Localized Basification of Catalytic Surfaces enhances the Selective Oxidation of L-Sorbose over Supported Pt Catalysts modified with Tertiary Amines

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Modification of supported Pt catalysts with strongly adsorbing tertiary amines is shown to be an efficient method to increase the reaction rate in the direct oxidation of L-sorbose to 2-keto-L-gulonic acid with molecular oxygen, and to increase the selectivity of the base-sensitive reaction.

The industrial production of vitamin C is based on the multistep synthesis developed by Reichstein and Gruessner[1] in 1934. The process includes the stoichiometric oxidation of 2,3;4,6-di-O-isopropylidene-α-L-sorbose to the corresponding carboxylic acid. An alternative method is the aqueous-phase oxidation with molecular oxygen, catalyzed by platinum metals.[2–4] Heyns[5] was the first to suggest direct oxidation of unprotected L-sorbose to 2-keto-L-gulonic acid (2-KLG) in a neutral aqueous solution, as shown in Scheme 1. However, the performance of supported Pt and Pd is poor: high catalyst : reactant mass ratio and long reaction times are necessary to obtain full conversion and selectivity is also only moderate.[5,6] We have attempted recently to overcome catalyst deactivation by promoting supported Pt and Pd catalysts with Pb and Bi.[6] The main role of Pb and Bi promotion is a geometric (blocking) effect which decreases the size of the active Pt or Pd ensembles. Upon promotion, the initial rate and selectivity increased but the overall performance of the catalysts was still poor due to oxidation and dissolution of promoters under the reaction conditions employed.

An alternative approach to increase the oxidation rate is the use of alkaline solutions. Bases have a complex effect on the reactivity of L-sorbose and on the adsorption strength of the acidic product 2-KLG. The considerable rate enhancement at higher pH is accompanied by a drop in selectivity, as shown in Fig. 1 (the average reaction rate and the selectivity to 2-KLG
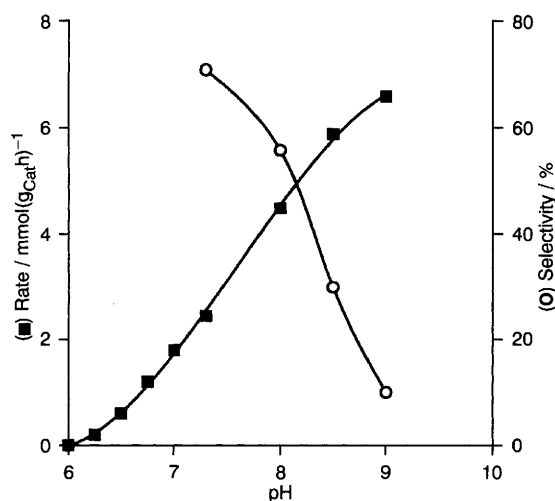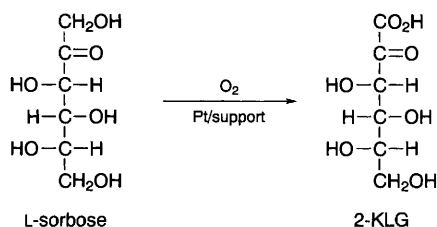
being determined at 30% conversion). An important factor in the low selectivity is the poor stability of 2-KLG in alkaline solutions even in the absence of a catalyst, as illustrated in Fig. 2. The addition of a Pt metal catalyst further accelerates product decomposition.

Here we report the application of tertiary amines as modifiers, which adsorb strongly on Pt and can also enhance the rate of the surface oxidation reaction. The nitrogen base modifier can interact with L-sorbose or one of the reaction intermediates on the Pt surface without increasing the pH of the bulk liquid, which would lead to product decomposition.

