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Catalytic oxidation of butyl acetate over silver-loaded zeolites

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Abstract

The performance of silver-loaded zeolite (HY and HZSM-5) catalysts in the oxidation of butyl acetate as a model volatile organic compound (VOC) was studied. The objective was to find a catalyst with superior activity, selectivity towards deep oxidation product and stability. The catalyst activity was measured under excess oxygen condition in a packed bed reactor operated at gas hourly space velocity (GHSV) = $15,000-32,000 h^{-1}$, reaction temperature between 150 and 500 °C and butyl acetate inlet concentration of 1000–4000 ppm. Both AgY and AgZSM-5 catalysts exhibited high activity in the oxidation of butyl acetate. Despite lower silver content, AgY showed better activity, attributed to better metal dispersion, surface characteristics and acidity, and its pore system. Total conversion of butyl acetate was achieved at above 400 °C. The oxidation of butyl acetate followed a simple power law model. The reaction orders, *n* and *m* were evaluated under differential mode by varying the VOC partial pressure between 0.004 and 0.018 atm and partial pressure of oxygen between 0.05 and 0.20 atm. The reaction rate was independent of oxygen concentration and single order with respect to VOC concentration. The activation energies were 19.78 kJ/mol for AgY and 32.26 kJ/mol for AgZSM-5, respectively. © 2008 Elsevier B.V. All rights reserved.

Keywords: Butyl acetate; Silver; Zeolites; Catalyst; Characterization; Activity; Kinetic

1. Introduction

The choice of the volatile organic compound (VOC) emission abatement technique depends on the characteristics of the effluent to be treated, such as the nature of VOC, its concentration and its flow rate [1]. Catalytic oxidation that can be effectively applied in a wide range of VOCs concentrations and waste gas flow rates presents an interesting solution for VOCs elimination [2]. The catalytic process permits the oxidation reaction to occur at a significantly lower temperature than that required by thermal oxidation processes. There are two types of catalysts that can be used in catalytic oxidation, i.e. metal oxides and supported noble metals [2,3-5]. The selection between a metal oxide or a noble metal is generally influenced by several factors such as the nature of the gaseous stream to be treated and the presence of contaminants. However, it is generally accepted that noble metals are more active than metal oxides but the latter are more resistant to poisoning [6]. Pt and Pd are the most common noble metals used for total oxidation of VOCs [7] and usually, they are supported on an oxide such as Al₂O₃ or SiO₂.

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In general, platinum exhibits higher activity than palladium for the total oxidation of VOCs [8].

Oxides of transition metals such as copper, chromium, manganese and nickel can tolerate higher levels of poisons but the activity shown by these oxides are usually lower than that of noble metal-based catalyst [4]. Silver has recently gained much interest for low temperature NOx reduction [9] and CO oxidation [10]. Thus, it could be a suitable catalyst for many redox reactions like VOC oxidation. Pioneering works by Cordi and Falconer [11] led to the conclusion that Ag/Al₂O₃ catalyst was very active for the complete oxidation of VOC to CO₂ and H₂O. VOC was hypothesized to diffuse along the alumina surface and reacted at the silver sites, where oxygen is adsorbed. As the oxidation occurred at high temperatures, VOC reacted in parallel on silver and alumina sites. Recently, Beak et al. [12] studied various transition metals such as Mn, Fe, Co, Ni, Cu, Zn and Ag for catalytic oxidation of toluene and methyl ethyl ketone and silver showed the best activity among the tested catalysts. Thus, it is of great scientific interest to study the performance of this metal in the complete oxidation of a wider range of organic substances.

The choice of the support is also important with γ -alumina being the most widely investigated. An important property pointed out by several researchers is that the hydrophobicity of

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the support [12,13]. The advantage of using a more hydrophobic support is that water vapor, both from the atmosphere and formed as a reaction product, will have lower tendency to adsorb on the catalyst, particularly at low reaction temperatures. The competitive adsorption between the organic and water molecules on the catalyst's active sites always results in lower catalytic activity [12,14]. Recently, zeolites have gained much interest to be used as supports or even as catalysts for oxidation reactions [6,15]. The merit of zeolite-based catalyst is that the active metal components can be exchanged with the existing cations in the zeolite. Consequently, better metal dispersion is obtained down to nearly molecular level [13,16]. This property, coupled with the size and shape features of the zeolites, allow the materials to be used as an effective catalyst in many reactions. However, different metal exchanged zeolites will have different behaviors in the reaction system due to differences in the metal dispersion, pore characteristics, hydrophobicity, Si/Al ratio and surface acidity.

