

Catalytic Wet Oxidation of phenol by $(\text{La}_{0.8}\text{Sr}_{0.2})\text{Mn}_{0.98}\text{O}_3$ catalyst in batch reactor

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The catalytic performances of a Mn based perovskite-like catalyst, $(\text{La}_{0.8}\text{Sr}_{0.2})\text{Mn}_{0.98}\text{O}_3$, in Catalytic Wet Oxidation (CWO) of a phenolic solution under milder conditions of temperature (398 – 498 K) and pressure ($P_{\text{O}_2} = 4$ bars), in a batch reactor, have been investigated. Aim of this study is the evaluation of the effect of temperature, catalyst loading, phenol concentration and stirrer speed on phenol conversion.

Experimental data obtained from the different test conditions are best-fitted to evaluate the effective reaction order and apparent activation energy.

1. Introduction

The contamination of aqueous streams by organic compounds is a problem of great interest today since the growing demand of quality water resources.

In particular phenol compounds as pollutants have been object of investigations not only because phenol can be considered a model molecule but also because phenol or its derivatives are present as raw materials or intermediates in several industrial processes (pharmaceutical, petrochemical, plasticizer, agriculture amongst others).

There are different strategies for the remediation of water contaminated with organic compounds. An effective technique for a broad range of organic compounds is the adsorption on activated carbon (Hobby and Gimbel 2004). Adsorption does not ultimately destroy the pollutants, therefore the active carbons have to be disposed or reactivated, which increases the costs of the method.

The conventional biological treatment is widely applied for the handling of residual wastewaters. The main disadvantage of biological treatment is the incapability of treatment for highly polluted and toxic waste streams in industrial wastewaters. Biological treatment is neither suitable for chemical oxygen demands (COD) above 10 g l⁻¹ nor for water which includes toxic compounds (Debellefontaine et al 1995) due to biomass poisoning.

The wet oxidation (WO) process, in particular the catalytic one (CWO), is considered to be an attractive method for concentrations of organic loads of about 10-100 g l⁻¹

(Debellefontaine et al 1995). The use of a catalyst results in a significant reduction of the temperature and pressure and an increase of the oxidation rate of refractory compounds and is therefore improving the economy of the process because the oxidation of organic pollutants can be realized under milder conditions compared to the non catalyzed processes. A key aspect in this process is the catalyst choice, many are the catalysts tested (Luck, 1999; Masende et al., 2003), so far those with the best performances are noble metals based thus difficult to employ since their high cost.

The target is to find a material fulfilling important requirements as cheap cost, activity at low temperature and pressure, stability and that it is environmentally friendly.

Under this light this work deals with CWO process of phenol carried out at low pressure with a LSM catalyst, an unusual material for this kind of applications. Certain perovskite-type oxides (ABO_3), with lanthanum in the A-site and a transition metal in the B-site, have been studied as potential oxidative catalysts for waste gas purification ever since it was discovered that some have comparable catalytic activities to conventional $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts (Bell et al. 2000). Aim of this work is to investigate on the activity of a potentially promising material since its relatively low cost and its proved activity as oxidation catalyst, as well as on the optimization of the process parameters as temperature, catalyst amount and agitation speed.

2. Experimental

2.1 Catalyst

The catalyst employed in this work was a commercial (Praxair) perovskite-like $(\text{La}_{0.8}\text{Sr}_{0.2})\text{Mn}_{0.98}\text{O}_3$.

The physical properties supplied by the manufacturer are: $d_{50} = 0,9 \mu\text{m}$, surface area = $5,0 \text{ m}^2 \text{ g}^{-1}$.

2.2 Catalytic activity tests

Catalytic activity tests were conducted in a stirred batch reactor ("4563 Mini reactor", produced by the Parr Instrument Company, Illinois, USA).

It consists of a moveable cylindrical stainless steel 0,6 l vessel with a flat gasket seal. It is equipped with a gas inlet valve, a gas outlet valve, a liquid outlet valve and a rupture disc as a pressure relief device. Temperature and pressure can be checked by an internal fixed thermocouple and by a pressure gauge. The vessel can be heated by a cylindrical heater; inner liquid solution can be stirred by a stirring system.

The reactor was loaded with 0,5 l of phenolic solution at fixed concentration and with the catalyst in powder form. The reactor was then sealed and pressurized with oxygen through gas inlet valve to an initial pressure of 4 bars (40 MPa).

Reactant not converted and products obtained during the reaction were detected by HPLC (Shimadzu 10 A VP system equipped with a diode array detector). The column employed was a Pinnacle II C18 with a length of 250mm and an inner diameter of 4,6mm. The stationary phase is C18 or ODS silica supported with a media particle diameter d_p of $5 \mu\text{m}$. The mobile phase employed in this work was a mixture of acetonitrile (35%) and water (65%) sent through the column with a flow rate of $0,7 \text{ ml min}^{-1}$. The water employed in the mobile phase was deionized, micro filtrated and furthermore acidified with 1 ml of H_3PO_4 (3 M) resulting in a pH of 2,8.

