Effects of alkaline additives on conversion of 2,4,5-trichlorophenol over Pd-Rh/C catalysts

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Effects of alkaline additives on conversion of 2,4,5-trichlorophenol (TCP) over Pd-Rh/C catalysts were studied at 80°C and 1 Atm. The catalysts were prepared by incipient wetness impregnation of carbon support and characterized by BET surface area, temperature programmed reduction (TPR) and X-ray diffraction (XRD) methods. The dechlorination of TCP occurs mainly via two pathways: hydrodechlorination and hydrolysis. The dechlorination of TCP can be accelerated significantly by alkalis. The addition of alkali had increasing effect on the initial reaction rate, conversion and crystallite size of Pd. The initial TCP dechlorination activity without alkali was found to be in the following order: 0.97%Pd/C>0.8%Pd/0.19%Rh/C>0.98%Rh/C. The selectivities of mono and di-chlorophenol were also improved with Pd/C catalyst.

Keywords: Hydrodechlorination, 2,4,5-Trichlorophenol, Pd/Rh/C catalyst, Alkaline additives

Chlorophenol (CP) compounds are the subjects of many studies due to their environmental significance as persistent and potentially hazardous substances[1]. The majority of CPs is formed during the natural chlorination of organic material, biodegradation of plant protecting chemicals or disinfections of drinking water[2-4]. Chlorophenols such as 2,4,5-trichlorophenol are used as fungicides, as wood preservers and as plant growth regulators.

Currently several efforts are directed to destroy unwanted stocks and to depollute soils, ground and wastewaters in which these compounds are accumulated. Among the most common methods for the destruction of these chloroarenes are incineration, pyrolysis, hydroysis, chemical and biochemical degradation[5,6]. In addition, attempts are also being made to destroy chlorophenols with catalytic hydrogenation processes.

As a viable alternative, catalytic hydrodechlorination (HDC) is a promising process whereby the chlorinated waste can be converted into products of commercial value[7]. It is simple, safe, effective, and it ensures, in many instances, the regeneration of the initial raw material[8]. In liquid-phase HDC, the addition of a base that serves as a proton scavenger can help to maintain the palladium metal active[9-11]. Catalyst support and additives have

been found to play important role by reducing the detrimental effects of hydrogen chloride released as the reaction proceeds[12,13]. Also the aim of selecting active carbon as the support is the high activity of Pd supported on carbonaceous carriers, in part, to the hydrogen spillover onto various amorphous and structured carbon[14].

This work focuses on the carbon supported palladium catalysts with alkali additives (Li_2CO_3, K_2CO_3 and NaOH) to improve the catalytic activity of the solids in the liquid-phase HDC of 2,4,5-trichlorophenol (TCP). In addition, the influence of Rh metal, on the catalytic performance is also studied with an aim to steer the selectivity towards the intended mono and di-chlorinated compounds.

Experimental Procedure

Materials

The TCP (2,4,5-trichlorophenol) (>99%) was purchased from Across Organics. Stock solution of TCP was prepared using deionized water (18 MΩ). High purity 10.3% H_2 in N_2 mixture was used in the catalytic hydrodechlorination experiments. A commercial active carbon (CECA-France) with 65 μm mean particle diameter was used without further treatment. K_2CO_3, Li_2CO_3 and NaOH were purchased from Merck.

Catalyst preparation

Various catalysts *viz*. Pd/C, Rh/C and Pd/Rh/C were prepared by incipient wetness impregnation of carbon support. Catalysts were prepared by dissolving $PdCl_2$ and $Rh(NO_3)_3$ in HNO_3 acid solution. Pd and Rh loading of the catalyst was adjusted by changing Pd and Rh concentration in the impregnation solution. After impregnation, the resulting pastes were dried at 110°C for 12 h. Then, samples were further heated at 400°C for 2 h. The metal loadings were determined using Thermo Elemental X Series ICP-MS.