Butyl acetate (BA) is generally used as a solvent in a variety of coating resins including epoxies, urethanes, cellulosics, acrylics and vinyls. The major applications for these surface coatings are wood furniture and fixtures, containers and closures, automotive refinishing and maintenance and marine coatings. Ester compounds are generally reported to be the most difficult organic solvent to completely oxidize [17] and little work has been reported on the catalytic oxidation of butyl acetate in the literature. As such, the quest for investigating the performance and behavior of zeolite catalysts in butyl acetate oxidation is a worthwhile effort. The objective of this research was therefore aimed at demonstrating the catalytic performance and behavior of silver exchanged zeolites in the complete oxidation of butyl acetate. The kinetic model to represent the oxidation behavior of butyl acetate over silver-loaded zeolites is also proposed. For the purpose of comparison, zeolite Y and ZSM-5 are used as the zeolite support materials.

2. Experimental

2.1. Catalyst preparation

Ion-exchange method generally results in a strong metal-support interaction and better dispersion of metal in the zeolite [16]. Hence, this method was applied to incorporate silver within the two tested zeolite supports, i.e. HY (Si/Al = 80) and HZSM-5 (Si/Al = 280) in the present study.



Fig. 1. Schematic of the reactor system.

The zeolite powder samples were supplied in their hydrogen form from Zeolyst International, USA. Silver metal was loaded on the zeolites using ion exchange method as described by Canizares et al. [16]. In this procedure, 10 g of the zeolite powder was added to 20 ml of 0.05 M AgNO3 solution. The mixture was then stirred at room temperature for 24 h. The ion exchange process was repeated until maximum possible equilibrium exchange was achieved. All the above procedures were performed in the dark due to the sensitivity of silver to light. The suspension was then filtered and dried at 80 °C, followed by calcination at 550 °C for 6 h. Before the catalysts were used in the reactor, they were converted into pellet using a hydraulic pellet making press. The pellets were then crushed and sieved into particle sizes of between 250 and 300 $\mu m.$ The particle size range was selected to limit the pressure drop across the catalyst bed as well as particle diffusion during the reaction [18].

2.2. Experimental setup

The activity of the catalysts was measured in a 9.3 mm i.d. stainless steel reactor of 450 mm length fixed in an experimental setup as shown in Fig. 1. The temperature in the reactor was monitored using a K-type temperature probe. Three sets of the probes were placed on the inlet, outlet and the centre of the catalyst bed to monitor the temperature change along its length. About 5 °C temperature difference was observed within the reactor in the axial direction.

Feed gas supplies were obtained from Malaysia Oxygen Berhad (MOX). Nitrogen gas was purged in the VOC saturator to generate the VOC vapor continuously. The purified air was simultaneously used as the makeup gas for a simulated air stream. The feed gases were pre-mixed in the mixing chamber to obtain homogeneous gas mixture before entering the reactor or by-passing it to the outlet point. The gas hourly space velocity (GHSV) was measured at inlet conditions and is defined as

$$GHSV = \frac{Q}{V_{cat}}$$
(1)

where Q is the inlet volumetric flow rate, ml/h and V_{cat} is the volume of the catalyst bed, ml.

