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Wacker oxidation catalysis in a supported aqueous phase

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Adsorption of palladium (II) and copper (II) salts onto the controlled pore glass CPG-240, in the presence of water, yields a supported aqueous phase Wacker oxidation catalyst. Conversions of 1-heptene to 2-heptanone of up to 24% under batch conditions are observed. The activity and selectivity of the catalysts are sensitive to water content, oxygen pressure and temperature.

Keywords: Wacker oxidation catalysis; supported aqueous phase; (SAP) catalysis

1. Introduction

The partial oxidation of olefins can be accomplished by a variety of methods [1]. Those reactions that use molecular oxygen as the oxidant are attractive due to the ready availability of oxygen and the absence of unwanted reduction by-products formed in the reaction. The Wacker reaction, eqs. (1)–(4), is probably the best known example of a partial olefin oxidations that uses molecular oxygen as the oxidant. As discovered by J. Smidt in the late fifties, the reaction consists of the palladium/copper catalyzed oxidation of an olefin to a ketone or aldehyde in an aqueous solvent [2]. Although molecular oxygen is the oxidant it is the oxygen of water which is incorporated into the product [3] (see reactions (1)–(4) below). The catalysis is homogeneous and thus is most appropriate for low molecular weight olefins that have appreciable water solubility. Cosolvents are typically added for the Wacker oxidation of higher olefins which are sparingly soluble in water [4].

The separation of catalyst and products is difficult for the Wacker oxidation of higher olefins; high temperatures are needed to distill the products from the catalyst. It is for this reason that an effective heterogeneous catalyst for the

Wacker oxidation of liquid olefins is desirable [5].

(1) $Pd^{2+}(CH_2=CHR) + H_2O \rightarrow Pd^0 + CH_3C(O)R + 2H^+$

(2) $2Cu^{2+} + Pd^0 \rightarrow Pd^{2+} + 2Cu^+$

(3) $2Cu^+ + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O$

(4)(net) $CH_2=CHR + \frac{1}{2}O_2 \rightarrow CH_3C(O)R.$

We have recently reported a new class of heterogeneous catalysts which are appropiate for liquid hydrocarbon substrates [6]. In Supported Aqueous Phase (SAP) catalysis the catalyst is associated with a supported water layer which is immiscible with the organic product and reactant phase. A water soluble transition metal complex serves as the catalyst; the complex resides in an aqueous layer immobilized in the pores of a high-surface-area hydrophilic solid. This arrangement is superior to a simple two-phase reaction in that the support provides the necessary interfacial area required for the reaction to proceed at a reasonable rate. Importantly, since the catalysis proceeds at the interface between an organic phase containing reactants and products, and an aqueous phase containing the catalytic species, SAP catalysis is usable with high molecular weight hydrocarbons which are water insoluble. Rhodium based SAP catalysts display good activity for the hydroformylation of a variety of olefins [6–8].

Water content has a dramatic effect on the catalytic activity of the SAP rhodium hydroformylation catalysts [6]. Specifically, at very low water content the catalysts show very little hydroformylation activity and at high water content the catalysts are inactive. Maximum activity was observed in the range 5 to 10 wt% water [6]. It was postulated that water in the catalytic phase is necessary to increase the mobility and thus the catalytic activity of the water soluble complex. At high water contents the water may fill the pores and thus decreases the interfacial area between the catalytic and substrate phases; under these conditions little activity would be expected.

The fact that water is involved in the catalytic cycle of Wacker oxidation catalysis, vide supra, lead us to develop SAP Catalysts for this reaction. Here we report on the preparation and use of SAP Wacker oxidation catalysts. The influence of several reaction parameters on the activity and selectivity of the SAP Wacker catalysts have been investigated.

2. Experimental

The controlled pore glass, CPG-240, was obtained from Electronucleonics and used as received as the support for all the supported aqueous phase catalysts prepared here. Palladium chloride (AESAR), copper chloride dihydrate (Baker), solvents and olefin were purchased in the highest purity available and used as received. Deionized water was used for the catalyst preparation.

CATALYST PREPARATION

Pd : Cu = 1 : 1 (molar); 10% by weight salt loading: 0.50 g $PdCl_2$ and 10.0 g CPG-240 were stirred in 40 ml ethanol for 2 hours at room temperature. The solvent was then removed at room temperature by rotary evaporation. A solution of 0.48 g of $CuCl_2.2H_2O$ in 20 ml water was then added to the flask containing the $PdCl_2$-impregnated CPG-240. The slurry was stirred for 30 min at room temperature at which time the water was removed at room temperature under vacuum. The catalyst was obtained as a free-flowing brown powder and stored at room temperature under a static nitrogen atmosphere. The water content was determined by thermogravimetric analysis to be 15 weight percent; in a typical reaction with 0.5 g catalyst and 15 mL total reaction volume this corresponds to a water content in the reaction of 0.5 volume percent (vide infra).