Catalyst characterization

BET surface areas were measured with Quantachrome Monosorb 17S apparatus using single point BET method. X-ray powder diffraction patterns of samples were obtained on a Rigaku D/Max ultima+ diffractometer using CuKα (λ = 1.5405) radiation. Samples were scanned from 15 to 50 (in 2Θ) at a rate of 0.04°/min. Metal crystallite sizes were calculated from the broadening of Pd(111) and Rh(111) peaks using Scherrer equation, $t = C\lambda /Bcos\Theta$, where λ is the x-ray wavelength (A°), B is the full width at half maximum, Θ is Bragg angle, C is a factor depending on crystallite shape (taken to be one), and t is the crystallite size (A°).

Catalytic activity experiments

Liquid-phase hydrodechlorination of TCP was carried out in a three-necked glass reactor at a stirring speed of 250 rpm. The reaction vessel (100 mL) was placed in a temperature-controlled heating oil bath. A proportional and integral controller with a precision of ±1°C was used to control the reaction temperature. The reactor was equipped with a hydrogen mixture supply, thermocouple port, reflux condenser and side sampling port. 10.3% H_2/N_2 mixture at a constant volumetric flow rate (250 mL min^{-1}) was sparged via a sintered glass from the bottom of the reactor and this also helped to better stir the reaction mixture. All the reactions were conducted with initial concentration of 0.084 M of TCP at 1 Atm of pressure. Catalyst (0.2 g) was mixed in 80 mL of reaction solvent mixture. A methanol-water mixture (50/50) was used as reaction solvent.

The effect of alkalis over 0.97% Pd/C catalyst in methanol-water (50/50) mixture on HDC of TCP was also studied. 0.5 grams of alkali (K_2CO_3, Li_2CO_3, NaOH) are added into reaction mixture of 80 mL. After adding alkali, the reaction mixture was stirred for an hour to ensure the complete dissolution.

In all the experiments, the reaction mixture was flushed with nitrogen flow (500 mL min^{-1}) before catalytic activity tests. All experiments were carried out at 80°C. After the temperature leveled out at the reaction temperature, reaction medium was sparged with 10.1% hydrogen/nitrogen gas mixture, and then reaction time was registered. As the reaction progressed, an aliquot of sample was withdrawn from sampling port by a 100 μL syringe. After dilution, samples were filtered and the concentration of reaction products was followed by HPLC (Spectra system UV6000LP) using a C_{18} column as stationary phase and a mixture of methanol and water (70:30, *v/v*) as mobile phase. The entire reaction products were also identified in a HP 5973a GC-MS with the help of NIST library.

Results and Discussion

Catalyst characterization

All catalysts had the BET surface area of 950 ± 15 m^2/g. The surface area of the catalysts did not vary significantly, indicating that the observed changes in activity were due to the metal catalysts. The actual metal loadings and average crystallite sizes determined from X-ray diffractograms are listed in Table 1. The catalysts are labeled according to their actual metal content, e.g. 0.97%Pd/C. A representative XRD diffraction pattern of 0.97%Pd/C is shown in Fig. 1. In XRD patterns of 0.97%Pd/C and 0.98%Rh/C, the peaks were rather weak and broad. Rh_2O_3 and metallic Rh were detected on fresh 0.98%Rh/C catalyst. On fresh 0.97%Pd/C catalyst, strong Pd and weak PdO phases were identified but,
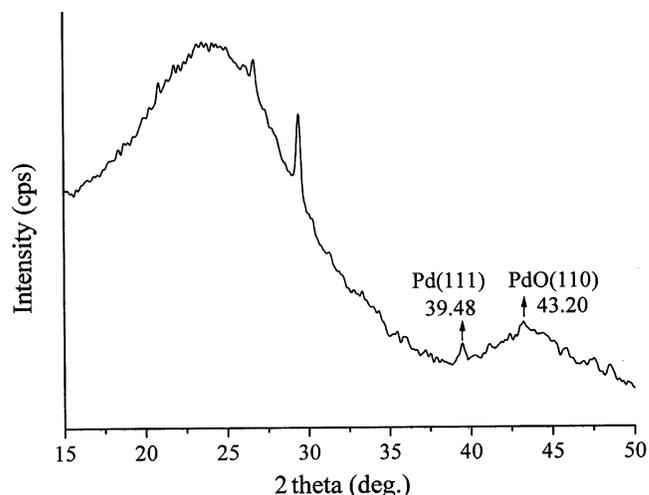