The catalytic activity was determined under different process variables as tabulated in Table 1. The reactor was operated under excess oxygen condition at different temperatures and feed concentrations at GHSV of between 15,000 and 32,000 h⁻¹. In this study, the VOC conversion and corresponding carbon dioxide

Table 1		
Process variables in	the catalytic oxidation	study

Process variables	Unit	Value
Weight of catalyst	g	0.23
Feed flow rate	ml/min	117-250
GHSV	h^{-1}	15,000-32,000
Feed VOC concentration	ppm	1,000-4,000
Feed O ₂ concentration	%	18.3-19.6
O ₂ /VOC molar ratio	-	95.5-98.0
Reaction temperature	°C	200-500
Pressure	atm	1.7

yield were the main process parameters. The reaction was operated under steady state in which all process variables remained constant with time at any given point in the reactor before any measurement was made. The fractional conversion (X_{VOC}) is defined as

$$X_{\rm VOC} = \frac{N_{\rm initial} - N_{\rm final}}{N_{\rm initial}} \tag{2}$$

where N_{initial} is moles of VOC present initially and N_{final} is moles of VOC present after the reaction complete.

The VOC concentration was monitored using an offline Hewlett Packard, Model 5890 series II gas chromatograph equipped with an FID and Hewlett Packard 3396 Series II integrator. The separation of the gaseous products was achieved using a HP Plot Q capillary column (Divinyl benzene/styrene porous polymer, 30 m long \times 0.53 mm i.d. \times 40 μ m film thickness).

3. Results and discussion

3.1. Catalyst characterization

The silver loading content was analyzed by inductive couple plasma (ICP) using the standard method of analysis and 2.5 wt.% silver was found to be loaded in AgY zeolite while it was 3.2 wt.% in AgZSM-5 catalyst. Thus, protons in HZSM-5 were more readily exchangeable compared to those in Y zeolite. The SEM micrograph of AgY and AgZSM-5 are shown in Fig. 2. The SEM image reveals bright and dark contrast under a secondary electron detector and quantum back scattered electron, i.e. QBSD detector. It is known that elastically backscattered intensity is a function of the incident angle of the electron beam with respect to the metal planes [19]. Therefore, Fig. 2 indicates that the bright fields in the image are silver-rich regions and the dark fields are zeolite support regions.

The TEM images of AgY and AgZSM-5 are shown in Fig. 3. The TEM image showed both catalysts with uniform uni-dimensional pore structure at different orientations. A small portion of AgY porosity disappeared as the beam of TEM focused, showing low stability of this material when bombarded with high-energy electrons. Still, most of the pore structures were retained even after prolonged exposure to the beam. However, AgZSM-5 did not encounter the same problem.

Fig. 4(a) shows the XRD pattern of AgY. From the XRD peaks at $2\theta = 38$ and 44, it is clear that the metallic silver phase was successfully formed [12]. The intensity gradually increased as the silver loading increased as observed in AgZSM-5 (Fig. 4(b)). The structure and crystalline structure of ZSM-5 was not significantly changed as the characteristic peaks in the region of $2\theta = 20-25^{\circ}$ were still maintained.

3.2. Role of the silver in VOC oxidation

Catalytic oxidation of organics involves the use of a solid catalyst. The role of a catalyst is basically to allow the reaction to proceed via an alternative pathway or mechanism those results in the lower activation energy. Consequently, the reaction rate



Fig. 2. SEM image at magnification of $5000 \times$ of (a) AgY and (b) AgZSM-5.

is accelerated and corresponding change to the pre-exponential factor usually result. Therefore, the overall change to the rate of reaction would be a combined effect of a reduction in the activation energy and the value of the pre-exponential factor of the reaction.

In order to study the role of silver in oxidation of butyl acetate, blank runs were carried out to provide the background data (Table 2). It was found that no conversion took place within the investigation temperature range for the experimental run without

Table 2 Background data on the role of silver in butyl acetate catalytic combustion

Catalyst	Butyl acetate conversion (%)				
	300 °C	400 °C	500 °C		
No catalyst	0	0	0		
HZSM-5	0	5	14		
AgZSM-5	69	97	100		



Fig. 3. TEM image of (a) AgY and (b) AgZSM-5.

catalyst. The result indicated that the thermal oxidation occurring on the wall of the reactor was negligible. In the presence of HZSM-5 support in the reactor, almost no conversion was detected below 350 °C and at 400 °C; only 14% conversion was achieved. These conversions were attributed to thermal oxidation and that catalyzed by sites other than silver. These sites were likely to be acid sites that have been widely reported in the literature [6,18]. It could be deduced from the result that the thermal combustion was also negligible below 350 °C and started to be significant at 400 °C. Any improvement in the conversion beyond that caused by thermal oxidation when the metal exchanged HZSM-5 was used could therefore be attributed to the positive effect of the metal. In this study, the incorporation of silver onto HZSM-5 was found to markedly improve the conversion with significant conversion of 69, 97 and 100%, respectively achieved at 300, 400 and 500 °C. This result suggested the dominant role of metal sites in the oxidation process of butyl acetate.