Catalytic tests were carried out by varying temperature, phenol concentration, catalyst loading and the stirrer speed. Blank experiments (i.e. with no catalyst) at 423 and 448 K were conducted as well.

Table 1: Schedule of the experiments conducted. (*) test conducted at different phenol concentration: $1,25 \cdot 10^{-3}$ M, $3,75 \cdot 10^{-4}$ M, $6,25 \cdot 10^{-4}$ M, $7,50 \cdot 10^{-4}$ M.

398 K		423 K		448 K		473 K		498 K	
g_{cat}/l	stirrer speed (rpm)	g_{cat}/l	stirrer speed (rpm)	g_{cat}/l	stirrer speed (rpm)	g_{cat}/l	stirrer speed (rpm)	g_{cat}/l	stirrer speed (rpm)
		-	0 700	-	0 700	-	0 480 700		
					0 320 480 700				
				1.5	3.5				
	0		0 160 320 480 (*) 640 700						
2.0	320 480 640 700	2.0		2.0	480	2.0	480	1.0	480
				2.5	480				
	0 480 640 700			3.0	480				
				3.5	480				
	0 480 640 700			4.0	480				

3. Results and discussion

3.1 Kinetic of the catalytic wet oxidation of phenol

The kinetic analysis of the reaction was performed for all the situations enumerated in Table 1; the experimental data displays (with a satisfying best-fit) a first-order-like kinetics with respect to phenol concentration, confirming some literature findings (see e.g. Portela-Miguel et al. (1997)):

$$\frac{dC_{phl}}{dt} = kC_{phl} \quad (1)$$

where C_{phl} is the concentration of phenol (mol cm^{-3}) and k (s^{-1}) is the effective reaction rate taking into account intermediate reactions, mass transfer phenomena, mixing and catalyst load.

As expected, as temperature increases, the effective rate of conversion increases since also correlated phenomena increase. The apparent activation energies estimated from the slopes of the straight lines in Arrhenius plots and calculated by means of the least squares techniques, in case of catalyst loading of 2 g l^{-1} , 3 g l^{-1} and 4 g l^{-1} , were respectively $32,5 \text{ kJ mol}^{-1}$, $42,7 \text{ kJ mol}^{-1}$ and $44,6 \text{ kJ mol}^{-1}$, confirming that catalyst loadings above 2.5 g l^{-1} introduce a change in the reaction regime, thus becoming kinetic controlled.

3.2 Effect of the initial phenol concentration

The catalytic wet oxidation of phenol was studied by varying the initial phenol concentration in order to determine its effect and possible reactant limitations on conversion under the same reaction conditions, namely, at 423 K , with an oxygen pressure of 4 bars and a stirrer speed of 480 rpm , with 2 g l^{-1} of catalyst loading. The experiments were carried out at phenol concentration of $1,25 \cdot 10^{-3} \text{ M}$, $3,75 \cdot 10^{-4} \text{ M}$, $6,25 \cdot 10^{-4} \text{ M}$, $7,50 \cdot 10^{-4} \text{ M}$.

Figure 1 shows the conversion x vs. time curves, modelled with a first-order-like kinetics, at different initial phenol concentrations. Though the time required to reach an asymptotic regime is almost constant as the initial phenol concentration increases, the imposed catalyst loading, along with the fixed agitation speed, doesn't allow a complete conversion of phenol at high initial concentration, probably due to mass transfer limitations between gas-phase and liquid-phase oxygen and transport limitations of phenol to the catalyst surface.

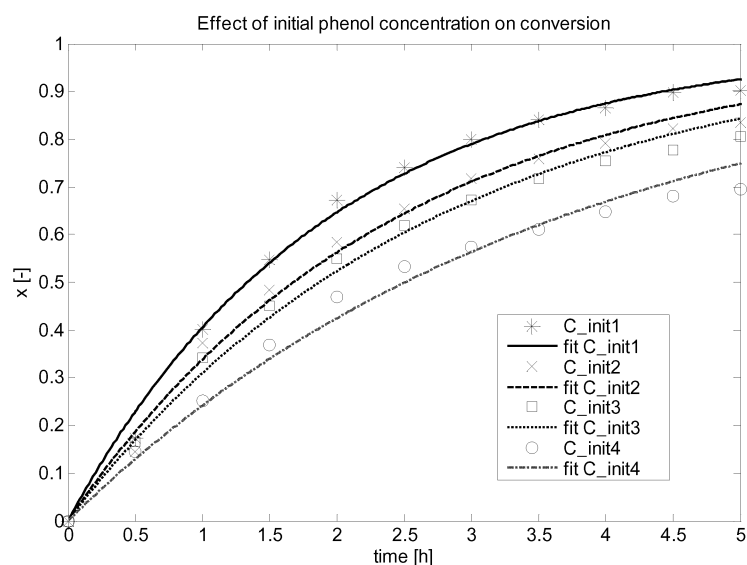


Figure 1 – Effect of different initial phenol concentrations ($C_{init1} = 3.75 \cdot 10^{-4} \text{ M}$, $C_{init2} = 6.25 \cdot 10^{-4} \text{ M}$, $C_{init3} = 7.50 \cdot 10^{-4} \text{ M}$, $C_{init4} = 1.25 \cdot 10^{-3} \text{ M}$) on phenol conversion at 423 K , oxygen pressure = 4 bar , stirrer speed of 480 rpm and catalyst loading = 2 g l^{-1} .