OXIDATION REACTION CONDITIONS

All oxidations were performed in a 25 mL Parr mini reactor fitted with an automatic stirrer, liquid sampling valves, and a thermostated furnace. The stirring speed was kept constant at 400 rpm for all the runs. After first loading the SAP catalyst and hexane solvent to the reactor water was added to the system by one of two procedures: (i) the water was simply added neat by syringe; and (ii) the water was supplied by first impregnating the desired amount of water onto 1.2 times its weight of CPG-240 followed by the addition of the water saturated CPG to the Parr reactor. These procedures were developed for the preparation of SAP rhodium catalysts as described previously [7].

ANALYTICAL METHODS

Thermogravimetric analyses were performed in air on a DuPont 951 thermogravimetric analyzer. Gas chromatography (GC) analyses of products were performed on a HP5890 series II equipped with a 25 m long SP capillary column.

3. Results

The only oxidation product of 1-heptene observed with the SAP Wacker catalysts prepared here was 2-heptanone. Thus the oxidation activity of the catalysts is defined as the conversion to 2-heptanone. In addition to partial oxidation significant isomerization to 2-heptene and 3-heptene is observed with the SAP catalysts. The internal olefins are not oxidized under the reaction

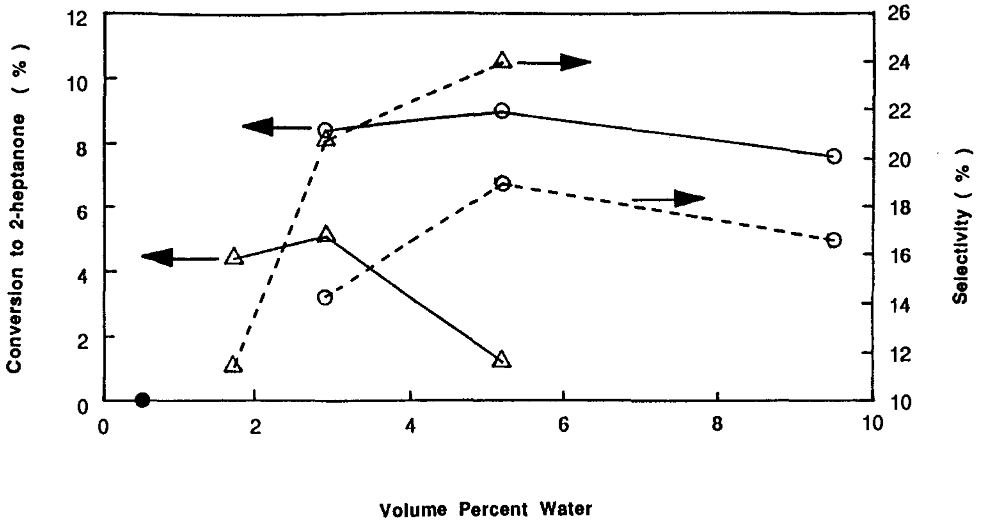

Fig. 1. Influence of water content on reaction selectivity and conversion to 2-heptanone. The solid lines show conversion to 2-heptanone and the corresponding dashed lines show reaction selectivity as defined in the text. Two methods of water addition are represented in the plot; method I with △ and method II with ○. The solid dot represents the data point for the catalyst to which no water was added. Reaction conditions: 30% 1-heptene in hexene, $T = 100\,^{\circ}\mathrm{C}$, $P = 60$ psig O_2, $t = 3$ h, 1-heptene/Pd = 210.

conditions employed due to their lower reactivity. The selectivity of the reaction is defined as:

$$\frac{\text{moles 2-heptanone}}{\text{moles 1-heptene converted}}.$$

The influence of water on the reaction is shown in fig. 1. Data for both methods of introducing water, as described in the experimental section are shown. The volume percent water is defined as:

$$\frac{\text{volume water}}{\text{total liquid volume}} \times 100.$$

For catalysts in which water was added by method II some residual water surely remains within the added CPG after the reaction system comes to equilibrium. This water is included in calculating the total volume percent water even though it is not directly involved in defining the reactivity of the system. In all cases the activity of the catalyst was higher when water was added via water saturated CPG-240, i.e. procedure II.

There is a marked decrease in the conversion to 2-heptanone at water contents greater than 3 volume percent when procedure I is used. By contrast, when procedure II is used, the conversion to 2-heptanone is weakly dependent on the amount of added water for additions larger than 3 volume percent water.

