ROLE OF ZEOLITES IN CATALYTIC ABATEMENT OF VOLATILE ORGANIC COMPOUNDS (VOCs) POLLUTION

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ABSTRACT

This article reviews the role of zeolites in the abatement of VOC emission to the atmosphere. The incorporation of metal species into zeolites' lattice structure through ion exchange will convert these materials into effective catalysts for VOC removal. The most active metals are noble metals (Pt and Pd) and some transition metals (Cr, Co, Cu, Fe, Mn and V) but the activity varies with the type of VOC used. The high activity of zeolite catalysts is commonly associated with high metal loading, high metal dispersion and high total surface area offered by these materials. This property, coupled with the size and shape features of the zeolites, allow the materials to be used effective catalysts in extremely selective reactions Thermal and hydrothermal stability of zeolite catalysts received much attention among researchers as the activity of the catalyst should be sustained in a proionged high temperature operation in humid air stream. Hydrophobicity and thermal resistance are found to increase with an increase in SiO_2/Al_2O_3 ratio of zeolites. Chlorinated VOCs pose major challenge to the activity and viability of catalytic decomposition process. The decomposition of low H/Cl ratio VOCs is relatively low and problems of catalyst deactivation and formation of higher chlorinated species still remain unsatisfactorily resolved. The presence of water in feed stream can retard the activity of zeolite catalysts due to competitive adsorption but for low H/Cl ratio VOCs, it serves as H supplier to suppress the formation of higher chlorinated by-products in favour of HCl. Hydrophobic zeolites have recently gained much attention due to their ability to selectively remove one or more organic pollutants from humid air streams and can act as dual-function sorbent-catalyst.

INTRODUCTION

Volatile organic compounds (VOCs) are an important class of air pollutants, emitted from many industrial processes and transportation activities (Becker and Förster, 1998 ; Niu *et al.*, 1999). Catalytic combustion is one of the most promising technologies for the decomposition of VOCs due to its definitive character and save of energy. Catalytic oxidative decomposition is similar to thermal oxidation in that the gaseous impurities to be destroyed are reacted with oxygen at elevated temperature to form primarily carbon

dioxide and water vapour. It differs in that the reactions are made to occur at a relatively low temperature by the use of a solid catalyst. Typically, the reaction temperature is in the range of 150° to 480°C (Rafson, 1998), and is determined on the basis of the material being oxidized.

Noble metals (Pt and Pd) are among the most commonly used metal catalysts in investigations of VOC catalytic decomposition (Brink *et al.*, 2000). Apart from the higher specific activity, they are favoured because of their resistance to sulfur poisoning (Niu *et al.*, 1999) than oxide catalysts. In addition, highly dispersed Pt and Pd catalysts are easily prepared using a number of support materials (Zhang *et al.*, 1997). According to Zwinkels *et al.* (1993), there is correlation between the rate of hydrocarbon oxidation and metal-oxygen bond strength. Generally, this correlation can be presented as so-called volcano plot (Figure 1). A clear maximum in the curve is observed for platinum-group metals.

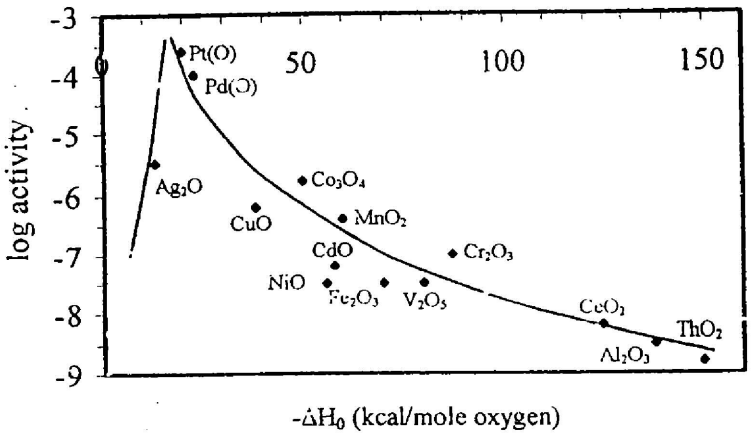

Figure 1 . Volcano-type plot indicating specific activity in hydrocarbon oxidation as a function of the metal-oxygen bond strength (Zwinkels *et al.*, 1993).