Fig. 1—XRD pattern of 0.97%Pd/C catalyst

Table 1—Pd and Rh contents, metal crystallite sizes, catalytic HDC initial activity of TCP and time for 6 h conversion (X_{6h}) over Pd/Rh/C catalysts

Actual metal loading % (w/w)	Alkali additives	TCP consumption rate (mmol.$g_{cat}^{-1}min^1$)	Turnover frequencies (min^{-1})	X_{6h}	Metal crystallite size determined from XRD (nm)
0.97%Pd/C	Li_2CO_3	7.44	0.40	0.32	
0.97%Pd/C	NaOH	13.2	2.08	0.78	Pd (111)- 40.6
0.97%Pd/C	K_2CO_3	14.5	2.65	0.84	
0.97%Pd/C	-------	5.28	0.23	0.69	
0.80%Pd/0.19%Rh/C	-------	4.18	0.17	0.66	Pd (111)- 19.3 Rh (111) *ND
0.98%Rh/C	-------	3.51	0.13	0.39	Rh (111)- 35.3

*ND: Not detected

on 0.8%Pd/0.19%Rh/C catalyst, only Pd(111) metallic phase at $2\theta = 40.03°$ corresponding to cubic symmetry was detected.

From XRD patterns it is observed that the addition of Rh to Pd shifted the position of Pd metallic phase and changed the available phases in 0.8%Pd/0.19%Rh/C catalyst. In X-ray diffractogram of 0.8%Pd/0.19%Rh/C catalyst, 2θ signal of Pd shifted to higher values from Pd (111) 39.49 to Pd (111) 40.03. Similar shifts were reported over different supports, such as, in Pd/Fe-SiO$_2$ and Pd/Fe-TiO$_2$. The 2θ values of metallic Pd changed from Pd (111) 40.15 to Pd (111) 40.56[17]. These shifts to higher 2θ values can be regarded as, to an extent, indication of alloying. Since the TPR patterns of the catalysts did not show any significant consumption of hydrogen, the samples were not reduced with hydrogen before the reaction and they were used without any activation.

Dechlorination of TCP without alkali

Based on the results of previous studies[15,16] the best conditions like ratio of methanol-water mixture, ratio of Rh-Pd over carbon support, initial concentration of TCP, calcinations and reaction temperatures, H$_2$ partial pressure, etc. were selected for the present study. Hydrodechlorination of TCP in water/methanol (50/50) mixture was followed by the disappearance of TCP and was also confirmed by the appearance of stoichiometric amounts of chloride. Concibido et al.[18] observed faster polychlorinated ethylene (PCE) dechlorination rates in (50/50, v/v) water/methanol mixture. Progress of product distributions from HDC of TCP in methanol/water (50/50) at 80°C over 0.97%Pd/C catalyst is depicted in Fig. 2 as a representative plot. The 2-CP and 4-CP were found to
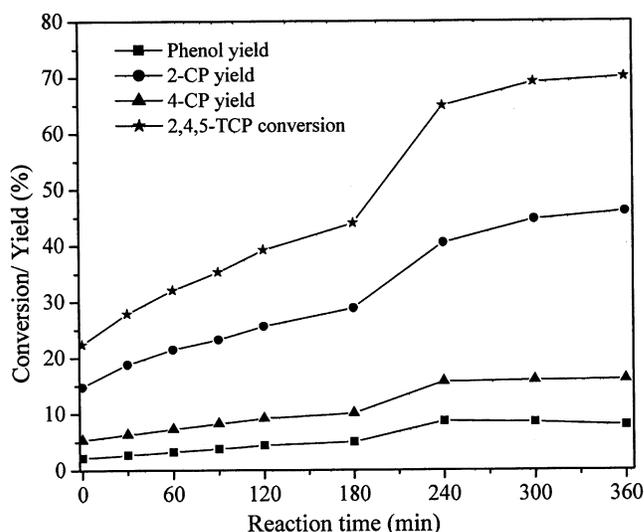