Fig. 4. XRD image of (a) AgY and (b) AgZSM-5.

3.3. Catalyst activity of AgY and AgZSM-5

For the purpose of comparison, the oxidation of butyl acetate was studied over two silver-supported catalysts, namely AgY and AgZSM-5. This was based on one of the objectives of this study that was to determine the better catalyst for the oxidation reaction with respect to the metal content, acidity of the catalyst and zeolite structure. Previous result showed that more silver was exchanged into ZSM-5 as compared to the Y zeolite. The ex situ characterization could give different results compared to that obtained in in situ characterize ex situ the types of acid sites in the catalysts. This was justified based on the fact that pyridine which is a base will have specific electronic interactions with acid sites in the samples. The interaction is specific to the chemical properties the materials and should be independent of working temperature or the presence of other feed components such as oxygen and VOC under its normal working conditions. The analysis was done on the exact form of the catalysts (undergone complete preparation steps and sieved to the desired particle sizes) that would be used in the reaction. Thus the question of active site availability and accessibility should not arise.

In the present study, the activity of the catalysts was measured within 5 h time on stream and during this period, no significant catalyst deactivation was observed. However, the study on activity decay beyond this time was not within the scope of the present work. Fig. 5 shows the butyl acetate conversion with time at



Fig. 5. BA conversion as a function of time at three different temperatures $(C_{BA} = 1000 \text{ ppm}; \text{GHSV} = 15,000 \text{ h}^{-1})$ on (a) AgY and (b) AgZSM-5.

three different temperatures (300, 350 and 400 $^{\circ}$ C) over AgY and AgZSM-5 catalysts. The conversion increased with an increase in temperature. Almost 100% conversion was obtained at 400 $^{\circ}$ C showing high catalytic activity of both catalysts. Despite having

higher silver loading, AgZSM-5 showed a relatively lower activity. This result indicated that active metal content alone could not result in a good catalyst. Other contributing factors are such as metal dispersion, available surface area, exchange site and other type of active site that could catalyze the reaction such as acid sites [6,8].

In order to identify the active site that contributed to the acidity of the two tested catalysts, the catalysts were examined using FTIR spectroscopy after pyridine adsorption. The samples were exposed in excess of pyridine for 1 h after being degassed at 200 °C overnight, followed by desorption of physically adsorbed pyridine at 200 °C under vacuum. Scanning of the IR spectra was done in the wave number range of 1400–1700 cm⁻¹. Fig. 6 shows the infrared spectra of pyridine adsorbed on the catalyst in the region 1700–1400 cm⁻¹. Pyridine bound to Brønsted acid sites is associated with an infrared absorption band at 1597 cm⁻¹ and that bound to Lewis acid sites is associated with a band at 1446 cm⁻¹ [6,18] while peaks at 1638 cm⁻¹ represents strong Brønsted acid sites [19].

It could be concluded that acidity in zeolite was mainly contributed by Brønsted acid and Lewis acid sites [19]. The IR spectrum in Fig. 6 shows that both types of acid sites presented in AgY. AgZSM-5 with predominantly Lewis acid sites, since the adsorption band attributed to Brønsted sites was low. However, the number of strong Brønsted was higher in AgY, suggesting the higher overall acidity of the material. Lower Si/Al zeolites such as the Y zeolite possessed higher acidity as aluminum atoms were associated with acid sites which could be in the form of Brønsted and Lewis acid sites [20].

