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Supported liquid phase catalysis in selective oxidation

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Abstract

The application of supported liquid-phase catalysis (SLPC) to selective oxidation examples is discussed to provide valuable alternatives to the purely homogeneous or heterogenous processes. Specific examples discussed are the Wacker type ethylene oxidation on heterogenous catalysts and the vinyl acetate production by ethylene acetoxylation. The potential industrial application of SLPC for these oxidations and the possible extensions of this technology to other oxidation processes are also discussed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Selective oxidation reactions have traditionally been thought of as purely homogeneous or heterogeneous catalytic processes. However, the salient features of both types of catalysis can be combined to comprise a more efficient process than the one achieved using the corresponding homogeneous or heterogeneous system independently. Such a combined catalytic process provides foundation for the concept of supported liquid-phase catalysis (SLPC).

SLPC research has formally existed since the late 1930's [1]. Remarkably, practical application of this technology has not been widespread since then. As researchers find that they can accentuate the strengths of both homogeneous and heterogeneous catalysis into the discipline of SLPC, more emphasis has been placed upon this concept for several classes of catalytic reactions in the literature.

This article will focus on the application of supported liquid-phase catalysis to selective oxidations. The remainder of this section will provide a general background of homogeneous and heterogeneous oxidation catalysis as well as present a review of the SLPC area. Sections 2 and 3 will illustrate these concepts through two example catalytic oxidations: (1) ethylene oxidation to acetaldehyde and acetic acid and (2) ethylene acetoxylation to vinyl acetate monomer. Each section will compare and contrast the reactions and mechanisms for the homogeneous and heterogeneous cases. The potential industrial application of SLPC for these oxidations will also be discussed. Finally, we will end by identifying the possible extensions of this technology to other oxidation processes.

1.1. Homogeneous vs. heterogeneous catalysis

Homogeneous catalysis has several potential advantages over the heterogeneous catalysis of the same

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reaction. These advantages include the possibility of achieving greater selectivities and the potential for a more efficient use of the metal atoms [2]. These benefits, however, are far outweighed by several engineering problems that are associated with homogeneous reactions. For example, many of these reaction media are corrosive in nature. Thus, the materials used for construction of the process equipment can be unattractively expensive. Another limitation of the liquid-phase process is the difficulty of separating the product from the catalyst. Additionally, the utility of the fully exposed metal atoms might be hindered by gas–liquid diffusion limitations. Heterogeneous processes of the same reactions are typically not plagued by these problems. Thus, several alternative heterogeneous catalytic processes have been proposed for processes (particularly oxidations) that are currently carried out with homogeneous catalysis [3]. Typically, these alternative catalytic systems are ''hybrids'' of both homogeneous and heterogeneous catalysis.

The ''hybrid'' catalyst is typically prepared by immobilizing or anchoring a soluble homogeneous metal complex to an inert support. Although it is not essential, these metal complexes can have the same structure in solution as in the solid state [4]. In some cases, the solid metal complex can give rise to the same mechanism and hence comparable selectivities and activities for the analogous homogeneous reaction. Moreover, it is possible for the solid metal complexes to become soluble in a compatible liquid film which can form at the surface and in the pore structure of the catalyst. As discussed in the following section, this type of catalyst is referred to as a supported liquid-phase catalyst.

1.2. Supported liquid-phase catalysis

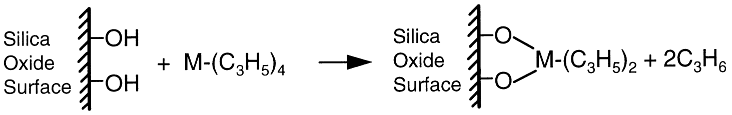
In SLPC, the liquid-phase complex or ligand is typically anchored on two types of surfaces: polymer supports and inorganic oxide supports. Polymer supports can easily be functionalized by ligand forming species, which can readily form ligand–metal complexes. Polystyrene has been widely used as a support in SLPC applications [5–7]. Examples of homogeneous complexes used with these supports include complexes of rhodium and mixed palladium-phosphines. These catalysts have been useful in the application of hydrogenation and isomerization of olefins [5,6].

