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DETERMINATION OF SUITABLE CATALYST FOR THE CATALYTIC OXIDATION OF TOLUENE TO BENZALDEHYDE USING COMBINED CrO_3/H_2O_2 OXIDANT SYSTEM

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ABSTRACT

The research is designed to determine the suitable catalyst for the oxidation of toluene to benzaldehyde using CrO_3/H_2O_2 oxidant system under appropriate conditions of temperature and reaction time. Nine (9) catalysts [CU_2O, CUO, $CU(CH_3COO)_2$, $CUSO_4.5H_2O$, $Co(CH_3COO)_2$, $Fe_2(SO_4)_3$ $.9H_2O$, $Fe_2(SO_4)_3$. $7H_2O$, Calcined$CaCO_3$, MnO_2] and Eight(8) oxidant systems [50%$KMnO_4$, Solid $KMnO_4$, Acidified $KMnO_4$, $KMnO_4/K_2Cr_2O_7$, H_2O_2, CrO_3, CrO_3/H_2O_2, Air] were used in the study. Thetoluene oxidation was carried out using each oxidant by separateapplication of all the nine catalysts either in aqueous or acidic medium. The results revealed that out of the various catalysts and oxidants used, only three (3) catalysts [CUSO4.5H2O, Fe $_2(SO_4)_3.9H_2O$, $Fe_2(SO_4)_3$. 7H $_2O$] and one oxidant(CrO_3/H_2O_2,) produced the targeted product.When the same three catalysts were applied on the oxidants in acidic medium, benzoic acids were produced but when applied on oxidants in aqueous medium benzylalcohols were produced. The percentage yield of the benzaldehydeproducts were calculated at various temperatures and reaction times. When $Fe_2(SO_4)_3.9H_2O$ was used as a catalyst,low yield of1.0% was obtained at 40ºCand 10minutes reaction time. The high yield of 1.25% was obtained at 50ºC and 10minutes reaction time. But when the temperature was raised to 60ºC and the reaction time was extended to 20 minutes, the yield dropped to 0.69%. When $CUSO_4.5H_2O$ was used as a catalyst, the low yield of 0.20% was obtained at 30ºC and 10minutes reaction time. The high yield of 1.66%was obtained at 40ºC and 10minutes reaction time. Similarly, when the temperature was raised to 60ºC and the reaction time was extended to 20 minutes, the yield dropped to 1.09%. However,when $Fe_2(SO_4)_3$. $7H_2O$was used as a catalyst, the low yield of 1.0% was obtained at 30ºC and 20minutes reaction time. The high yield of 1.90% was obtained at 40ºC and 20minutes reaction time. But when the temperature was raised to 60ºC and 10minutes reaction time, the yield dropped to 0.65%. Therefore, based on the percentage yield obtained from the three effective catalysts used, $Fe_2(SO_4)_3$. $7H_2O$ was found to be the most suitable catalyst for the oxidation of toluene to benzaldehyde using CrO_3/H_2O_2 oxidant system.

Keywords:Catalytic, Oxidation, Toluene,Chromium(vi)oxide/Hydrogen peroxide, Benzaldehyde

INTRODUCTION

Studies of catalysts and catalyzed reactions have multiplied over the years due to their variety of applications in industries. Catalytic studies cut across the entire field of chemistry including organic, inorganic and physical chemistry. This is because catalysis is concerned with controlling the rate and the direction of a chemical reaction. Literature revealed that the first row transition metals are suitable catalysts due to their low price and availability which will bring down the cost of production.A catalytic reaction is one in which more than one turn over or events occur per reaction centre or catalytically active site(Smith and Notheis,1999). Generally,for the selection of suitable catalysts consideration should be given to the reaction medium, nature of the catalyst, phase, reaction time and conditions of temperature and pressure. Similarly recent literature indicated that although some achievements have been obtained in the catalytic oxidation of toluene to benzaldehyde, its(benzaldehyde) yieldis still relatively low(Gepeng, 2010). Some other recent works investigated the production of benzaldehyde by liquid-phase homogenous catalytic oxidation of toluene using different catalysts (Gepeng, 2010).The choice of CrO_3/H_2O_2 oxidant system is based on the fact that although H_2O_2 is a very good oxidizing agent, but its decomposition is very slow that is why it is combined with CrO_3 which catalyzed its decomposition to release the O_2 needed for the oxidation process.Although, benzaldehyde has been produced for decades using different methods, yet the search for more efficient methods of its production is still on-going. This is due to the fact that almost all the existing methods suffer from one drawback or another. Thus, Some of the catalytic reactions were carried out in gas phase which required high pressure and cooling system to condense the product and residual reactants (Zhang *et al*.,2004). Some catalysts gave high yield but also produced side products thereby making the separation of benzaldehyde very difficult and expensive (Groot and de Bont, 1998).Therefore, this research is designed to determine appropriate catalyst for an efficient oxidation of toluene to benzaldehyde using CrO_3 / H_2O_2 oxidant system.

