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One-step heterogeneously catalytic oxidation of *o*-cresol by oxygen to salicylaldehyde

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Salicylaldehyde (selectivity = 57.3% at a conversion = 73.8%) was prepared for the first time by the oxidation of *o*-cresol in a single step using impregnated CuCo/C catalysts.

Salicylaldehyde is an important intermediate in the production of perfumes, drugs, dyes, plastics, photographic, agricultural and electroplating chemicals. Traditionally, salicylaldehyde was mainly obtained from Reimer–Tiemann reaction.[1] Generally, the yield of salicylaldehyde by this method is lower than 40%. Furthermore, an excess amount of chloroform over phenol is necessary. The recovery and recycling of unreacted chloroform and phenol are difficult to realize. There is one industrial process starting with phenol and formaldehyde to form salicyl alcohol, which is then homogeneously catalytically oxidised to give salicylaldehyde.[2,3] This method employs an excess amount of formaldehyde, heavy pollution should be inevitable. Salicylaldehyde can also be produced by side-chain chlorination of *o*-cresol and saponification of the resulting dichloromethyl group to form the aldehyde group.[4] The drawbacks of this process are the employment of a large amount of chlorine and the generation of poisonous effluents. In addition, the product that contains the chlorinated impurities does not meet food and drug grade specifications. The oxidation of *p*-cresol to *p*-hydroxybenzaldehyde using cobaltous compounds in the presence of a large amount of NaOH has also been reported.[5,6] The oxidation of *o*-cresol is very difficult. The selective oxidation of *p*-cresol to *p*-hydroxybenzaldehyde could not be applied in *o*-cresol.[7]

Herein we disclose a first report on the heterogeneously catalytic direct oxidation of *o*-cresol by oxygen to salicylaldehyde over copper and cobalt bimetallic oxides supported on activated carbon. This route is a green process. The catalyst is easily recovered. The main by-products are oxygenated hydrocarbon compounds, which are less poisonous and environmentally friendly.

The catalysts were prepared using a commercial activated carbon support (specific surface area 1100 $m^2\ g^{-1}$). This support was impregnated with an aqueous solution of mixed metal nitrates, using the incipient wetness method. After impregnation, the samples were first dried at 393 K and then calcined at 673 K in a vacuum quartz tube to afford the oxides.

The catalytic oxidation reactions were carried out in an autoclave of 600 ml capacity equipped with a magnetic-type stirrer (Parr Instrument. USA). In a typical experiment, *o*-cresol (15.0 g), methanol (120 ml), pyridine (1.5 ml) and catalyst (1.0 g) were added and the mixture was stirred at a constant speed of 600 rpm. Oxygen was pulse-charged under a pressure of 0.6 MPa into the reactor. The reaction was terminated by charging the cool water through the cooling coil inside. Product samples were collected using a liquid sampling valve and analyzed by liquid chromatography (HPLC, Shimadzu liquid chromatograph, Model LC-9A, equipped with Chrompak C18 15 cm column, UV 254 nm). Authenticated standard samples were used for the identity of the products. The total conversion and product distribution were evaluated with calibration curves which were obtained by injecting known amount of authenticated standard.

The main by-products detected in the reaction were salicylic acid and salicyl alcohol. The change of product distribution with time is depicted in Fig. 1. In this figure, the selectivity for salicyl alcohol is very high initially. It decreases rapidly with the reaction time. The appearance of salicyl alcohol suggests that aldehyde is a secondary product and produced by a consecutive reaction from the alcohol. The data on the conversion of *o*-cresol and selectivities for salicylaldehyde, salicylic acid and salicyl alcohol in the oxidation of *o*-cresol over different catalysts are illustrated in Fig. 2. It is found that copper oxide is in favour of alcohol product formation and cobalt oxide is beneficial for deep oxidation, especially for the formation of acid. The alcohol intermediate seems to be oxidised immediately after its formation, so no salicyl alcohol can be found using Co/C as a catalyst. The reason lies in the difference of the oxygen donation ability between copper and cobalt. Mixing the