The other class of surfaces for homogeneous complex anchoring are inorganic oxide supports. These include silica oxides, alumina oxides and mixtures thereof. Fig. 1 illustrates the preparation of an organic complex anchored to the surface of a silica oxide. The metal complexes are attached to the surface via reaction with surface hydroxyls.

If the reactants, products and/or reaction conditions are favorable, very thin condensed liquid films may form on the surface of these inert supports providing a ''homogeneous-like'' environment for the reaction to take place. This is considered to be the establishment of the supported liquid-phase.

There are three general roles the SLP can provide to these catalytic systems; (1) the film could serve the solvent, dissolving the anchored complex, (2) the materials comprising the liquid phase might be an important participant in the reaction and (3) the SLP could serve as a catalyst to the reaction. In all of the applications that will be discussed below, the SLP is used as a solvent for the oxidation reactions.

The concept of supported liquid-phase catalysis has been successfully applied to several processes in selective oxidation. In the following sections, two example processes will be discussed: (1) the Wacker reaction of ethylene to form acetaldehyde and (2) vinyl acetate production via acetoxylation of ethylene.



where M = metals (e.g. Mo, Pt or Pd)

Fig. 1. Example of metal complex anchoring to silica surface.

2. Ethylene oxidation

The major industrial route for producing acetaldehyde is the homogeneous oxidation of ethylene. This reaction is known as the Wacker process. Although this process has been popular for commercial use, much interest has been placed on the development of analogous heterogeneous Wacker catalysts. Some of these heterogeneous processes involves the presence of a supported liquid-phase.

2.1. *Homogeneous ethylene oxidation: the Wacker process*

The Wacker reaction was first discovered based on the work of Smidt et al. [8,35], who recognized that ethylene could be converted to acetaldehyde using a $PdCl_2$–$CuCl_2$ catalyst in acetic acid solution. The catalytic cycle occurs according to reactions 1–3 below [35]:

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow C_2H_4O + 2HCl$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$$2CuCl + \frac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

The oxidation of ethylene occurs in the presence of $PdCl_2$; this reaction reduces the palladium to metal. The metal is easily oxidized via reaction with $CuCl_2$, and the cycle is completed by reoxidation of the CuCl by oxygen. At pressures of 100–150 psig and temperatures between 100–110°C, this process yields approximately 95–99% selectivities based on ethylene.

2.2. *Heterogeneous catalyzed ethylene oxidation*

Several Wacker-type heterogeneous catalyst systems have been investigated in the literature [9,10,36]. One of the general problems encountered in the process is the catalyst stability [9]. The activity of the heterogeneous catalysts generally starts very high, but decreases over time due to reduction of Pd. The strategy for designing a successful solid catalyst that could conduct the Wacker chemistry is to combine Pd with a solid component which has the capability to support the redox cycle (i.e. Pd(0)—->Pd(2^+)) with great efficiency. One of the most effective of these type of catalysts to date is the Pd–V_2O_5 catalyst, typically supported on alumina [10,11]. Catalysts such as Pd–Ru–V_2O_5 and Pd–Ti–V_2O_5 have also been effective [9]. In these systems, the V_2O_5 assumes the role of reoxidizing the Pd(0).

These catalysts have slightly less comparable to activities and selectivities as the analogous homogeneous reaction. Their stability is typically good as well. Minor deactivation can be observed over the course of a 120 h laboratory run, however, the catalysts can be reactivated in the presence of oxygen [9].

Some researchers believe that the mechanism of the gas phase process is similar to that of the liquid-phase process, primarily due to the fact that selectivities and rates of olefin oxidations for both are comparable. For example, ethylene oxidation is faster than propylene oxidation to a similar proportion for both processes. Moreover, both oxidize propylene proportionally to acetone. Because there are so many significant similarities between the homogeneous and the heterogeneous cases, it was hypothesized that the active center for the latter catalyst is Pd^{2+}. A schematic representation of the proposed mechanism is reproduced in Fig. 2 below [9].