Fig. 2—Changes in 2,4,5-trichlorophenol with time over 0.97%Pd/C catalyst in (50/50) methanol/water mixture without alkali at 353 K, 0.1 atm (10.3%H$_2$/N$_2$) and C_{TCP} = 0.084 mol dm^{-3}

be the major intermediate products. The 0.97%Pd/C catalyst exhibited higher yields of 2-CP and 4-CP. Maximum yields of 2-CP and 4-CP were 46 and 16% after 6 h of reaction. No ring hydrogenation products were detected, and phenol was detected as final product in most cases after six hours of reaction time. However, with 0.8%Pd/0.19%Rh/C catalyst, in addition to 2-CP and 4-CP the other products were 2,4-DCP and 2,5-DCP. Maximum yields of mono- and dichlorinated (MCP and DCP) were 47 and 12% respectively after 6 h of reaction time. An increase in the concentration of rhodium in Pd/Rh/C catalysts led to a decrease in selectivity and yield also. Over 0.98%Rh/C catalyst, the conversion of chlorinated compounds was found to be lower than those obtained with other catalysts at all times of reaction. However,

2-CP and 4-CP were found to be the major intermediate products. After the addition of rhodium, yield of chlorinated compounds (15%) was found to decrease. Thus, Palladium supported on carbon appeared to be better catalyst for hydrodechlorination of TCP in liquid phase under applied conditions among the catalysts tested.

The initial HDC activity for TCP was found to be in the following order: 0.97%Pd/C>0.8%Pd/0.19% Rh/C>0.98%Rh/C. Addition of Rh caused a decrease in the activity as well as selectivity. This behaviour may be a consequence of dilution of Pd by Rh.

Effect of alkalis on the conversion and products of dechlorination of TCP

Figure 3 (a, b, c) shows that the conversions of TCP in the presence of alkalis are different than that in the absence of alkali. At a reaction time of 6 h, typical conversions of TCP are 86, 78 and 32% in presence of potassium carbonate, sodium hydroxide and lithium carbonate respectively. Thus, potassium carbonate and sodium hydroxide accelerate the decomposition of TCP significantly while lithium carbonate promotes it less than the others.

Based on the identified conversion products, the probable reaction pathways of TCP dechlorination with alkalis are shown in Scheme 1. The two parallel pathways for dechlorination are, hydrodechlorination and hydrolysis. The hydrolysis follows the ionic reaction, generating catechol and resorcinol.

Further, mono-chlorinated products were not observed with potassium carbonate additive. After the dechlorination, maximum yield of 2,4-DCP (50%) was obtained at 6 h. Moreover, aromatic structures, such as phenol, catechol, resorcinol, etc., were also observed in the products. When sodium hydroxide was used, catechol and resorcinol were not present in the product distribution, but phenol, mono and di-chlorinated products were obtained. Sodium hydroxide additive produced lower yield of 2,4-DCP than what was obtained with potassium carbonate. In comparison with sodium hydroxide additive, phenol yield decreased from 47 to 18% with potassium carbonate additive over 6 h of reaction time. Also, mono and di-chlorinated products were not obtained by adding lithium carbonate, which had the lowest strength of basicity, and only phenol was obtained in the products.

