

# Single Step Selective Oxidation of *para*-Chlorotoluene to *para*-Chlorobenzaldehyde over Vanadium Silicate Molecular Sieves

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Selective formation of *para*-chlorobenzaldehyde (>65%) in a single step from *para*-chlorotoluene is reported for the first time using H<sub>2</sub>O<sub>2</sub> as an oxidant and vanadium silicate molecular sieves as the catalyst.

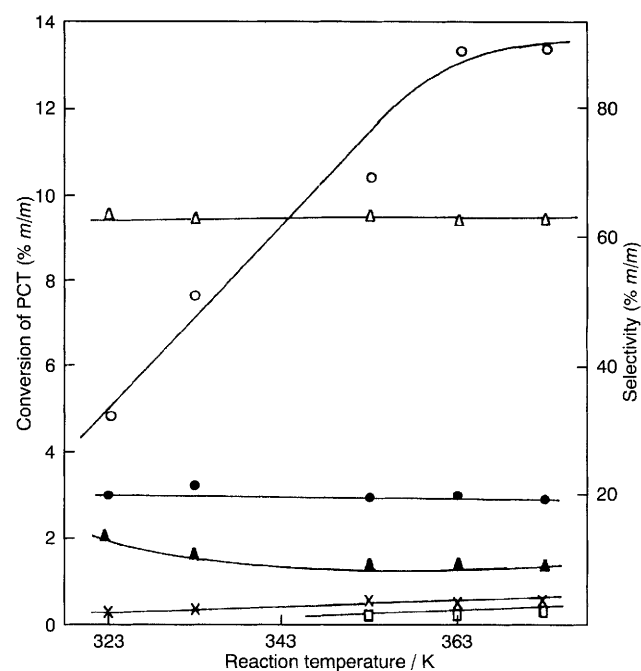
*para*-Chlorobenzaldehyde (*p*-CIBZD) is an important intermediate in the production of dyes, optical brighteners, agricultural chemicals and pharmaceuticals.<sup>1</sup> *p*-CIBZD is produced mainly by chlorination of *para*-chlorotoluene (PCT) to form *para*-chlorobenzal chloride which is then subjected to acid hydrolysis.<sup>1,2</sup> It is also produced by the hydrogenation of 4-chlorobenzonitrile in the presence of an acid and a nickel catalyst.<sup>3</sup> Apart from these catalysts, acetates of Co<sup>II</sup>, Mn<sup>II</sup> and Cu<sup>II</sup> have also been described for the oxidation of chlorotoluenes to the corresponding aldehydes and acids by molecular oxygen in acetic acid media.<sup>4–6</sup> However, with these catalysts there are a number of problems, such as the formation of *para*-chlorobenzoic acid, catalyst removal from the product and requirement of a stoichiometric amount of the catalyst. Recently, novel microporous vanadium silicate molecular sieves with MFI (VS-1) and MEL (VS-2) structures have been found to catalyse the transformation of the primary carbon atom of unactivated alkanes and activated arenes to the corresponding alcohols and aldehydes with aqueous H<sub>2</sub>O<sub>2</sub>.<sup>7</sup> However, the potential of these catalysts in the oxidation of the primary carbon atom of the deactivated chloroaromatics has not yet been exploited. Here we disclose the first report on the selective formation of *p*-CIBZD from PCT and aqueous H<sub>2</sub>O<sub>2</sub> in one step using vanadium silicate molecular sieves.

VS-1, VS-2, silicalite-1 and silicalite-2 were prepared as described in the literature.<sup>7–9</sup> These materials were found by powder X-ray diffraction to be highly crystalline. In addition, the presence of vanadium in the framework of MFI (Mobil five or ZSM-5) and MEL (Mobil eleven or ZSM-11) structures were confirmed by IR, ESR and <sup>51</sup>V MAS NMR spectroscopy. The V-silicalite-1 and V-silicalite-2 (vanadium impregnated silicalite-1 and silicalite-2) samples were prepared by impregnating silicalite-1 (silica polymorph of MFI) and silicalite-2 (silica polymorph of MEL) with VOSO<sub>4</sub> solution by maintaining the concentration of vanadium similar to VS-1 and VS-2. All the catalysts were characterized for their surface area, crystal size and adsorption properties. The properties of the catalysts are given in Table 1.

The reactions were carried out in a stirred autoclave (Parr instrument, USA) in the temperature range 323–373 K under autogenous pressure. In a typical experiment hydrogen peroxide (30%, 5.3 g) was added to a solution of PCT (2 g) and acetonitrile (25 ml). The catalyst (0.2 g) was then added and the mixture was stirred for 12 h at the required temperature. Product samples were analysed using a gas chromatograph (Blue star, India Model 421) equipped with a flame ionization detector and a capillary column (50 m × 0.2 mm i.d.) coated with methyl silicon gum. Reference substances and GC-MS (Shimadzu

GC-MS-QP-2000 a) were used for the identification of the products.