The results of the Pd–V_2O_5 and Pd–Ru–V_2O_5 catalysts do provide hope for viable alternatives to the homogeneous processes. However, a remaining problem is how to fully utilize the metal surface to achieve the maximum catalyst efficiency; additionally, the question of how these catalyst stabilities are affected by more practical reaction conditions, remain. These challenges could potentially be answered through the design of an appropriate supported liquid-phase catalyst.

2.3. *Supported liquid-phase catalysis for ethylene oxidation*

Smidt et al. [8] briefly mentioned the process where a palladium/copper solution deposited on porous support particles could catalyze the Wacker reaction. The first workers to thoroughly investigate this heterogeneous catalyst system were Komirama and Inoue [12].

In this process, the pore walls of porous alumina is coated with a thin film of a hydrochloric acid solution of $PdCl_2$ and $CuCl_2$. It is not mentioned in this work how selective this process is towards acetaldehyde

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow C_2H_4O + 2HCl \qquad (1)$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl \qquad (2)$$

$$2CuCl + \frac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O \qquad (3)$$

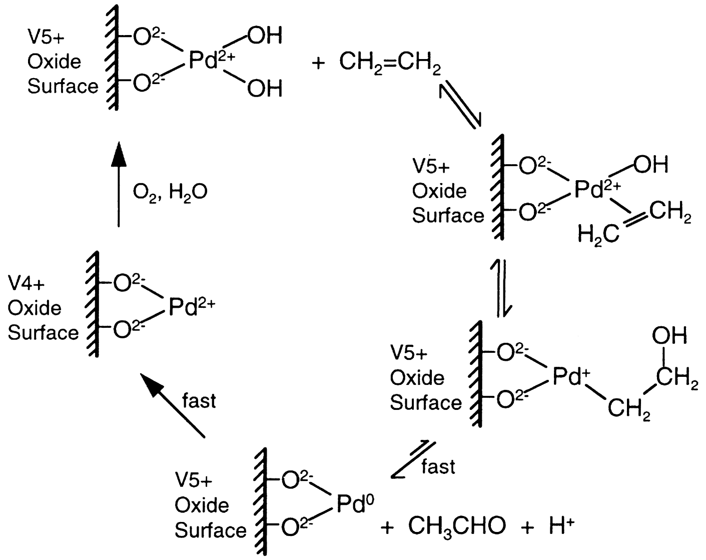


Fig. 2. Proposed mechanism for gas-phase Wacker oxidation of ethylene on a Pd/V_2O_5 catalyst [9].

production or how the activity compares to the liquid-phase reaction. Regardless, this process suffers from serious constraints. The solvent that solubilizes the liquid-phase, evaporates during the reaction. To circumvent this, the ethylene–oxygen reagent mixture can be bubbled through a water saturator to compensate for the loss of the solvent due to evaporation. Unfortunately, the presence of additional water can cause pore filling which subsequently results in activity loss due to the gas–liquid diffusion barriers [13].

A more promising approach has been the development of a SLP catalyst that incorporates a molten-salt as the solvent for the supported liquid-phase. Molten salts are excellent candidates for this use because they form mixtures over wide temperature ranges, and they also are capable of solubilizing materials such as water, metals and oxides. Rao and Datta applied this concept to selective ethylene oxidation [13]. $PdCl_2$/$CuCl_2$ was deposited as a thin film (30–70 Å thick) on the walls of the porous silica support. The molten salt used in this example was a KCl/CuCl mixture. The authors report that such a catalyst is active and selective towards acetaldehyde production under mild conditions. It is at least seven times as stable as the SLP catalysts whose liquid layers contain an aqueous solvent. Additionally, the molten salt catalyst loses virtually no activity over a 140 h laboratory run in contrast to the Pd–V_2O_5 catalysts.

One advantage of the SLP process over the homogeneous case is the more efficient utilization of the active centers due to the fact that the liquid is present in a very thin layer. The gaseous reactants will have better access to the solvated metals due to the shorter diffusion path; moreover, the reaction velocity can be optimized by using an optimal liquid loading on the catalyst [13].

This area of supported liquid-phase catalysis provides a desirable alternative to the liquid phase-process in ethylene oxidation to acetaldehyde. However, a great deal of process work needs to be conducted to determine the viability for industrial application. Obtaining catalyst lifetime data and discovering the optimal process conditions will be an important measure to take towards this end.