The butyl acetate conversion against reaction temperature is shown in Fig. 7. Both AgY and AgZSM-5 catalysts exhibited high catalytic activity in the oxidation of this organic with the total conversion achieved at a temperature above 400 °C. The T_{50} value (temperature at which 50% conversion was achieved) for butyl acetate oxidation was 230 °C for AgY and it was 280 °C for AgZSM-5. It could be concluded from the results of acidity



Fig. 6. Infrared spectra of pyridine-adsorbed on (a) AgY and (b) AgZSM-5.



Fig. 7. Comparison of the performance of different zeolite supports AgY and AgZSM-5 on combustion of butyl acetate ($C_{BA} = 1000 \text{ ppm}$; GHSV = 15,000 h⁻¹).

characterization that strong Brønsted acidity appeared to play an important role in determining the catalytic behavior of the catalysts. In particular, a higher activity was expected due to its larger number of strong Brønsted sites, especially in AgY. While the mechanism of VOC oxidation on the metal site is well described in the literatures [2–4], it is reported elsewhere that the oxidation of VOC could also be initiated by the chemisorption on Brønsted sites and acidity plays an important role in VOC oxidation process [5,15]. In the presence of both types of active sites, the activity of the catalyst was greatly enhanced.

Among the two catalyst tested, AgZSM-5 gave lower catalytic activity at low temperature. At 150 °C, there was no conversion of butyl acetate but once the reaction temperature was increased above 200 °C, the oxidation activity markedly improved. This result might be explained by the fact that due to capillary condensation, water vapor formed could easily block the micropores of Ag/zeolite preventing the occurrence of oxidation at low temperature. In view of this observation, a hydrophobic support should be preferable to minimize the pore blockage by water vapor on the catalyst surface.

The surface area and pore accessibility of a catalyst may be one of the factors that result in the better performance of AgY as compared to AgZSM-5. Y zeolite has larger pore size than ZSM-5 (7.4 Å versus 5.5 Å). As there was a least resistance for diffusion of reactants/products in and out of the larger pores in AgY catalyst, higher catalyst activity was achieved. During oxidation of butyl acetate, the catalyst was observed to become darker at high temperature (above 400 °C), which indicated the deposition of carbonaceous material. The problem was more noticeable in AgY compared to AgZSM-5.

In catalytic oxidation of VOC, the completion of the reaction is equally important as the by-product could be significantly hazardous as the original substance. Therefore, this aspect of the reaction was also studied by measuring the carbon dioxide yield during the reaction. Fig. 8 shows the comparison of the carbon dioxide yield in the oxidation of butyl acetate over AgY and AgZSM-5. Increasing carbon dioxide yield with higher reaction temperature suggested favorable result with respect the completeness of the reaction. AgY also showed better yield at



Fig. 8. Carbon dioxide yield in the oxidation of butyl acetate over AgY and AgZSM-5 (GHSV = $32,000 \text{ h}^{-1}$; $C_{VOC} = 1000 \text{ ppm}$).

all the temperatures tested. The oxidation performance of silverloaded zeolites in present study was better than the work reported by Ojala et al. [21] where noble metal, mono- and bimetallic platinum and palladium supported on γ -Al₂O₃-La and γ -Al₂O₃-Ce were tested. They reported that 100% conversion of butyl acetate was only achieved at 500 °C and the carbon dioxide yield was only about 60%. In addition, T_{50} of butyl acetate over a fresh catalyst was around 280 °C. Silver-loaded zeolites have the potential to be used as effective oxidation catalysts like noble metal over butyl acetate.

3.4. Kinetic study

The dependence of the rate of butyl acetate oxidation on the partial pressure of butyl acetate and oxygen was tested using the power law rate Eq. (3) as given below

$$(-r_{\rm v}) = k_{\rm s} P_{\rm v}^n P_{\rm o}^m \tag{3}$$

in which $(-r_v)$ is the rate of reaction, mol/h g_{cat}, k_s is the reaction rate constant; P_v and P_o are the partial pressure of VOC and oxygen, respectively. The *n* and *m* are reaction orders and the *n* value was estimated by varying the VOC partial pressure between 0.004 and 0.018 atm. Similarly, the reaction order *m* was obtained by varying partial pressure of oxygen between 0.05 and 0.2 atm. The rate of VOC decomposition can be obtained under differential reactor mode when the conversion was kept below 10%. The rate it can be expressed in term of the VOC conversion (X_{VOC}), flow rate ($F_{VOC,in}$) and weight of the catalyst, W_{cat} in Eq. (4) treating the reactor operated under differential mode [22]

$$(-r_{\rm v}) = \frac{X_{\rm VOC}F_{\rm VOC,in}}{W_{\rm cat}} \tag{4}$$

Table 3
Experimental data for the combustion of butyl acetate under differential reactor mode