The results of the PCT oxidation over VS-1, VS-2, V-silicalite-1 and V-silicalite-2 are summarized in Table 1. The catalysts are compared under similar reaction conditions. The main products of the reaction are *para*-chlorobenzylalcohol (*p*-CIBZA), *para*-chlorobenzaldehyde (*p*-CIBZD) and 3-methyl-6-chlorophenol (3M-6ClPh). Small amounts of 2-methyl-5-chlorophenol (2M-5ClPh) and other products (hydroxy chlorobenzyl alcohols and hydroxy chlorobenzaldehydes) were also detected. Among the catalysts tested, VS-1 exhibited the higher catalytic activity; however, the selectivity for *p*-CIBZD over VS-1 and VS-2 was found to be comparable. Silicalite-1 was almost inactive under the reaction conditions and a blank run (no catalyst) also failed to give any product. Even V-silicalite-1 and V-silicalite-2 catalysts were found to be



**Fig. 1** Conversion of PCT (○) and the selectivities for *p*-CIBZA (●), *p*-CIBZD (△), 3M-6ClPh (▲), 2M-5ClPh (×) and others (□) as a function of the reaction temperature. Reaction conditions: catalysts (VS-1) = 0.2 g, PCT = 2 g, solvent (acetonitrile) = 25 ml, H<sub>2</sub>O<sub>2</sub>:PCT (mol ratio) = 3, reaction time = 12 h.

**Table 1** Oxidation of *para*-chlorotoluene<sup>a</sup>

Catalyst	Si : V (mol ratio)	Surface area/ m <sup>2</sup> g <sup>-1</sup>	Turnover number <sup>b</sup> (TON)	Crystal size/μm	Product distribution (% m/m)					<i>p</i> -CIBZD : <i>p</i> -CIBZA
					<i>p</i> -CIBZA	<i>p</i> -CIBZD	3M-6ClPh	2M-5ClPh	Others	
VS-1	118	475	75.8	0.2	20.7	63.6	9.7	3.4	2.6	3.1
VS-2	125	432	41.6	1.5	21.0	65.6	8.2	2.1	3.1	3.1
V-Si-1 <sup>c</sup>	118	n.d. <sup>d</sup>	9.8	n.d. <sup>d</sup>	23.1	53.0	13.7	—	10.2	2.3
V-Si-2 <sup>c</sup>	125	n.d. <sup>d</sup>	12.3	n.d. <sup>d</sup>	22.5	57.0	7.5	—	13.0	2.5

<sup>a</sup> Reaction conditions: catalyst = 0.2 g, PCT = 2 g, reaction temperature = 373 K, solvent, (acetonitrile) = 25 ml, H<sub>2</sub>O<sub>2</sub>:PCT (mol ratio) = 3, reaction time = 12 h. <sup>b</sup> Moles of PCT converted per mole of vanadium. <sup>c</sup> V-impregnated silicalite-1 and silicalite-2. <sup>d</sup> n.d. = not determined.

ineffective for the enhancement of PCT oxidation. The higher catalytic activities of VS-1 and VS-2 are believed to be because of those vanadium ions which are incorporated in the framework positions of VS-1 and VS-2 during hydrothermal synthesis. The oxidation turnover of PCT under identical conditions over VS-1, VS-2, V-silicalite-1 and V-silicalite-2 were found to be 75.8, 41.6, 9.8 and 12.3, respectively. The corresponding selectivities for *p*-CIBZD were 63.6, 65.6, 53.0 and 57.0, respectively. Earlier studies show that oxyfunctionalization of primary carbon atoms of unactivated alkanes appears to be a characteristic feature of vanadium silicates.<sup>7</sup> It is believed that the reaction proceeds by a Fenton-type radical mechanism where side chain (benzylic oxidation) and ring oxidation of PCT take place together.<sup>7</sup>

Fig. 1 illustrates the conversion of PCT and the selectivities for the products as a function of the reaction temperature using VS-1 as the catalyst. It is found that the reaction temperature is one of the most important factors affecting catalytic activity; however, selectivity for the products remained unaffected. The conversion of PCT was increased from 4.9 to 13.4% (*m/m*) when the reaction temperature was raised from 323 to 363 K, whereas an increase in the PCT conversion was not observed beyond 363 K, probably owing to a greater decomposition of H<sub>2</sub>O<sub>2</sub> at higher temperature (373 K).

In addition, the ratio of *p*-CIBZD:*p*-CIBZA (aldehyde:alcohol) increases with the reaction time which suggests that the aldehyde is a secondary product and produced by a consecutive reaction from the alcohol.<sup>7</sup>

In the oxidation of larger molecules like *ortho*-chlorotoluene (OCT) and *meta*-chlorotoluene (MCT), VS-1 gave less than 2% conversion which may be attributed to the surface reaction owing to its smaller pore diameter than both OCT and MCT.

In summary, novel vanadium silicate molecular sieves (VS-1 and VS-2) appear to be efficient catalysts for the one step synthesis of *para*-chlorobenzaldehyde. A higher yield of *p*-CIBZD was obtained by raising the reaction temperature.

We thank P. Ratnasamy for helpful discussion and encouragement. T. S. thanks U. G. C., New Delhi for financial support.

Received, 12th December 1994; Com. 4/07555B

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