Metal (Group V_B to II_B) oxides are, in general, less active than the noble metals but are more resistant to poisoning (Sinquin *et al.*, 2000). The most active oxides have a p-semiconductor nature and the most frequently used ones are the oxides of V, Cr, Mn, Fe, Co, Ni and Cu. Chromium oxide is claimed to be one of the most active catalysts in chlorinated VOC destruction (Padilla *et al.*, 1999), but the authors reported the formation of highly toxic by-products such as chromium oxychloride ($Cr_2O_2Cl_2$) and phosgene ($COCl_2$).

ZEOLITES

Zeolites are members of a family of minerals called tectosilicates, which includes dense-phase materials such as the feldspars and the various form of silica (Marcus and Cormier, 1999). They are microporous, high-internal-surface-area crystalline materials with an open three-dimensional framework consisting of tetrahedral AlO_4^{-5} and SiO_4^{-4} units linked through shared oxygens. The general framework formula of zeolites is $(AlO_2)_x(SiO_2)_{(n-x)}$, where n is the number of tetrahedra per unit cell and $n/2 \geq x$. There are

40 known naturally occurring zeolites and more than 150 synthetic ones (Chen *et al.*, 1994).

Molecular sieving and shape-selective catalysis of Zeolites

Zeolites are unique porous solids due to their crystalline structure and strictly regular pore and cage dimensions (Blauwhoff *et al.*, 1999). Figure 2 visualizes this specific property of zeolites which make them in many cases superior over other (amorphous) solids. As can be seen, zeolites possess strictly regular pore and cage.

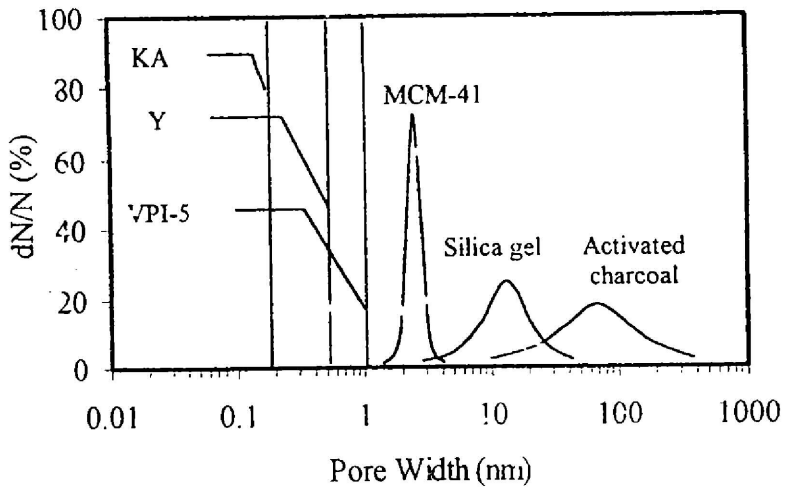

Figure 2 : Pore width distributions for selected porous solids (Weitkamp *et al.*, 1999).

Molecular sieving is the selective adsorption of molecules, whose dimensions are below a certain critical size, into the intracrystalline void system of a molecular sieve (Chen *et al.*, 1994). This property is so important and easy to understand that molecular sieve is taken to be synonym for zeolite. Example of molecular sieving is the separation of *para*-xylene/*meta*-xylene mixtures with zeolite HZSM-5 as adsorbent and separation of the low-octane unbranched C_5/C_6 alkanes from their high-octane branched isomers (Blauwhoff *et al.*, 1999).

Shape-selective catalysis can be described as the combination of catalysis with the molecular sieve effect (Weitkamp *et al.*, 1999). In the case of shape-selective catalysis in zeolites, the combination of both properties, viz. pores of molecular dimensions and catalytically active sites inside these pores, is exploited to control the selectivity of catalytically conducted reactions.