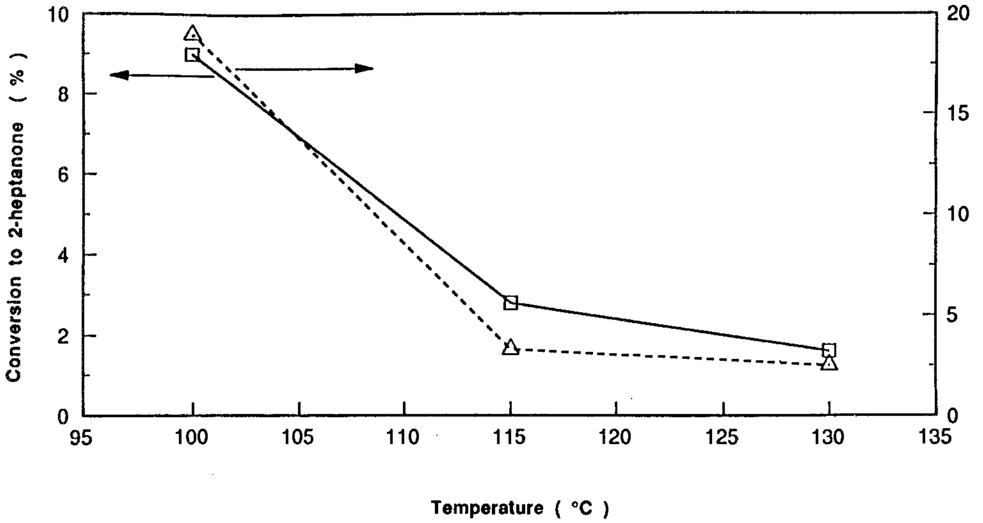

Fig. 2. Oxidation of 1-heptene as a function of reaction temperature: □——□, conversion of 1-heptene to 2-heptanone; △- - - -△, selectivity of the oxidation reaction. Water addition to 5.2 volume % was made by method II (see text). Reaction conditions: 30% 1-heptene in hexene, $P = 60$ psig O_2, $t = 3$ h, 1-heptene/Pd = 210.

The maximum activity is observed at approximately 5 volume percent water. The selectivity of the reaction also peaks at about the same amount of added water when using procedure II. The selectivity observed for procedure I increases as the activity drops for water contents larger than 3 volume percent.

Additional reactions were carried out in which 1-heptene was added after the catalyst and solvent were saturated with oxygen at the reaction temperature. This pretreatment of the catalyst resulted in slightly improved conversion to 2-heptanone but dramatically lower selectivity. The results were similar for the whole range of water content investigated. Thus this procedure was discontinued for the subsequent experiments. In all other reactions water was added following procedure II.

The influence of the reaction temperature on the activity and selectivity of the reaction is shown in fig. 2. Both activity and selectivity decrease with increasing temperature. At higher temperatures the reaction is dominated by isomerization which results in a greater overall conversion of 1-heptene but a much lower reaction selectivity.

In fig. 3 the results obtained from the variation of oxygen partial pressure are shown. Activity and selectivity both increase with an increasing oxygen partial pressure.

The influence of catalyst loading and the relative Cu/Pd concentration on the activity and selectivity of the reaction is shown in table 1. The selectivity increases slightly with an increase in both loading (compare entrees 18 and 17) and the Cu/Pd ratio (compare 15 versus 17 and 18). There is a slight increase in

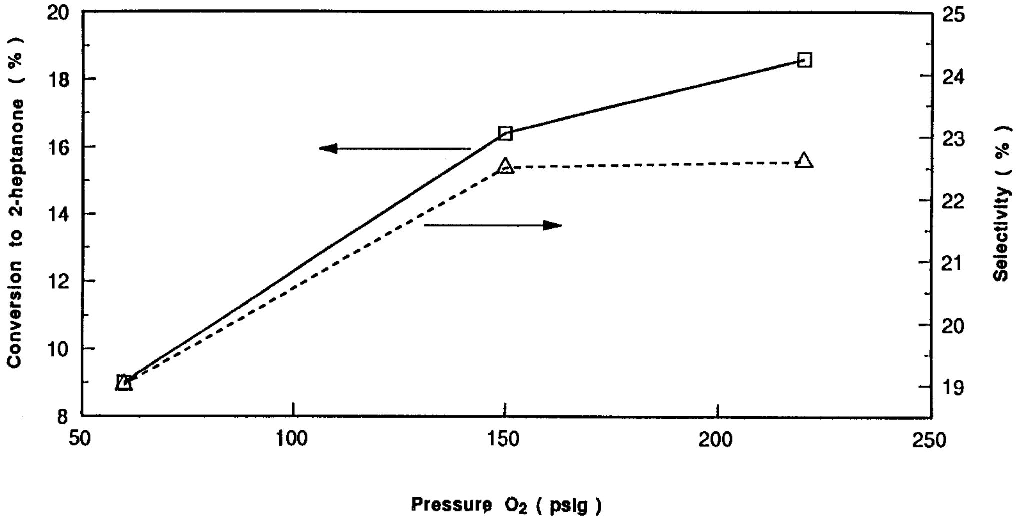

Fig. 3. Oxidation of 1-heptene as a function of oxygen partial pressure: □——□, conversion of 1-heptene to 2-heptanone; △----△, selectivity of the oxidation reaction. Water addition to 5.2 volume % was made by method II (see text). Reaction conditions: 30% 1-heptene in hexene, $T = 100\,^{\circ}\mathrm{C}$, $t = 3$ h, 1-heptene/Pd = 210.

selectivity and a nearly linear increase in conversion to 2-heptanone as both [Pd] and [Cu] are doubled.