Conversion of TCP increases when the strength of basicity increases. In addition, it is observed that the nature of alkali changes the product distribution
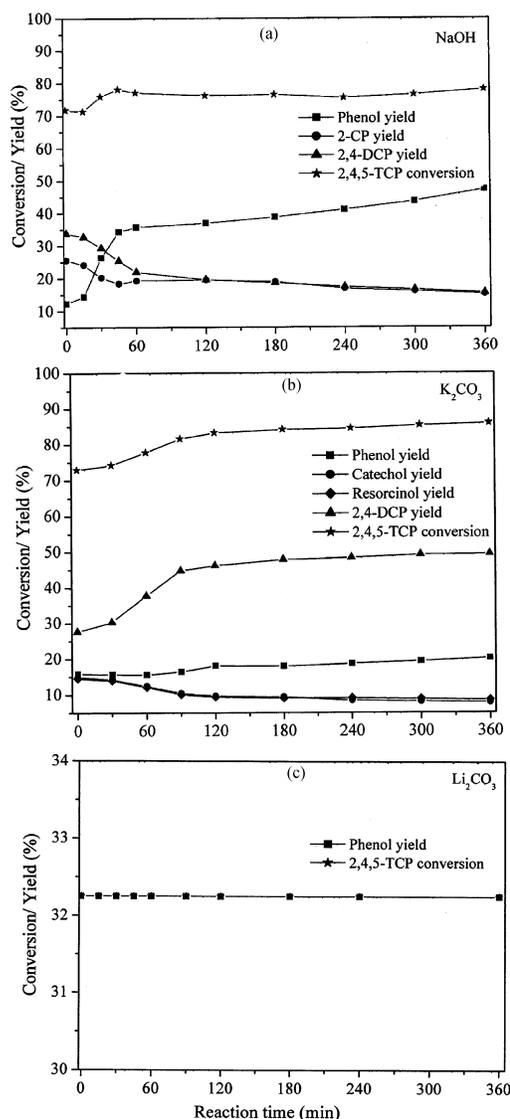

Fig. 3—Effects of alkalis, (a) NaOH, (b) K_2CO_3, (c) Li_2CO_3, on the conversion/yield of TCP in (50/50) methanol/water over %0.97 Pd/C catalyst at 353 K, 0.1 atm (10.3%H_2/N_2) and C_{TCP} = 0.084 mol dm^{-3}

which indicates that the HDC reaction was structure sensitive. However, it is very difficult to come to a conclusion about sensitivity/insensitivity to the catalyst structure from present experimental results.

There have been conflicting reports regarding the effects of alkalies on the catalytic activities. Aramendia et al.[19] studied hydrodechlorination of 3-chloropryridine and chlorbenzene over alkali-modified zirconia-supported palladium catalysts. The alkali carbonates (Li, Na and K) used in the reaction were found to play an important role by lowering the detrimental effects of hydrogen chloride released as the reaction proceeds. There is no general consensus
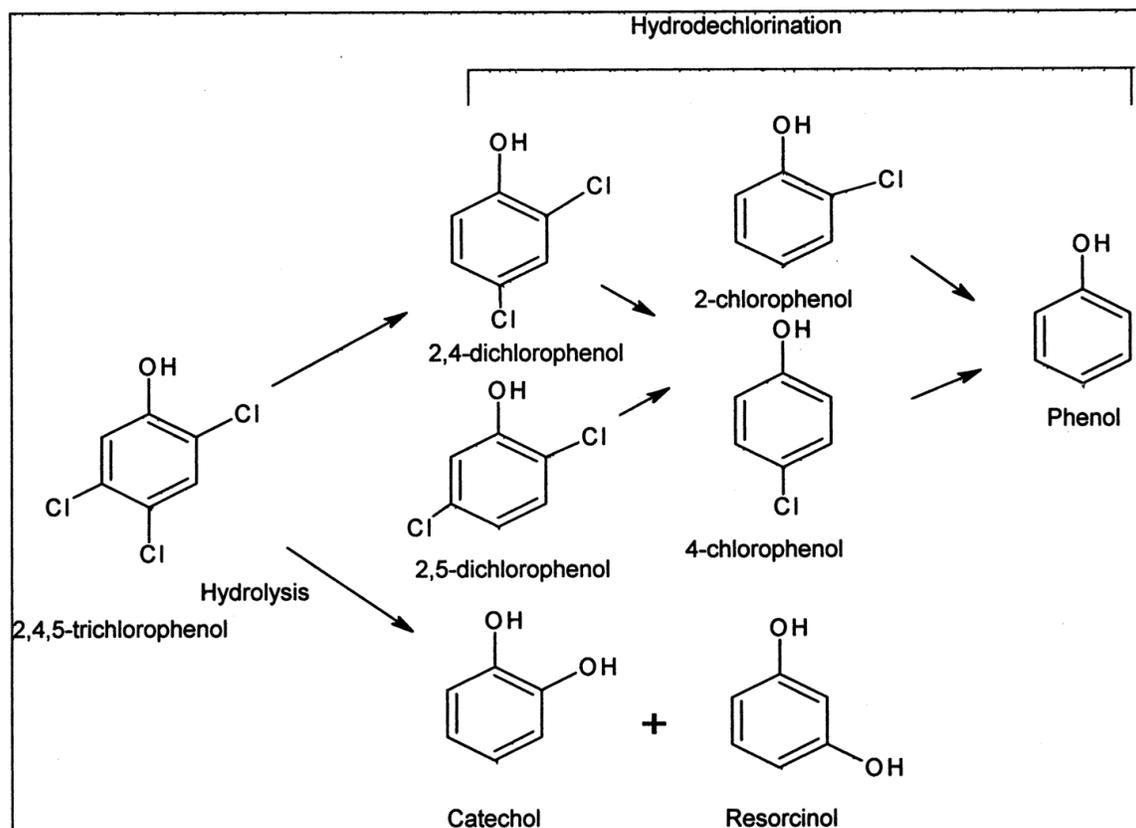
Scheme 1—Probable dechlorination pathways for TCP in presence of alkalis in liquid phase.

