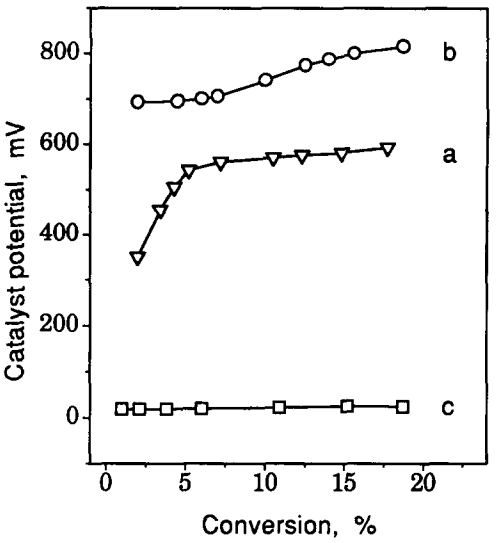

Fig. 4. Potential of the 0.9 wt.-% Bi–5 wt.-% Pt/alumina catalyst during the oxidation of (a) cinnamyl alcohol and (b) cinnamaldehyde with oxygen, and during the (c) hydrogenation of cinnamyl alcohol (aqueous Na_2CO_3 + DBS, 40°C).

3.4. Selectivity to aldehyde intermediate

In certain cases not only the reaction rate, but also the selectivity is influenced by the oxidation state (potential) of the catalyst. Fig. 4 shows the catalyst potential–conversion relationship during the oxidation of cinnamyl alcohol to cinnamaldehyde (curve a) and its further oxidation to cinnamic acid (curve b) at a controlled pH of 11. There is about a 200 mV potential gap between the two processes under identical conditions, which indicates that the aldehyde intermediate is not oxidized to a considerable extent until the alcohol reactant is present on the surface. However, if the rate of oxygen supply is increased, the steady-state catalyst potential will be higher and

the separation of alcohol and aldehyde oxidation becomes poor. Similarly, when using the unpromoted Pt/alumina catalyst, lower selectivities can be expected based on the curves shown in Fig. 2. The experimental observations are in good agreement with the expectations: only 88.5% selectivity to cinnamaldehyde at 10% conversion was obtained in the air-oxidation of cinnamyl alcohol over Pt/alumina, whereas the selectivity of a Bi–Pt/alumina ($Bi/Pt_s = 0.5$) was 99% at 10% conversion and decreased below 97% only at 99% conversion.

An interesting mechanism has been proposed recently for the interpretation of poor conversions obtained in the partial oxidation of some alcohols [39]. Based on the dehydrogenation mechanism of alcohol oxidation, the authors suggested that the product carbonyl compound can be re-reduced by the hydrogen formed in the reaction and finally an equilibrium alcohol–ketone mixture is obtained. If this mechanism were valid, the C=C double bond should be rapidly (and irreversibly) hydrogenated during the oxidation of cinnamyl alcohol. However, not even traces of the saturated alcohol or aldehyde could be detected by GC analysis. Fig. 4, curve c shows that the hydrogenation of cinnamyl alcohol to phenylpropanol occurs at more negative potentials, by at least 300 mV, compared to the oxidation of cinnamyl alcohol. This high potential gap between the two processes indicates that the reduction of the product or reactant during the oxidation reaction is impossible. The likely interpretation of the moderate yields [39] is the chemical poisoning of the catalyst, which prevents the further oxidation of the reactant.

4. Conclusions

The measurement of the steady-state catalyst potential during the oxidation of alcohols over supported noble metal catalysts offers a unique possibility for gaining an insight into the processes occurring on the solid/liquid interface. It provides a key for controlling the rate of oxygen supply, avoiding over-oxidation of the active metallic sites and optimising the reactor performance.

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