MATERIALS AND METHOD

The materials and reagents used are toluene, Hydrogen peroxide, Chromium vi oxide, Sulphuric acid, Potassium permanganate, Acetic acid, distilled water, Acetone, Nine (9) Catalysts; CU_2O, CUO, CU(CH3COO)2, CUSO4.5H2O, Co(CH3COO)2, Fe2(SO4)3.9H2O, Fe2(SO4)3. 7H2O,CalcinedCaCO3 and MnO2.

METHODOLOGY

Eleven(11) different oxidants were prepared according to standard procedure (Farouq, 2008). The substrate, toluene was prepared as described below. The followingCatalysts; CU_2O, CUO, Calcined$CaCO_3$ and MnO_2 were weighed and used in powdered form while $CU(CH_3COO)_2$, $CUSO_4.5H_2O$, $Co(CH_3COO)_2$, $Fe_2(SO_4)_3.9H_2O$, $Fe_2(SO_4)_3$. $7H_2O$ were prepared as described below. The oxidation reaction was conducted in acid or aqueous medium using different oxidants and catalysts on the substrate. The products of the oxidation reactions were tested for the presence of alcohols, aldehydes and acids using the spotstest (Shriner *et al.*, 1998). Furthermore, GCMS analysis was employed with a view to determining the yield and also to investigate the effects of temperature and reaction time on the products.

Preparation of Toluene

1M Toluene Solution in Benzene was used in the experiment. The solution was prepared by transferring 10ml of toluene into $100cm^3$ volumetric flask and the flask was filled to the mark with benzene. The flask was stopped and shaken properly to ensure uniform mixing. The solution was then kept for further use.

Preparation of Catalysts

1.40g of $Fe_2(SO_4)_3.9H_2O$ was dissolved in $50cm^3$ of distilled water in a beaker and the content was transferred into $1000cm^3$ volumetric flask. The beaker was rinsed five times with about $50cm^3$ of distilled water in each case and the washings were transferred into the volumetric flask. The flask was then filled to the mark with distilled water. The flask was stopped, shaken properly and then kept for further use. The same procedure was used in the preparation of $Fe_2(SO_4)_3.7H_2O$, $CUSO_4.5H_2O$,Co(CH3COO)2 and CU(CH3COO)2 catalysts solutions.

Oxidation of Toluene using combine oxidant of CrO_3/H_2O_2 and Catalysts

0.5g of CrO_3, $50cm^3$ distilled water, $50cm^3$ of prepared $Fe_2(SO_4)_3.9H_2O$ were added into the reaction flask followed by $50cm^3$ of prepared 1M solution of toluene. The content was heated to 80ºC, then$25cm^3$ of 100 volumes of H_2O_2 were added. The mouth of the reaction tank was properly closed with rubber cork to prevent escape of gases. The temperature was maintained at 80ºC with continuous stirring for 5hours. At the end, the organic layer was separated and distilled to about $10cm^3$ and analyzed for the presence of oxidation products. The same procedure was repeated with each of $Fe_2(SO_4)_3.7H_2O$ and $CUSO_4.5H_2O$ in place of $Fe_2(SO_4)_3.9H_2O$.

Analysis of the Oxidation products

Oxidation products were tested for the presence of Alcohols, Aldehydes and Carboxylic acids using spot test.

RESULTS

Table 1.1: Preliminary spot Test for Alcohols, Aldehydes and Carboxylic acids

Reagents	Alcohols	Aldehydes	Carboxylic acid	Inference
Jone's reagent	+ve	-	-	Effective
2,4-dinitrophenyl hydrazine reagent	-	+ve	-	Effective
Saturated $NaHCO_3$ Solution	-	-	+ve	Effective

Table 1a. Results of the analysis of the oxidation products using 50% $KMnO_4$ Solution

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	50%$KMnO_4$	AQUEOUS	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	_	_	_
			$Fe_2(SO_4)_3.7H_2O$	_	_	_
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected

Table 1b. Results of the analysis of the oxidation products using solid $KMnO_4$ crystals

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	Solid $KMnO_4$	AQUEOUS	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	_	_	_
			$Fe_2(SO_4)_3.7H_2O$	_	_	_
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected

Table 1c. Results of the analysis of the oxidation products using acidified $KMnO_4$ solution

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	Solid $KMnO_4$	ACID	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	_	_	+
			$Fe_2(SO_4)_3.7H_2O$	_	_	+
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected, + = detected