Metal-exchanged zeolites

Zeolites have wide potential to be used as catalyst for gas-phase decomposition of VOC. These materials can be formulated to carry active metal catalysts through metal exchange procedure to give near molecular level metal dispersion in their pores (Weitkamp *et al.*, 1999). The presence of multivalent cations within the zeolite matrix has been found to increase its activity by creating highly acidic centers through hydrolysis of charged

cations (Becker and Förster. 1998). The for the decomposition of VOCs, among others, the following systems have been investigated : Cu-Y and Pd-Y/benzene (Becker and Förster, 1998), Pd-HFAU/*o*-xylene (Dégé *et al.*, 2000) and Cr-ZSM-5/TCE (Chintawar and Greene, 1997) and the results are very promising (Table 1). Chintawar and Greene (1997) and Becker and Förster (1998) claimed that for most zeolite catalysts studied, high activity of transition metal-exchanged zeolites as catalysts for deep oxidation as well as partial oxidation reactions has been noticed.

Zeolite Hydrophobicity

Hydrophobicity and thermal resistance are found to increase with an increase in SiO_2/Al_2O_3 ratio of zeolites (Marcus and Cormier. 1999). Hydrophobic zeolites have recently gained much attention due to their ability to selectively remove one or more organic pollutants from humid air streams (Dégé *et al.*, 2000). More hydrophobic zeolites such as ZSM-5 types, dealuminated faujasites and silicalite are found to be especially effective for such applications (Marcus and Cormier. 1999). This property is expected to eliminate some of the problem associated with catalyst poisoning in the presence of high humidity.

THE EFFECT OF HUMIDITY

Most of the industrial waste gases are often saturated with water vapour. Moisture can cause considerable problems with the practical application of catalytic emission control in the sense that it generally inhibits or poisons the oxidation catalyst especially at low temperatures (Becker and Förster, 1998). The fact that the catalysts are more reactive in the absence of water shows that while water is a necessary reagent for the hydrolysis reaction (Sinquin *et al.*, 2000), its presence also has an inhibiting effect on the decomposition reaction (Ng *et al.*, 1998). Patterson *et al.* (1999) in their research concluded that without water replenishing the surface hydroxyl groups the hydrolytic activity is not sustainable. Thus the development of low-temperature water-resistant catalysts is highly desirable

Zeolites are generally very unstable and lose their activity easily in the presence of high humidity. Water vapour can influence the activity of metal-exchanged zeolite catalysts in two ways. First, water molecules compete with reactant molecules for the surface active sites and therefore, affect the adsorption and activation of VOC and oxygen. Second, the accumulation of water in the pores by adsorption and capillary condensation can affect the interaction between active metal species and zeolite support, and can even deactivate some surface active sites (Holmgren *et al.*, 1999). Zeolites also might undergo some dealumination at sufficiently high temperature in the presence of high humidity. This can be identified by a sharp drop in specific surface area, loss in crystallinity and ultimately leads to the collapse of the structure.

Hydrophobic catalysts have been intensively investigated for humid VOC decomposition applications for their high low affinity towards water and higher hydrothermal stability (Chintawar and Greene, 1997 ; Niu *et al.*, 1999). Water adsorption capacity using thermal gravimetry method has been the best way of demonstrating hydrophobicity of the catalysts. Successful application of these zeolites has been reported. Niu *et al.* (1999) reported the synthesis of siliceous zeoliteY on treating NaY zeolite with $SiCl_4$ followed

Table 1 : Review of zeolite catalysts for VOC decomposition study.