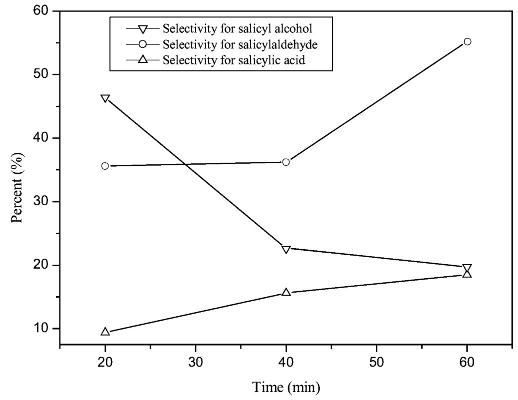

Fig. 1 Influence of reaction time on catalytic performance. Reaction conditions: *o*-cresol = 15.0 g, catalyst CuCo/C (Cu:Co = 0.6 : 1, mol ratio) = 1.0 g, solvent = 120 ml, pyridine = 1.5 ml, temperature = 363 K, pressure = 0.6 MPa.

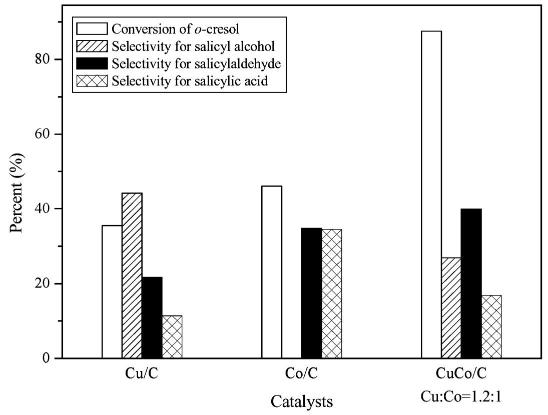

Fig. 2 Catalyst performance over different catalysts. Reaction conditions: *o*-cresol = 15.0 g, catalyst = 1.0 g, solvent = 120 ml, pyridine = 1.5 ml, temperature = 363 K, time = 90 min, pressure = 0.6 MPa.

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Table 1 Catalytic oxidation of *o*-cresol[a]

Catalysts	Cu : Co (mol ratio)	Conversion (mol %)	Product distribution (mol %)				Salicylaldehyde/ Salicylic acid
			Salicylaldehyde	Salicylic acid	Salicyl alcohol	Others	
CuCo/C	0.3 : 1	52.1	47.1	24.3	11.7	16.8	1.9
CuCo/C	0.6 : 1	65.5	46.5	29.6	8.0	15.9	1.6
CuCo/C	1.2 : 1	73.8	57.3	21.8	7.5	13.4	2.6
CuCo/C	2.4 : 1	74.6	49.9	26.2	9.3	14.6	1.9

[a] *Reaction conditions: o*-cresol = 15.0 g, catalyst = 1.0 g, solvent (methanol) = 120 ml, pyridine = 1.5 ml, reaction time = 50 min, reaction temperaure = 353 K, reaction pressure = 0.6 MPa.

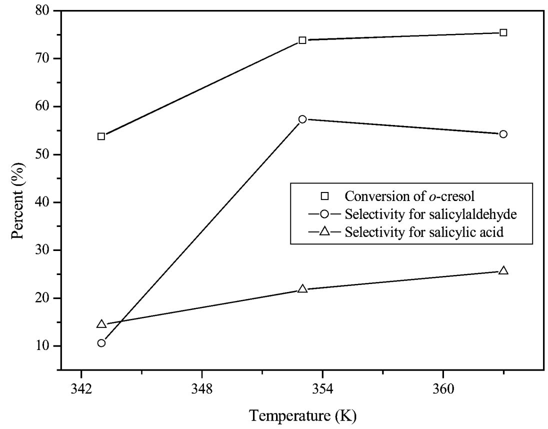

Fig. 3 Influence of temperature on catalytic performance. Reaction conditions: catalysts CuCo/C (Cu:Co = 1.2 : 1, mol ratio) = 1.0 g, *o*-cresol = 15.0 g, solvent = 120 ml, pyridine = 1.5 ml, time = 50 min, pressure = 0.6 MPa.