Table 1d. Results of the analysis of the oxidation products using acidified mixture of $KMnO_4$ and $K_2Cr_2O_7$ Solution

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	$KMnO_4/K_2Cr_2O_7$	ACID	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	+
			$Fe_2(SO_4)_3.9H_2O$	_	_	+
			$Fe_2(SO_4)_3.7H_2O$	_	_	+
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected, + = detected

Table 1e. Results of the analysis of the oxidation products using Aqueous H_2O_2 Solution

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	H_2O_2	AQUEOUS	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	+	_	_
			$Fe_2(SO_4)_3.7H_2O$	+	_	_
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected, + = detected

Table 1f. Results of the analysis of the oxidation products using CrO_3 solution

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	CrO_3	AQUEOUS	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4$ $5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	_	_	_
			$Fe_2(SO_4)_3.7H_2O$	_	_	_
			CALCINED $CaCO_3$	_	_	_
			MnO_2	–	–	–

KEY: −= not detected

Table 1g. Results of the analysis of the oxidation products using CrO_3 in Acetic Acid

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	CrO_3	Acetic acid	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4$ $5H_2O$	_	_	_
			$Fe_2(SO_4)_3.9H_2O$	_	_	+
			$Fe_2(SO_4)_3.7H_2O$	_	_	+
			CALCINED $CaCO_3$	_	_	_
			MnO_2	–	–	–

KEY: −= not detected, + = detected

Table 1h. Results of the analysis of the oxidation products using CrO_3/H_2O_2 in Aqueous

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	CrO_3/H_2O_2	AQUEOUS	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4$ $5H_2O$	_	+	_
			$Fe_2(SO_4)_3.9H_2O$	_	+	_
			$Fe_2(SO_4)_3.7H_2O$	_	+	_
			CALCINED $CaCO_3$	_	_	_
			MnO_2	–	–	–

KEY: −= not detected, + = detected

Table 1i. Results of the analysis of the oxidation products using Air as Oxidant

SUBSTRATE	OXIDANT	MEDIUM	CATALYST	PRODUCT ANALYSIS		
				ALCOHOL	ALDEHYDE	ACIDS
TOLUENE	AIR	DILUTE ACETIC ACID	CUO	_	_	_
			CU_2O	_	_	_
			$CU(CH_3COO)_2$	_	_	_
			$Co(CH_3COO)_2$	_	_	_
			$CUSO_4\ 5H_2O$	_	_	+
			$Fe_2(SO_4)_3.9H_2O$	_	_	+
			$Fe_2(SO_4)_3.7H_2O$	_	_	+
			CALCINED $CaCO_3$	_	_	_
			MnO_2	_	_	_

KEY: −= not detected, + = detected

Table 2a: Results of GCMS analysis of the product obtained using $CUSO_4\ 5H_2O$ as a Catalyst

Reaction Temp.(ºC)	Reaction Time(min.)	Product	Yield (%)
30	10	Benzaldehyde	0.20
	20	Benzaldehyde	0.38
	30	-	-
40	10	Benzaldehyde	1.66
		Benzoic acid	0.56
	20	Benzaldehyde	1.22
	30	-	-
50	10	Benzaldehye	1.23
	20	Benzaldehyde	1.50
	30	-	-
60	10	Benzaldehyde	1.23
	20	Benzaldehyde	1.09
	30	-	-

Table 2b: Results of GCMS analysis of the product obtained using $Fe_2(SO_4)_3.9H_2O$ as a Catalyst

Reaction Temp.(ºC)	Reaction Time(min.)	Product	Yield (%)
30	10	-	-
	20	-	-
	30	-	-
40	10	Benzaldehyde	1.0
	20	Benzaldehyde	1.1
	30	-	-
50	10	Benzaldehye	1.25

	20	Benzaldehyde	1.20
	30	-	-
60	10	Benzaldehyde	1.10
	20	Benzaldehyde	0.69
	30	-	-

Table 2c: Results of GCMS analysis of the product obtained using $Fe_2(SO_4)_3.7H_2O$ as a Catalyst

Reaction Temp.(ºC)	Reaction Time(min.)	Product	Yield (%)
30	10	Benzyl alcohol	0.75
	20	Benzaldehyde	1.0
	30	-	-
40	10	Benzaldehyde	1.60
	20	Benzaldehyde	1.90
	30	-	-
50	10	-	-
	20	-	-
	30	-	-
60	10	Benzyl alcohol	0.84
		Benzaldehyde	0.65
		Benzoic acid	1.94
	20	Benzoic acid	1.50
	30	-	-