The catalysts were prepared by *in situ* modification of a 5 mass% Pt/Al₂O₃ (Engelhard, No. 7004; Pt-dispersion = 0.30, determined by transmission electron microscopy) or 5 mass% Pt/C (Engelhard, Escat 21, dispersion = 0.25 determined by hydrogen chemisorption). The catalyst (0.6 g) was suspended in water (40 ml) at ambient temperature; after reduction with hydrogen for 30 min, a nitrogen atmosphere was introduced and the modifier (dissolved in 2 ml water) added and the suspension allowed to stir for at least 90 min. The molar ratio of modifier to surface Pt atoms (Pt$_S$) was varied between 0.05 and 0.33 : 1. L-Sorbose (2.2 g) was added after catalyst modification, and the pH adjusted to 7.3 and controlled during the reaction by automatic titration with 0.4 mol dm⁻³ Na₂CO₃. (Catalyst composition and pretreatment conditions, reaction temperature and pH were optimized for the unmodified reaction in a previous study.[6]) The slurry was heated to 50 °C and the oxidation reaction initiated by replacing the nitrogen flow with oxygen. The product composition was determined by HPLC analysis.[6]

The influence of the pK_a value of the modifier on the catalytic performance of the 5 mass% Pt/Al₂O₃ system is illustrated in Table 1. Using pyridine (3, pK_a = 5.25[7]) as modifier, the average reaction rate and the selectivity to 2-KLG was
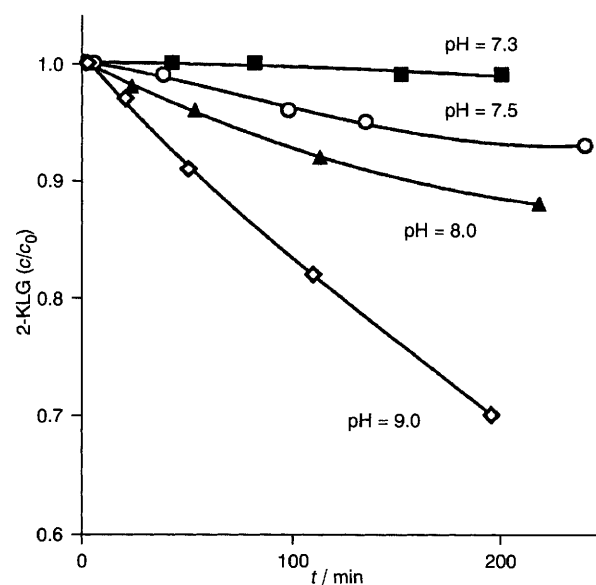
Scheme 1

L-sorbose → 2-KLG (O₂, Pt/support)

Fig. 1 Influence of pH on the average reaction rate and selectivity in the direct oxidation of L-sorbose to 2-KLG; (5 mass% Pt/Al₂O₃, standard conditions)

Fig. 2 Influence of pH on the non-catalytic decomposition of 2-KLG in oxygen at 55 °C; (c_0 = 50 g⁻¹ l, aqueous solution)

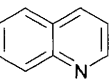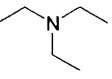practically the same as that obtained with unmodified Pt/Al₂O₃ under otherwise identical conditions.Trialkyl- and triaryl- amines of higher basicity, such as triethylamine 4, tributylamine and triphenylamine led to considerable rate enhancement accompanied with only a moderate decrease of selectivity to 2-KLG. For comparison, unmodified Pt/Al₂O₃ afforded similar reaction rates at a bulk pH of 9, but the selectivity was about six times lower at 30% conversion (Fig. 1).

Weakly basic aromatic amines, like pyrazine 1 or quinoline 2 decrease the reaction rate without any influence on the selectivity. They behave as strongly adsorbed, inert species which cover a fraction of active sites. Interestingly, the influence of amines on the oxidation rate is determined by the basicity of the nitrogen atom, and the chemical structure of the modifier is only of secondary importance.

On the contrary, structural alterations in the nitrogen-base modifier have a strong influence on the selectivity of the oxidation reaction. The characteristic feature of the direct oxidation of L-sorbose to 2-KLG over Pt/Al₂O₃ is a good initial selectivity (93% at 10% conversion), which decreases at higher conversions due to various side and consecutive reactions. No positive effect on selectivity was observed with trialbylamines throughout the whole conversion range, compared to the unmodified reaction. Modification by heteroaromatic com- pounds such as pyridine, quinoline, acridine or pyrazine provided a 5 to 10% increase in the initial selectivity, but the advantage of the modified catalysts disappeared above 20% conversion.