copper and cobalt oxides forms a bimetallic oxide catalyst. With this catalyst, the product selectivity lies somewhat between the single Cu and Co catalysts. It is worth noting that the mixed bimetallic catalyst exhibits much higher activity than either of the single oxide catalyst. In other words a synergetic effect occurs which, in turn, suggests the formation of new active catalytic species on the surface.

The influence of the Cu/Co ratio on catalytic activity in the oxidation of *o*-cresol was studied (Table 1). The conversion of *o*-cresol increases with the increase of the Cu/Co ratio and slows down after the ratio of Cu/Co reaches 1.2 : 1, which indicates that a saturation of the concentration of the active sites is reached. The selectivity for salicylaldehyde passes a maximum at a ratio of 1.2 : 1. An excess amount of copper results in a decrease of selectivity for salicylaldehyde from the maximum of 57.3%.

It is considered that the nucleophilic lattice oxygen (O^{2-}) is responsible for the selective oxidation and electrophilic oxygen species (O_2^-, O^-) lead to deep oxidation.[8,9] The Co^{2+}, Co^{3+} and O^{2-} ions form a dynamic circle which acts as a convertor for oxygen species from the dissolved molecular oxygen into the lattice oxygen. The reduced active centres are reoxidised by the adsorbed molecular oxygen to generate new active centres. The possible reaction mechanism for the initial steps of oxidation is considered as follows: the physical adsorption of the side methyl of *o*-cresol on the active centre, the formation of the C–O bond and the dissociation of the C–H bond. If one C–O bond is formed, the product is alcohol, and if one C–H bond in the adsorbed benzyl species is activated and dissociates, another C–O bond will be formed and aldehyde is produced. The attack of electrophilic oxygen species (O_2^-, O^-) on the C=O double bond makes it difficult for the adsorbed aldehyde to escape from the catalyst surface, which results in the formation of an acid product and decreases the selectivity for salicylaldehyde. In the catalytic oxidation, copper plays a bifunctional factor: the hindrance of the electrophilic species (O_2^-, O^-) and facilitating the formation of nucleophilic O^{2-} species.

The dependence of the reaction temperature on the conversion and selectivity were investigated in the temperature range between 343 and 363 K using the CuCo/C (Cu : Co = 1.2 : 1, mol ratio) catalyst (Fig. 3). It can be seen that the conversion of *o*-cresol and selectivity for salicylic acid increase with increasing reaction temperature. The selectivity for salicylaldehyde is found to pass through a maximum at 353 K. A further increase in temperature causes a decrease in the selectivity due to the further oxidation of salicylaldehyde to salicylic acid at higher temperatures. This postulate is well supported by the fact that the total selectivities for salicylaldehyde and salicylic acid at 353 and 363 K are nearly the same.

Pyridine is an essential additive in the catalytic oxidation of *o*-cresol. In the absence of pyridine the reaction results in an excessive formation of tar and acid. It is postulated that pyridine is adsorbed on the catalytic active centre which, in turn, inhibits the further oxidation of the aldehyde product to form by-products. In the selective oxidation of alcohol employing palladium-supported hydrotalcite as a catalyst, Uemura *et al.*[10] also found that pyridine was an important additive for their reaction.

In summary, this is a first report on the direct preparation of salicylaldehyde from *o*-cresol by the heterogeneously catalytic method. The route is economy and environmentally friendly, so it has a potential industrial application on a large scale as an alternative to stoichiometric processes. This research realized 57.3% selectivity for salicylaldehyde at 73.8% conversion of *o*-cresol.

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