DISCUSSION OF RESULTS

The preliminary tests(table 1.0) were conducted to test the workability of the spot tests reagents in identifying the oxidation products in to alcohols, aldehydes and carboxylic acid. Although the spot tests might not be sensitive enough to detect small quantities of above mentioned products, however, the aim was to identify those reactions that give substantial amount of the target products that can be used for further analysis. The choice of catalysts was based on their availability and low prices. Out of the nine (9) catalysts employed, only three(3) [$Fe_2(SO_4)_3.7H_2O$, $CUSO_4.5H_2O$, $Fe_2(SO_4)_3.9H_2O$] yielded detectable oxidation products comprising of alcohols, aldehydes and carboxylic acids. However, the identity of the products and their yields could not be detected using the spot tests. Therefore, GCMS analysis was employed on the aldehyde products. Furthermore, in order to investigate the effect of temperature and reaction time on the yield, the reactions were repeated at different temperatures(30, 40, 50 and 60ºC) and reaction times(10, 20 and 30mins).

Table 3.0 showed the result of the reaction with $Fe_2(SO_4)_3.7H_2O$ as a catalyst, gave three different products that is, benzylalcohol,benzaldehydeand benzoic acid. At 30ºC and 10minutes reaction time, a very small amount of benzyl alcohol was produced(0.75%).When the reaction time was increased to 20minutes,benzaldehydes was produced instead of benzyl alcohol. This suggests that the first product of the reaction was benzylalcohol which was oxidized further to benzaldehyde when the reaction time was increased. At 40ºC, benzaldehyde was produced in both 10 and 20minutes reaction times. However, at 60ºC and 10minutes reaction time, three products were identified;benzyl alcohol, benzaldehyde and benzoic acid. But when the reaction time was doubled to 20minutes, the product was exclusively benzoic acid. This suggests succession of oxidation reaction from alcohol to aldehyde and finally to acid. It further shows that high temperature and long reaction time result in over oxidation to acid.

Table 4.0 gave the result of the oxidation products with $Fe_2(SO_4)_3.9H_2O$ as catalyst. Before the reaction, the result was expected to be the same with that of $Fe_2(SO_4)_3.7H_2O$,simply because the main compounds are the same $Fe_2(SO_4)_3$, the only difference was in the water of crystallization. Interestingly, the products were not entirely the same indicating that the water of crystallization serves to modify the catalytic property. On using $Fe_2(SO_4)_3.9H_2O$, the product was exclusivelybenzaldehyde. The yield which was withinthe range of 1.0 to 1.25% did not indicate the presence of either benzylalcohol or benzoic acid. But when the temperature was raised to 60ºC and the reaction time was extended to 20minutes, the yield dropped to 0.69%. This could not be explained as no other product was identified. Ordinarily, over oxidation to benzoic acid was expected but the GC/MS spectrum of the product did not show the presence of the expected benzoic acid. The possible explanation might be deactivation of the catalyst with the increase in temperature.

Table 5.0 shows the GCMS result of the products obtained when $CUSO_4.5H_2O$ was used as the catalyst. Almost all the products here were benzaldehyde with only a record of benzoic acid at 40ºC. The yield was very low at 30ºC and it fluctuated withinthe range of 1.22 to 1.66%. However, the yield tends to drop when the reaction was carried out at 60ºC for 20minutes. This is very similar to the observation made in the previous case where the yield declined at 60ºC. The expectation was further oxidation to benzoic acid at higher temperature but the GC/MS data did not show presence of benzoic acid. Therefore, the low yield can be attributed to either reversed reaction or deactivation of the catalyst with temperature. Another possible reason might be due to evaporation or fast decomposition of the hydrogenperoxidewhich is the source of oxygen for oxidation. The unavailablility of the oxygen will certainly result in lower product yield and that is the most plausible of all the possibilities.

In general the yield was very low which might have resulted from different reasons. On the one hand, the reaction time was very short compared to many such reactions that range between 2 to 10 hours. For example,Acharyya et al, 2014 used $CUCr_2O_4$ and obtained 57.5% conversion after 10hours of the reaction. On the other hand, the temperature of the reaction was very low compared to most of what was recorded in the literature. For example Wang et al 2005 carried out their reaction at 190ºC on copper based catalyst and obtained 7% conversion. It was expected that the yield will actually improve with increase in temperature and reaction time. The yield is also expected to increase with increase in temperature,but at high temperature, there is the possibility that the reactants might turn to vapour.

CONCLUSION

Although temperature and reaction time played greater roles in this oxidation process, however, suitable catalyst accounted for the high yield of the target product. In view of this therefore, the most suitable catalyst for the oxidation of toluene to benzaldehyde using CrO_3 /H_2O_2 oxidant system is $Fe_2(SO_4)_3.7H_2O$.

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