3. Vinyl acetate production

The oldest of the vinyl acetate processes involves the gas-phase acetoxylation of acetylene [14]. This process, practiced in only a few locations today, is based upon vapor phase reaction on a supported zinc acetate catalyst, usually on carbon. The reaction generally gives high yields ranging from 92–98% based on acetylene. Although the acetylene process for vinyl acetate production gave excellent yields, the expense and scarcity of acetylene made the process unattractive, and in the early 1960's, many processes involving ethylene evolved.

Information on both homogeneous and heterogeneous catalyzed ethylene acetoxylation reactions have appeared in the literature. The homogeneous process is based upon Wacker chemistry [15]. Unlike acetaldehyde production, however, the most widely used process for vinyl acetate production today is the gas-phase reaction. Although this reaction occurs over an heterogeneous catalyst, there has been much support that the reaction actually contains a mixture of both homogeneous and heterogeneous catalysis. Below, we will discuss the advantages and disadvantages of the individual reactions and mechanisms and will compare them to the possible presence of the supported liquid phase mechanism.

3.1. Homogeneous route to vinyl acetate monomer

The homogeneous acetoxylation of ethylene is analogous to the Wacker process for acetaldehyde production mentioned above. This reaction was first studied by Moiseev and coworkers [15]. The process uses a catalyst composed of a Pd^{2+} salt, generally palladium chloride, and a copper salt, all of which is dissolved in an acetic acid solvent. This catalytic reaction system yields very little vinyl acetate; and when a substantial amount of water is present, produces mostly acetaldehyde. However, when alkali metal salts are added, the yield to vinyl acetate production is dramatically improved [16].

The mechanism of this reaction has received considerable attention in the literature. The compilation of the mechanism is shown below. The reaction involves the coordination of ethylene by palladium; the Pd can be present as either palladous chloride or acetate. The coordination activates the ethylene to nucleophilic attack by the acetate forming a acetoxypalladium complex. This complex undergoes beta elimination of the hydrogen to generate vinyl acetate and a hydridpalladium complex. Evolution of HCl or acetic acid generates palladium(0), which is readily oxidized back to Pd^{2+} by cupric chloride [17].

$$
\begin{aligned}
&\mathrm{C_2H_4 + PdX_2 + HX \longrightarrow [C_2H_4PdX_3]^- + H^+}\\
&\mathrm{[C_2H_4PdX_3]^- + AcOH \longrightarrow [C_2H_4PdX_2(OAc)]^- + HX}\\
&\mathrm{[C_2H_4PdX_2(OAc)]^- \longrightarrow [C_2H_4PdX(OAc)] + X^-}\\
&\mathrm{[C_2H_4PdX(OAc)] \longrightarrow CH_2CH - OAc + Pd + HX}\\
&\mathrm{X = ClorOAc}
\end{aligned}
$$

The homogeneous process for vinyl acetate poses the same engineering challenges as for the acetaldehyde process. These problems are attributed to the rise of the vapor phase heterogeneous process, which is still most widely used in industry today.

3.2. Heterogenous route to vinyl acetate monomer

The vapor phase process for vinyl acetate monomer production involves the acetoxylation of gas-phase ethylene over a palladium based catalyst usually supported on either silica or alumina. Pd/Au alloy is known to enhance the reaction. Alkali metals salts are added to promote the reaction as well. The debate about the active centers of the catalysts have centered on palladium being present as Pd(0) or Pd(2^+). Mosieev et al. [18] argues that Pd(0) centers make up the active sites, which is formed from the direct involvement of acetate ions. Their evidence suggests that zero valent palladium metal catalyzed vinyl acetate reaction is highly selective and makes no acetaldehydes.

Others have argued more convincingly, that the active centers come in the form of some type of palladium acetate. Some evidence suggests that the reaction takes place with a Pd(1^+)-OAc intermediate [19–21]. This species supposedly forms as a result of acetic acid adsorption on the surface. In contrast, Augustine and Blitz [22] have observed the presence of a $Pd(OAc)_2$ acetate on the surface of Pd crystallites.