Temperature (oC)	AgY			AgZSM-5		
	P _o (atm)	$P_{\rm v}$ (atm)	$-r_{\rm v}$ (mol/h-g _{cat})	$P_{\rm o}$ (atm)	$P_{\rm v}$ (atm)	$-r_{\rm v}$ (mol/h-g _{cat})
	0.20	0.004	0.0169	0.20	0.004	0.0239
200	0.15	0.009	0.0390	0.15	0.009	0.0521
300	0.10	0.013	0.0589	0.10	$\begin{tabular}{ c c c c } \hline AgZSM-5 \\ \hline \hline $P_{\rm o}$ (atm) & $P_{\rm v}$ (atm) \\ \hline 0.20 & 0.004 \\ 0.15 & 0.009 \\ 0.10 & 0.013 \\ 0.20 & 0.004 \\ 0.15 & 0.009 \\ 0.10 & 0.013 \\ 0.20 & 0.004 \\ 0.15 & 0.009 \\ 0.10 & 0.013 \\ 0.05 & 0.018 \\ \hline \end{tabular}$	0.0749
300 350 400	0.05	0.018	0.0952	0.05	0.018	0.1139
	0.20	0.004	0.0236	0.20	0.004	0.0361
Temperature (oC) 300 350 400	0.15	0.009	0.0534	0.15	0.009	0.0769
350	0.10	0.013	0.0806	0.10	0.013	0.1241
	0.05	0.018	0.1231	0.05	Pv (atm) 0.004 0.009 0.013 0.018 0.004 0.009 0.013 0.013 0.018 0.004 0.009 0.013 0.018 0.004 0.009 0.013 0.013 0.013 0.013 0.013 0.018	0.1897
	0.20	0.004	0.0263	0.20	0.004	0.0523
100	0.15	0.009	0.0614	0.15	0.009	0.1109
400	0.15 0.009 0.0390 0.15 0.009 0.15 0.009 0.0390 0.15 0.009 0.10 0.013 0.0589 0.10 0.013 0.05 0.018 0.0952 0.05 0.018 0.20 0.004 0.0236 0.20 0.004 0.15 0.009 0.0534 0.15 0.009 0.10 0.013 0.0806 0.10 0.013 0.05 0.018 0.1231 0.05 0.018 0.20 0.004 0.0263 0.20 0.004 0.15 0.009 0.0614 0.15 0.009 0.10 0.013 0.0981 0.10 0.013 0.05 0.018 0.1531 0.05 0.018	0.1668				
	0.05	0.018	0.1531	0.05	0.018	0.2657

Table 4

Reaction rate constants, reaction order, activation energies and pre-exponential factor estimated from power law model for oxidation of butyl acetate

Catalyst T	Temperature (°C)	Rate constant, k_s'	React	ion order	Activation energy, E_a (kJ/mol)	Pre-exponential factor, A
			m	п	_	
	300	8.31	0	1.03		
AgY	325	8.86	0	1.04		
	350	9.25	0	1.09	19.78	469.74
	375	12.80	0	1.02		
	400	17.40	0	1.06		
AgZSM-5	300	6.59	0	1.02		
	325	7.24	0	1.06		
	350	14.53	0	1.09	32.26	5420.23
	375	11.26	0	1.05		
	400	15.46	0	1.06		
	400	15.46	0	1.06		

The nonlinear analysis was used to determine the reaction parameters representing the experimental data [22]. The results for oxidation of butyl acetate are tabulated in Table 3. By fitting the data to Eq. (3), the reaction orders and rate constant could be estimated and the results are summarized in Table 4. On both tested catalysts, the reaction order with respect to VOC was close to 1.0, while those of oxygen showed zero values. In agreement with findings by Garetto et al. [13] on propane oxidation on supported Pt catalyst, the rate of butyl acetate oxidation process showed higher dependency on the concentration of organic substance compared to oxygen. However, this relationship is only true under oxygen excess condition.