Experiments were performed in order to determine the amount of Pd and Cu that leached into the filtrate. Analysis for Pd and Cu was done in the following manner: the contents of the reactor were filtered at 100 °C through a stainless steel HPLC sintered filter. The liquid was analyzed for Cu or Pd by atomic absorption spectroscopy and in all cases no metals were found. The sensitivity of the analysis was 1 ppm for Cu and 2 ppm for Pd.

4. Discussion

Large quantities of water are required to activate the glass supported palladium and copper salts for Wacker oxidations of 1-heptene. By comparison

Table 1
Oxidation of 1-heptene as a function of palladium and copper concentration [a]

Run	Relative metal concentration		Salts (%)	Conversion to 2-heptanone (%)	Selectivity (%)
	[Pd]	[Cu]			
18	1	2	10	11	26
15	1.5	1.5	10	16	23
17	2	4	20	24	29

[a] Reaction conditions: 30% 1-heptene in hexane, 5.2% water, 100 °C, 150 psig O_2, 3 h.

maximum catalytic activity for SAP rhodium hydroformylation catalysts was observed at 8 wt% water on the catalyst under reaction conditions where the volume percent was less than 0.5%. At a similar water content for the Wacker SAP catalysts virtually no activity for either oxidation or isomerization is observed. Furthermore at water levels that resulted in hydroformylation catalysts of little activity significant conversion is observed in the Wacker SAP catalysts. These apparently conflicting results are rationalized from the affinity of the respective catalysts for water under ambient conditions. The SAP rhodium catalysts contain sulfonated triphenylphosphine and are hygroscopic at room temperature (the dried catalysts were observed to adsorb water from the atmosphere). Conversely, the SAP Wacker catalysts lose water in air at room temperature. It is postulated then, that more water needs to be present in the SAP Wacker system to sufficiently hydrate the supported palladium and copper salts to activate the catalysts. However the pores must remain open to allow the reaction to proceed. Thus the water must partition between the gas, liquid, and CPG and not fill the pores.

As it was noted before [7a] the addition of water, to activate rhodium SAP catalysts, method II is superior to method I. We suggest that in method I, droplets of water collide with SAP catalyst particles, soaking them and disturbing the even distribution of the Pd and Cu salts on the support. In this sense then, some of the catalyst particles may be damaged upon coming in to contact with water droplets resulting in lower catalyst activity. In contrast, method II provides for a controlled release of the water from the wet support into the SAP catalysts.

Olefin isomerization increases dramatically as a function of temperature with the SAP Wacker catalysts. Under homogeneous reaction conditions isomerization is generally not as pronounced a problem in Wacker catalysis. Also homogeneous Wacker catalysts generally do not show a dependence on oxygen partial pressure as is observed in the SAP catalysts investigated here. The oxygen dependency suggests that reoxidation of the palladium via the $Cu^{2+}/Cu^{+}/O_2$ couple may be slow in the heterogeneous case. Interestingly, a hydroquinone containing polymer supported Wacker catalyst showed a similar oxygen dependence on activity and selectivity [5]. The rate of copper reoxidation, and thus palladium reoxidation as well, could also be influenced by oxygen diffusion in the heterogeneous catalysts; diffusion limitations are common in heterogeneous systems. If the reoxidation of palladium metal to palladium(II) is slow then it is possible that palladium metal is partially responsible for olefin isomerization. Palladium(II) salts themselves can show isomerization activity [9]. As the copper/palladium ratio is increased it should increase the efficiency of the reoxidation of the palladium and thus increase reaction selectivity. From Table 1 however it is seen that as the molar ratio of Cu/Pd is increased there is only a slight increase in reaction selectivity.

Importantly conversion to 2-heptanone is directly proportional to the total palladium concentration. This suggests that more palladium sites become available for Wacker oxidation as the palladium concentration increases.

An advantage of the SAP Wacker oxidation catalysts is that the Cu^{2+} is confined to the glass support. Aqueous Cu^{2+} is very corrosive to steel; by supporting the copper-palladium redox couple on the glass the reaction can be done in an all metal reactor with significantly reduced corrosion.

Acknowledgements

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