In general, the mechanism can be thought of as the scheme outlined below [20]: ethylene is dissociatively adsorbed onto the palladium surface; oxygen is adsorbed on palladium; acetic acid is adsorbed on the catalyst where the adsorbed oxygen then abstracts a hydrogen from the adsorbed acid; the combination of the adsorbed ethylene and acetic acid results in vinyl acetate which ultimately desorbs.

$$\begin{gathered}
C_2H_4 + 2Pd \Leftrightarrow CH_2 - CH - Pd + PdH \\
O_2 + 2Pd \Leftrightarrow 2Pd - O \\
CH_3COOH + Pd \Leftrightarrow Pd - CH_3COOH_{ad.} \\
Pd - CH_3COOH_{ad.} + PdO \Leftrightarrow Pd - OCOCH_3 + Pd - OH \\
Pd - OCOCH_3 + CH_2CH - Pd \\
\Leftrightarrow Pd - CH_2CHOCOCH_{3ad.} + Pd \\
Pd - CH_2CHOCOCH_{3ad.} \Leftrightarrow Pd + CH_2CHOCOCH_3 \\
Pd - OH + PdH \Leftrightarrow Pd - H_2O_{ad.} \Leftrightarrow Pd + H_2O
\end{gathered}$$

It is probable that the gas–solid type mechanism involving adsorbed species on the catalyst surface catalyzes the vinyl acetate reaction. However, there is strong evidence as well that a liquid-phase type mechanism is also occurring under reaction conditions, and thus, supported liquid phase catalysis is thought to be a very important factor in the vinyl acetate reaction.

3.3. Supported liquid-phase route to vinyl acetate monomer

As pointed out, the heterogeneous vinyl acetate process typically occurs on a Pd/Au catalyst supported on a porous support such as silica or alumina. Under typical plant operating conditions, the absorption of acetic acid and water to the support can be substantial. [24,25]. Crathorne et al. [23] claims that this absorbed acetic acid exists in a liquid layer that is about 3 monolayers in thickness up to temperatures comparable to industrial conditions on a silica catalyst. Table 1 shows the amount of acetic acid retained on the surface of a silica catalyst containing various components.

Table 1
Influence of catalyst components on acetic acid adsorption at 400°C – catalyst base is silica [23]

Loading (wt%)			CH_3COOH adsorbed
Pd	Cd	K	(μmol g^{-1})
—	—	—	422
2.4	—	—	600
—	1.9	—	385
—	—	1.9	801
—	1.9	1.9	733
2.4	1.9	1.9	948

The study shows that the presence of palladium and alkali metal acetate (KOAc in particular) enhances the adsorption of acetic acid. This acid retention feature was thought to be very important in the overall scheme of reaction.

KOAc plays two very critical roles in enhancing the vinyl acetate reaction. Firstly, the presence of KOAc is essential to establish the supported liquid phase. KOAc is known to form a dimer species with acetic acid [26]:

$$KOAc + AcOH \Leftrightarrow KH(OAc)_2$$

And thus, one role of the KOAc is to immobilize the acetic acid molecules, which increases the reaction rate for vinyl acetate production and suppresses direct ethylene combustion [25,27]. This salt has a melting point of 148°C and is believed to be present in molten condition under normal operating conditions. This molten layer is considered foundational for the establishment of the supported liquid phase. In turn, the potassium acetate also helps to establish the active phase of the catalyst.

The second enhancing role of KOAc involves the solvation of the palladium complexes formed during reaction. For example, KOAc is known to form complexes with palladium acetate [25]:

$$\begin{gathered}
Pd(OAc)_2 + KOAc \Leftrightarrow KPd(OAc)_3 \\
KPd(OAc)_3 + KOAc \Leftrightarrow K_2Pd(OAc)_4
\end{gathered}$$