A further enhancement in selectivity to 2-KLG was achieved using saturated cyclic amines as modifiers. Hexa- methylenetetramine (5, pka = 8.87,⁸ Table 1) proved to be the most efficient studied. After optimizing the modifier: catalyst

ratio, selectivities as high as 98 and 81% were obtained at 20 and 30% conversions, respectively. When the reaction parame- ters were optimized using various supported Pt and Pd catalysts and 5 as modifier, a Pt/C catalyst proved to be the best. It provided 95 and 81% selectivities at 30 and 50% conversions, respectively.

As concerns the nature of base catalysis in the L-sorbose → 2-KLG transformation, it is most likely that the oxidation of the aldehyde intermediate is accelerated *via* a rapid hydration to the corresponding geminal glycol.⁹ The formation of a carboxyl group from the glycol intermediate is an oxidative dehydroge- nation step, which is usually much faster on platinum metals than the direct oxygen insertion to the carbonyl group of the aldehyde.³,⁴ The negligible hydration of some carbonyl com- pounds is in accordance with the high selectivity observed in the Pt-catalysed oxidation of secondary alcohols to ketones and aromatic alcohols to aldehydes in aqueous alkaline medium.

It seems that the outstanding promoting effect of 5 is due to its unique structure. The other tested aromatic and cyclo- aliphatic nitrogen compounds (*e.g.* quinoline) can adsorb horizontally on a flat Pt surface, with the nitrogen atom laying on a Pt atom. In contrast, when 5 is adsorbed on a flat Pt surface, at least one of the four nitrogen atoms cannot directly interact with the metal surface. It is not fully understood yet what is the role of the special structure of 5 in the interaction with the partially oxidized intermediate and in the favoured oxidation at C-1. Preliminary electrochemical model studies on polycrystal- line Pt show that under the reaction conditions employed 5 is partially adsorbed on the Pt surface, but does not take part in the surface oxidation process. Accordingly, 5 can only act as a localized base on the Pt surface.

In summary, the reaction rate and selectivity in the oxidation of L-sorbose with oxygen (a base-sensitive reaction) can be enhanced by modification of supported Pt catalysts with tertiary nitrogen bases and working in a neutral solution. The highest selectivity to 2-keto-L-gulonic acid was obtained using hexa- methylenetetramine in a very low modifier: reactant molar ratio of 1 : 1700.

The present study demonstrates that modifying the surface of metal catalysts with adsorbed nitrogen bases provides a local tuning of the base strength at the site where the reaction occurs, without influencing significantly the pH of the reaction solution. This concept may also be used beneficially in other heterogeneously catalysed reactions.

Table 1 Activity and selectivity of supported 5 mass% Pt catalysts modified with tertiary amines under standard conditions (cat : sorbose = 0.27 : 1, T = 50 °C, pH = 7.3, n = 1100 rpm, 1 bar O_2)

Catalyst	Modifier (Md)		Md/Pt₅ mol atom⁻¹	pK_a	S^a(%)	Rate^b/ mmol(g_{cat}h)⁻¹
Pt/Al₂O₃	—		—	—	71	2.64
Pt/Al₂O₃		1	0.2	0.65	73	1.53
Pt/Al₂O₃		2	0.2	4.9	71	1.69
Pt/Al₂O₃		3	0.2	5.25	72	2.54
Pt/Al₂O₃		4	0.2	11	58	6.64
Pt/Al₂O₃		5	0.1	8.87	81	1.23
Pt/C	—		—	—	51	10.0
Pt/C	5		0.1	8.87	95	4.56

^{a} Selectivity at 30% conversion (defined as [2-KLG produced]/[sorbose converted] × 100). ^{b} Average rate between 0 and 30% conversion.

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