The apparent activation energy, E_a and pre-exponential factor, A of butyl acetate oxidation was obtained from Arrhenius plot as shown in Fig. 9. The activation energy calculated from the plot was 19.78 kJ/mol for AgY and 32.26 kJ/mol for AgZSM-5. The lower value of activation energy correctly suggested the higher activity of AgY compared to AgZSM-5. This was an interesting finding bearing in mind that AgZSM-5 had higher silver loading. Thus, the exchange sites and pore characteristics of the zeolites were also expected to play significant roles in catalytic activity of metal exchanged zeolites. The overall rate of reaction was also found to be influenced by the value of pre-exponential factor, but to a lesser extent. Fig. 10(a) and (b) show parity plot of rate of reaction of butyl acetate oxidation where predicted data are plotted against experimental data at different temperatures for AgY and AgZSM-5, respectively. The rates of reaction for both catalysts were suc-



Fig. 9. Arrhenius plot for determining activation energy, E_a and pre-exponential factor, A.



Fig. 10. Predicted vs. experimental reaction rate of butyl acetate combustion at different reaction temperature on (a) AgY and (b) AgZSM-5.

cessfully predicted by this model between 300 and 400 °C with deviations within $\pm 5\%$. With differences in the metal loading, pore characteristics and hydrophobicity of the catalysts, no significant impact was detected on the fitting to the power law model. Thus, butyl acetate oxidation kinetics could be concluded to be satisfactorily presented by simple power law rate model.

4. Conclusions

Silver metal was successfully loaded into the HY (Si/Al = 80) and HZSM-5 (Si/Al = 280) zeolites using ion exchange method. The performance of silver-loaded zeolite for butyl acetate oxidation was found to depend on the pore characteristics, acidity and hydrophobicity of the zeolites. Both AgY and AgZSM-5 exhibited high catalytic activity in the oxidation of butyl acetate with the total conversion achieved at above 400 °C. Despite lower silver content, AgY showed better activity, attributed to better metal dispersion, surface characteristics and acidity, and its pore system. The main oxidation product was carbon dioxide. Power law model reasonably fitted the experimental data for the oxidation of butyl acetate over both AgY and AgZSM-5 catalysts. Under differential reactor mode, the reaction order, *m* with respect to oxygen was found to be close to zero while the reaction order with respect to VOC, *n* took a positive value close to 1. The activation energy estimated from Arrhenius equation gave a value of 19.78 kJ/mol for AgY and 32.26 kJ/mol for AgZSM-5, respectively. This result correctly suggested the higher activity of AgY as compared to agZSM-5.