The two complexes, $KPd(OAc)_3$ and $K_2Pd(OAc)_4$, can potentially dissolve in the $KH(OAc)_2$ solution to form the active centers of the catalyst. These complexes can either pyrolyze to form acetic acid or react with ethylene to produce vinyl acetate. Both actions will reduce the palladium back to metal. Based on all of these factors, the mechanism for supported liquid phase catalysis can be considered as an heterogeneous analogue of the Wacker reaction [23,28]:

$$\begin{gathered}
Pd + \frac{1}{2}O_2 + 2AcOH \Leftrightarrow Pd(OAc)_2 + H_2O \\
Pd(OAc)_2 + AcO^- \Leftrightarrow Pd(OAc)_3^- \\
Pd(OAc)_3^- + C_2H_4 \Leftrightarrow VAM + AcOH + AcO^- + Pd
\end{gathered}$$

In the above scenario, Pd is readily oxidized to palladium acetate in the presence of oxygen and acetic acid. The presence of KOAc then establishes an equilibrium with the palladium acetate which dissolves in the KOAc/AcOH melt that is present. The subsequent complex is then reduced by gaseous ethylene, forming vinyl acetate, acetic acid, acetate ion and palladium metal.

The likelihood that a similar mechanism to the above one is very good. The fact that capillary condensation of acetic acid occurs on silica has been established [23], however, the effect is expected to be much less for alumina [24]. Nevertheless, the resulting arguments about the dissolution of KOAc, the complexes formed and reaction mechanism are very plausible. Because the catalyst has features (such as KOAC) that promote the occurrence of the liquid layer, it is reasonable to conclude that the liquid-phase is important in the reaction. This does not completely discount the presence of truly heterogeneous mechanisms, involving solid Pd(0), Pd(1^+) and Pd(2^+) complexes. On the contrary, it is probable that all three species exist and contribute to the reactions.

The presence of this liquid layer is undoubtedly influenced by conditions such as temperature, pressure and acetic acid concentration. Because much of the literature has studied many different conditions, most of which are not completely applicable to the practical plant conditions, it is difficult to establish the amount of each phase that is present. Nevertheless, the foregoing arguments suggest opportunity for the presence of solvated complexes is quite high.

The compilation of the role of the supported liquid-phase catalyst for vinyl acetate production is shown in Fig. 3 [27]. The mixture of the acetic acid, KOAc and water melt comprises the liquid film. The molten salt melt is believed to provide a protective coating on the surface of the catalyst which impedes ethylene combustion. The resulting isolated palladium sites are then available for preferential adsorption of ethylene and oxygen that leads to vinyl acetate formation rather than to CO_2. Some form of palladium acetate is present and can be dissolved in the liquid layer. The vinyl acetate is believed to be formed on these small clusters of palladium acetate or on palladium acetate dense surfaces [27].