about the structure-sensitivity or insensitivity of the hydrodechlorination reaction[20,21]. Sajiki and Hirota[22] found that the addition of a nitrogen-containing base, such as pyridine, to a Pd/C catalyst inhibited the hydrogenolysis activity. On the other hand, potassium alkalis and sodium alkalis accelerated the dechlorination of o-chlorophenol in supercritical water[23].

The results of present investigations show that the rate of hydrodechlorination of TCP over catalysts depended on nature of alkali additive and the metal crystallite size as well as the reaction conditions (Table 1). Base addition to the reaction mixture improved the catalytic activity over palladium catalyst. K_2CO_3, Li_2CO_3 and NaOH addition to the reaction mixture clearly accelerated the initial HDC rate. All the three alkali metals improved the catalytic activity of Pd catalysts. Thus, the addition of alkali induced a increase in the initial catalytic activity and notably, K_2CO_3 and NaOH addition improved the final conversion (after 6 hours of reaction time) in the catalytic hydrodechlorination of TCP over 0.97% Pd/C. The addition of K_2CO_3 addition had positive effect on extending selectivity and conversion. With increasing strength of basicity, initial consumption rate, turnover frequencies and conversion of TCP increased. In periodic table, the strength of basicity of the alkaline metals increases from K to Li while anion does not play any important role. This improvement depends on the ionic radii of alkali metal added. Therefore, the larger the ionic radii ($Li^+<Na^+<K^+$), the greater the TOF of supported palladium catalyst. However, the decline in the activity of Pd/C catalysts is related to the decrease in the crystallite size of Pd.

It was also observed that the HCl produced in the process did not affect the palladium catalysts, which preserved the catalytic activity even after three usages. This was found from experiments from the three consecutive use of the same catalyst.

Conclusion

The study shows that potassium carbonate, lithium carbonate and sodium hydroxide are effective additives for the dechlorination of TCP in liquid phase. The dechlorination of TCP proceeds mainly via two pathways, hydrodechlorination and hydrolysis

where the hydrolysis is the major side-reaction depending upon the alkalis used and its concentration. Potassium carbonate accelerated the hydrodechlorination more than other alkali additives tried. In contrast to hydrodechlorination, in case of hydrolysis, potassium carbonate promoted the dechlorination more than sodium hydroxide. Dechlorination of TCP in presence of alkalis helped to remove generated HCl, and also inhibited the formation of toxic chlorinated byproducts of smaller size. The selectivity of mono-chlorophenol was found to improve with Pd/C catalysts. The addition of alkali led to an increase on the initial reaction rate and conversion.

Acknowledgement

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