Reference	Operating conditions				Remarks
	Catalyst	VOC	Temperature	Space velocity	
Chatterjee and Greene (1991)	H-Y, Cr-Y & Ce-Y (Si/Al=2.5)	Methylene chloride	300°-475°C	3,500 hr^{-1}	Catalytic activity and the oxygen chemisorption decreasing in the order : Cr-Y > H-Y > Ce-Y. H_2O reduced the conversion between 10%-60% and appeared to temporarily deactivate the catalysts. HCl and CO were major the components in product gas.
Karmakar and Greene (1992)	Co-Y, Ce-Y & Cr-Y (Si/Al=1.27)	CFC11 & CFC12	150°-400°C	10,500 hr^{-1}	Catalyst deactivation detected and, CCl_4 and $COCl_2$ by-product significantly presented in the product gas. Cr-Y was the most active and resistant to deactivation. Complete conversion was achieved at temperature >250°C for CFC11 and >400°C for CFC12.
Chintawar and Greene (1997)	Cr-Y & Co-Y (Si/Al=2.5)	Vinyl chloride, TCE & perchloroethylene	250°-400°C	2,400 hr^{-1}	Cr-Y showed better adsorption capacity for all reactants. The catalytic activity diminished with increasing Cl content of the reactant. High cation dispersion and acidity than corresponding γ-Al_2O_3 supported catalysts.
Becker and Förster (1998)	Na-, Cu- & Pd-Y (Si/Al=2.5)	Benzene, toluene & xylene	220°-350°C	45,000 hr^{-1}	Complete conversion was achieved at 350°C for all reactants. No significant difference between the activity of Na-Y and Cu-Y but Pd-Y activity significantly superior than the two. Further improvement in Pd-Y activity after H_2 pre-treatment.
Ono *et al.* (1998)	Cu-, Zn-, Mn-, Fe-, Co- & Ni-ZSM-5 (Si/Al=45)	Trimethylamine (TMA)	100°-400°C	11,000 hr^{-1}	The highest activity was achieved on Cu-ZSM-5 and Fe-ZSM-5 and the activity increased with increasing metal loading. Metals were found to weaken the strong acid sites of H-ZSM-5 and strongly interacted with TMA adsorbed.
Niu *et al.* (1999)	Pd-siliceous Y (Si/Al>150)	*n*-hexane	100°-400°C	6,000 ml/hr-g_{cat}	A catalyst with high Pd dispersion (≈55%), high thermal and hydrothermal stability than Pd/γ-Al_2O_3. Better *n*-hexane conversion at temperature >250°C.
Dégé *et al.* (2000)	Pd/FAU (Si/Al=4, 17 & 100)	*o*-xylene	150°-330°C	18,000 hr^{-1}	Coke retention within the zeolite pores at low temperature. Rate of *o*-xylene decomposition increased with Pd content. Increase in Si/Al ratio decreased the number of acid sites, the coke formation but increased the *o*-xylene decomposition efficiency.

Si/Al = SiO_2/Al_2O_3 ratio of the zeolites

by steam treatment. Excellent thermal and hydrothermal stability have been demonstrated.

DECOMPOSITION OF CHLORINATED VOCs

Until recently, the use of catalytic oxidizers was restricted to nonhalogenated streams because halogen, especially chlorine, would poison the catalysts used. Brink *et al.* (1998), for example, reported that despite were powerful oxidation catalysts, noble metals can easily form inorganic chlorides with deactivation as a likely consequence. As a general rule, catalytic activity decreases with increasing chlorine content (or Cl/C) of a molecule. Unfortunately, a clear correlation between the catalytic activity and the bond energy, thermal stability and heat of formation has yet to be established (Chintawar and Greene, 1997).

Catalytic oxidation of chlorinated VOCs constitutes one of the most significant challenge as far as deep or complete oxidation is concerned. Ideally, there should be only HCl as the chlorine-containing species in the product gas. Chintawar and Greene (1997) have shown that among the first row transition metals, including Ni and Mn, only Cr has the ability to catalytically destroy CE effectively. However, chromium residues are an environmental concern. Cr containing catalysts are also associated with the presence of elemental Cl_2 in the product gas due to well documented Deacon reaction (Brink *et al.*, 1998);

$$2HCl + \tfrac{1}{2} O_2 \rightleftharpoons Cl_2 + H_2O$$

Therefore, finding either an environmental friendly replacement or an active catalyst formulation containing very low levels of chromium would be worthwhile. The quest for ideal catalysts for chlorinated VOC decomposition has received much attention among researchers.

The addition of water as co-feed in the inlet gas has received considerable attention among researchers (Becker and Förster, 1998 ; Padilla *et al.*, 1999 ; Velasco *et al.*, 2000). Water can act as an H supplier to the decomposition of high Cl/H ratio substances to improve selectivity toward HCl (Velasco *et al.*, 2000) and to suppress Deacon reaction (Chatterjee and Greene, 1991). Beside water, hexane and toluene (Velasco *et al.*, 2000) and, methane and propane (Schneider *et al.*, 2000) have also been studied for the same positive role. Karmakar and Greene (1992) in their decomposition study of CFC11 on H-Y found that although nearly complete conversion is achieved, $COCl_2$, CCl_4 and CFC12 present in a significant amount in the product gas. Normally, selectivity toward deep oxidation products deteriorates with time due to catalyst deactivation. Brink *et al.* (2000) have extended the scope of the study to the removal of chlorine from catalyst surface. They came to the conclusion that removal of Cl from the surface (mainly in the form of HCl) by hydrocarbons is responsible for reducing the formation of by-products.