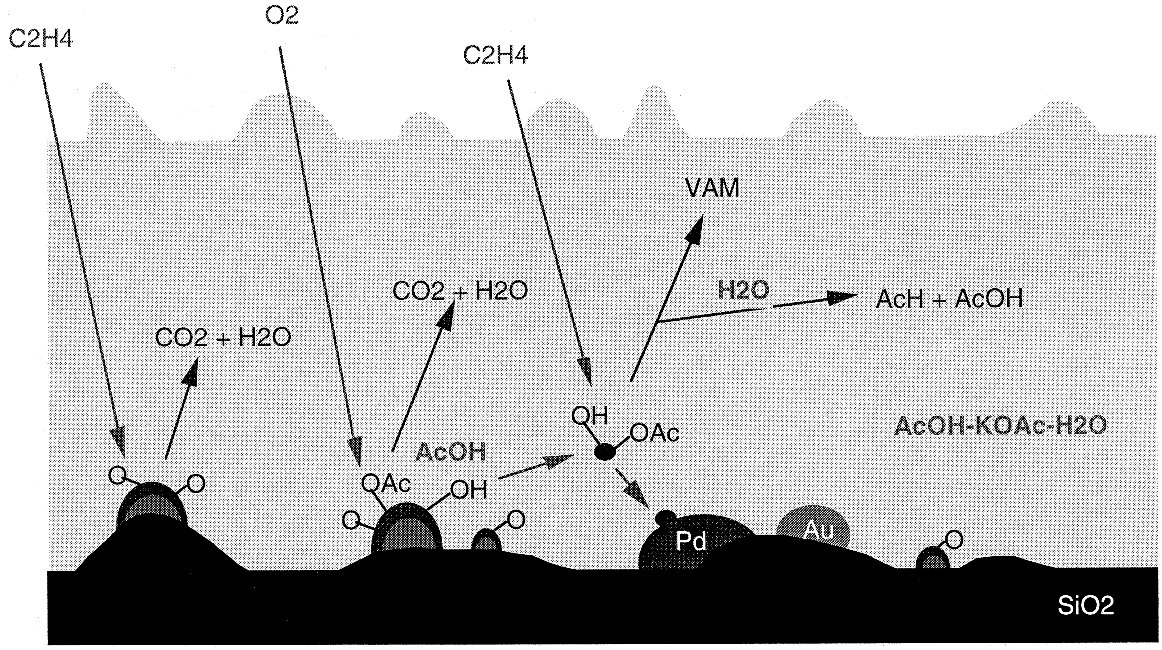


Fig. 3. Role of Pd–Au–KOAc–SiO_2 catalyst for ethylene acetoxylation to vinyl acetate [27].

Other viewpoints on the role of these complexes have been expressed. It has been argued that solvated Pd(II) complexes are responsible for the agglomeration of Pd particles and consequently deactivation [24,25,29,30]. Thus, the formation of these Pd(II) species would not be desirable because they become mobilized in the SLP, which ultimately leads to Pd particle growth. On the other hand, it has been argued that a certain amount of agglomeration of the metal is needed to obtain high rates [24]. These high rates would only be attainable when large crystallites, which protrude through the liquid film, are able to be accessed by the gaseous reactants.

Although much has been learned about the supported liquid-phase in vinyl acetate catalysis, there are remaining questions whose answers could lead to even further understanding. Pinpointing the actual active phase or phases present during the reaction and their respective mechanisms is needed. The determination of the solubility of the active complex(s) in the liquid films should also be made. Since much of the work thus far has been conducted under various conditions, the basis for comparison of how the active phases changes with reaction conditions is not established. More comprehensive studies to determine how the different phases change with reaction conditions such as temperature, pressures and species concentrations is needed. This information could provide the critical information researchers need to successfully design more active and selective vinyl acetate synthesis catalysts.

4. Extensions of supported liquid-phase catalysis for oxidation

A number of other selective oxidation reactions have been reported which have involved supported liquid-phases. Many of them have revolved around the use of molten salts as the liquid films. The oxidation of naphthalene in the presence of *p*-xylene to form phthalic anhydride is one example [31]. This system employs a $K_2S_2O_7$–V_2O_5 molten salt supported on silica.

Although it is not considered as a selective process, the oxidation of sulfur dioxide to sulfur trioxide is thought to take place with a catalyst containing a molten salt mixture on a support [32]. The catalysts for this system are usually vanadium pentoxide promoted by potassium salts supported on silica. Under typical reaction conditions (>420°C), a potassium pyrosulfate melt forms which helps to distribute the vanadium oxides in the pores of the support. There also has been evidence that the molten salt layer actually serves as a catalyst for this reaction [33].

More recent application of supported liquid films in selective oxidation has been in the gas-phase oxidation of benzene to phenol [34]. In this system, Pd and $Cu_3(PO_4)$ are impregnated by a H_2PO_4 solution onto silica. The evidence suggests that the phosphoric acid forms a liquid film on the surface which helps to increase catalyst activity over catalysts prepared with more volatile solvents. As a result of the liquid film, the copper ions will become mobile within the liquid film which enhances the opportunity of contact with immobilized Pd sites, thereby increasing activity.

5. Conclusions

It has been shown in this article that the application of supported liquid-phase catalysis to selective oxidation examples can provide valuable alternatives to the purely homogeneous or heterogeneous processes. The literature has reflected the growing interest in studying this area. However, in order for the mechanistic and kinetic understanding to be made, more in-depth studies on catalyst structure and phase compositions, in addition to the effects of process variables on the systems must be made. The answers to these challenging questions will provide invaluable information concerning the design of the most selective and active catalyst systems for selective oxidation as possible.

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