3.2 Effect of the catalyst loading

At a constant initial phenol concentration ($C_{\text{init}2}=6.25 \cdot 10^{-4}$ M), the effect of the catalyst loading on phenol conversion was studied at 448 K by varying the catalyst concentration from 1.0 g l^{-1} to 4.0 g l^{-1} . The data collected at 448 K put in evidence the dependence of phenol conversion on the catalyst concentration (Figure 2). With a constant initial phenol concentration, the initial rate of phenol oxidation per gram of catalyst decreased by increasing the catalyst loading till 2.5 g l^{-1} and became almost independent of catalyst concentration at higher loadings.

The behaviour of phenol oxidation rate at catalyst concentrations lower than 2.5 g l^{-1} suggests transport limitations of phenol to the catalyst surface. At higher catalyst concentrations, the reaction rate per gram of catalyst seems to be less affected by catalyst loading, indicating that a kinetic control seems to prevail on transport limitations.

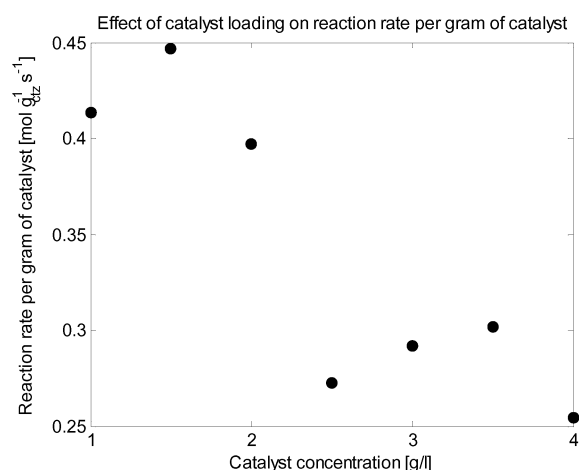


Figure 2 – Effect of catalyst concentration on reaction rate per gram of catalyst at 448 K, oxygen pressure = 4 bar, stirrer speed of 480 rpm and phenol initial concentration = $6.25 \cdot 10^{-4}$ M.

3.3 Effect of stirring speed

In a stirred batch reactor, the mixture is stirred vigorously in order to slurry the catalyst uniformly throughout the liquid. In order to observe the effect of the stirrer speed on the phenol oxidation rate, experiments were carried out at different stirring speeds. For the sake of brevity, the experiment developed at 423 K, with an oxygen pressure of 4 bars, a phenol initial concentration of $6.25 \cdot 10^{-4}$ M and 1 g l^{-1} of catalyst loading was taken as a paradigm of the whole experimental set.

Figure 3 presents the variation of phenol conversion with time at different stirring speeds. As the stirring speed increases from 0 rpm to 480 rpm, no appreciable differences on conversion are detected; on the other side, phenol conversion increases appreciably at 700 rpm, ensuring vigorous mixing and uniformity throughout. The existence of a threshold value is suggested in which the resistance due to phenol mass transfer to the catalyst particle has overcome.

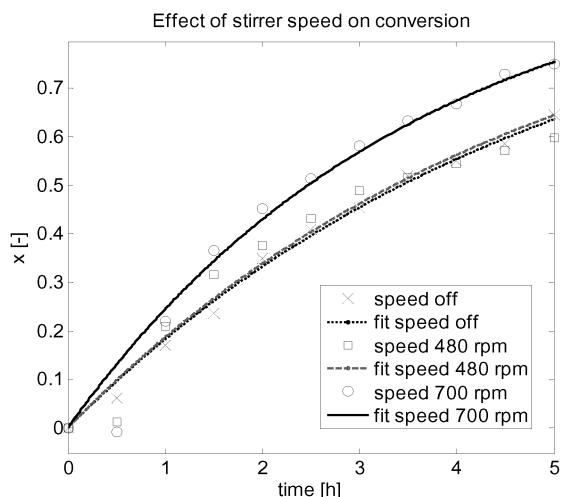


Figure 3 – Effect of stirrer speed on phenol conversion at 448 K, oxygen pressure = 4 bar, catalyst loading = 1 g l⁻¹ and phenol initial concentration = 6.25*10⁻⁴ M.

4. Conclusion

This study exploited the feasibility of a rather unusual catalyst for catalytic wet oxidation of phenol. This material, worth of note also because of its cheapness, allows to study the reaction in a range of low temperatures and oxygen partial pressures, else achievable employing noble metal based materials.

The oxidation of phenol in aqueous solution over a LSM catalyst was investigated above atmospheric pressure. The kinetic of the reaction exhibited first-order behaviour with respect to phenol concentration. The rates show a dependence on catalyst loading, decreasing as the catalyst concentration increased. These observations suggest transport limitations of phenol to the catalyst surface, as already advised by Satterfield (1970, p.5). Besides, an increase in stirring speed increased conversion of phenol appreciably, with a thresholding behaviour.

5. References

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