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References

- E.C. Moretti, Practical Solutions for Reducing Volatile Organic Compounds and Hazardous Air Pollutants, American Institute of Chemical Engineers, New York, 2001.
- [2] R. Rachapudi, P.S. Chintawar, H.L. Greene, Aging and structure/activity characteristics of Cr-ZSM-5 catalyst during exposure to chlorinated VOCs, J. Catal. 185 (1999) 58–72.
- [3] A.Z. Abdullah, M.Z.A. Bakar, S. Bhatia, Effect of hydrogen treatment on the performance of Cr-ZSM-5 in deep oxidative decomposition of ethyl acetate and benzene in air, Catal. Commun. 4 (11) (2003) 555–560.
- [4] H.L. Tidahy, S. Siffert, F. Wyrwalski, J.F. Lamonier, A. Aboukaïs, Catalytic activity of copper and palladium based catalysts for toluene total oxidation, Catal. Today 119 (2007) 317–320.
- [5] J. Tsou, P. Magnoux, M. Guisnet, J.J.M. Orfao, J.L. Figueiredo, Catalytic oxidation of volatile organic compounds; oxidation of methyl-isobutylketone over Pt/zeolite catalyst, Appl. Catal. B 57 (2005) 117–123.
- [6] R. Lopez-Fonseca, J.I. Gutiérrez-Ortiz, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Catalytic combustion of chlorinated ethylenes over Hzeolites, J. Chem. Technol. Biotechnol. 78 (2002) 15–22.
- [7] K. Everaert, J. Baeyens, Catalytic combustion of volatile organic compounds, J. Hazard. Mater. B 109 (2004) 113–139.
- [8] J.R. González-Velasco, A. Aranzabal, R. López-Fonseca, R. Ferret, J.A. González-Marcos, Enhancement of the catalytic oxidation of hydrogenlean chlorinated VOCs in the presence of hydrogen-supplying compounds, Appl. Catal. B 24 (2000) 33–43.
- [9] G.B.F. Seijger, P.V.K. Niekerk, K. Krishna, H.P.A. Calis, H. van Bekkum, C.M. van den Bleek, Screening of silver and cerium exchanged zeolite catalysts for the lean burn reduction on NOx with propane, Appl. Catal. B 40 (2003) 31–42.
- [10] C. Shi, M. Chenga, Z. Qua, X. Baoa, Investigation of the catalytic roles of silver species in the selective catalytic reduction of NOx with methane, Appl. Catal. B 51 (2004) 171–181.
- [11] E.M. Cordi, J.L. Falconer, Oxidation of volatile organic compounds on a Ag/Al₂O₃ catalyst, Appl. Catal. A 151 (1997) 179–191.
- [12] S. Baek, J. Kim, S. Ihm, Design of dual functional adsorbent/catalyst system for the control of VOCs by using metal-loaded hydrophobic Y-zeolites, Catal. Today 93–95 (2004) 575–581.
- [13] T.F. Garetto, E. Rincón, C.R. Apesteguía, Deep oxidation of propane on Pt-supported catalysts: drastic turnover rate enhancement using zeolite support, Appl. Catal. B 48 (2004) 167–174.
- [14] J.C. Wu, T. Chang, VOC deep oxidation over Pt catalysts using hydrophobic supports, Catal. Today 44 (1998) 111–118.
- [15] R. Lopez-Fonseca, J.I. Gutiérrez-Ortiz, J.L. Ayastui, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Gas-phase catalytic combustion of chlorinated VOC binary mixtures, Appl. Catal. B 45 (2003) 13–21.
- [16] P. Canizares, A.D. Lucas, F. Dorado, A.D. Asencio, Characterization of Ni and Pd supported on H-mordenite catalysts: influence of the metal loading method, Appl. Catal. A 169 (1998) 137–150.
- [17] P. Papaefthimiou, T. Ioannides, X.E. Verykios, Combustion of nonhalogenated volatile organic compounds over group VII metal catalysts, Appl. Catal. B 13 (1997) 175–184.

- [18] A.Z. Abdullah, M.Z.A. Bakar, S. Bhatia, Performance study of modified ZSM-5 as support for bimetallic chromium-copper catalysts for VOC combustion, J. Chem. Technol. Biotechnol. 79 (2004) 761–768.
- [19] Y.S. Ooi, R. Zakaria, A.R. Mohamed, S. Bhatia, Synthesis of composite material MCM-41/beta and its catalytic performance in waste used palm oil cracking, Appl. Catal. A 274 (2004) 15–23.
- [20] H.G. Karge, M. Hunger, H.K. Beyer, Characterization of zeolite-infrared and nuclear magnetic resonance spectroscopy and X-ray diffraction, in:

J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites: Fundamental and Applications, Springer Verlag, Berlin, Heidelberg, New York, 1999, pp. 198–326.

- [21] S. Ojala, U. Lassi, M. Härkönen, T. Maunula, R. Silvonen, R.L. Keiski, Durability of VOC catalysts in solvent emission oxidation, Chem. Eng. J. 120 (2006) 11–16.
- [22] H.S. Fogler, Elements of Chemical Reaction Engineering, 3rd ed., Prentice-Hall International, New Jersey, 1999, 254.