THERMAL AND HYDROTHERMAL STABILITY

Becker and Förster (1998) claimed that compared to alumina supporting Pd catalysts, Pd exchanged zeolite Y catalysts have higher and more durable activity in low-temperature catalytic combustion of benzene. Unfortunately, the catalysts are very unstable and lose their activity easily in steam because the hydrothermal treatment results in sharp dealumination of zeolites framework and ultimately leads to the collapse of the structure.

Luckily, an increase in SiO_2/Al_2O_3 of the zeolites has been demonstrated to significantly improve their hydrothermal stability (Chintawar and Greene, 1997). Recently, siliceous Y zeolite has been reported by Niu *et al.* (1999) to exhibit more excellent thermal and hydrothermal stability than common dealuminated Y zeolite. It can keep its structure perfectly even in 100% steam at 1000°C. For these characteristics, siliceous Y zeolite may be a potential support of catalysts for high-temperature catalytic combustion.

AD-CAT TECHNOLOGY

The presence of VOC pollutants in air is normally featured by high-volume/low-concentration. To cope with this situation, it is feasible to establish a combined adsorption/catalytic decomposition (Ad-Cat) process (Jiang *et al.*, 1999). It refers to an adsorption process complemented by a catalytic decomposition step to ultimately diminish the concentrated pollutant stream produced during the regeneration step. It can either be operated using the same dual-function sorbent/catalyst bed (Atwood *et al.*, 1998 ; Gan *et al.*, 2001) or the adsorption and catalysis decomposition are done separately (Jiang *et al.*, 1999).

In adsorption step, the VOC pollutant is trapped at, as-received conditions, and afterwards released to a relatively small amount of pre-heated air. As the recovered pollutant stream is highly condensed, adiabatic temperature rise in the sorbent/catalyst bed is high. The catalytic decomposition of this secondary air flow is, therefore, more efficient and economic in the sense of energy consumption. Study on this new concept of VOC removal has been initiated since as early as 1997 by Chintawar and Greene (1997). Atwood *et al.* (1998) in their study reported greater than 99 % TCE destruction using Cr-ZSM-5 and specific bed heating parameters significantly affected conversion and desorption/reaction time. As high as 80% -90% energy saving were also demonstrated.

Hydrophobicity of zeolites is known to increase with an increase in SiO_2/Al_2O_3 ratio. It should be noted that the hydrophobic nature of pentasil zeolites (ZSM-5, silicalite etc.) has been known for a long time. If the performance of adsorption/catalytic decomposition processes were to be carried out in a single vessel, it is interesting to search for an optimum SiO_2/Al_2O_3 ratio of the ZSM-5 type zeolites which gives preferred performance both as a sorbent and a catalyst. Chintawar and Greene (1997) in their work found that TCE adsorption capacity of ZSM-5 in humid stream increased by 68 % with an increase in the SiO_2/Al_2O_3 ratio from 30 to 120. SiO_2/Al_2O_3 ratio of 80, however, gives preferred performance as dual-function sorbent/catalyst.

CONCLUSIONS

Catalytically active metal species can be incorporated into zeolites' lattice structure through ion exchange to produce effective catalysts for VOC decomposition. The most active metals are noble metals (Pt and Pd) and some transition metals (Cr, Co, Cu, Fe, Mn and V) but the activity varies with the type of VOC used. Metal-exchanged zeolite catalysts commonly demonstrate near molecular level dispersion with specific surface area almost similar to that of parent zeolites. Hydrophobicity and thermal resistance are found to increase with an increase in SiO_2/Al_2O_3 ratio of zeolites. Major setback of catalyst deactivation and formation of higher chlorinated species always attributed to the decomposition of low H/Cl ratio VOCs. This problem can partly be solved by introducing

water in feed stream to serve as H supplier to suppress the formation of higher chlorinated by-products in favour of HCl. Hydrophobic zeolites with certain optimum SiO_2/Al_2O_3 ratio can be tailored for use as dual-function sorbent-catalyst for their high affinity toward organics.

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