

INFLUENCE OF NH₃ DURING THE CATALYTIC OXIDATION OF A 1-METHYLNAPHTHALENE / 1,2-DICHLOROBENZENE MIXTURE OVER Pt/ZEOLITE CATALYSTS

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Introduction

Reducing the emissions of toxic substances such as POPs (persistent organic pollutants) is one of the major problems faced by industrialized countries. POPs include a wide range of pollutants, which are semi-volatile, bioaccumulative, persistent and toxic. Their presence in the environment is harmful to humans but also to the ecosystems. Hence, these pollutants have received special attention for the last 10 years [1]. POPs are the by-products of incomplete combustion and are formed in many types of combustion and thermal processes, including waste-to-energy incineration. As the APC (Air Pollution Control) technology has greatly improved over the last years, new R&D routes are investigated to control POPs trace emissions. The catalytic oxidation technology is the most suitable for low temperature destruction of these pollutants present at low concentrations. The metal oxides or noble metals supported have been studied during the past few years to destroy these pollutants. Recently, acids zeolites have gained interest as alternative catalysts to noble metals and metal oxides [2-5]. Thus, the faujasite type zeolite proved to be a promising catalyst for the degradation of 1,2-dichlorobenzene [4, 5] and a mixture of benzofurane / 1,2-dichlorobenzene [6]. This study focuses on the catalytic oxidation of a mixture of 1-methylnaphthalene (1-MN), a model molecule representative of polycyclic aromatic hydrocarbons (PAHs), and 1,2-dichlorobenzene, a precursor of dioxins. The experiments were carried out on Pt/zeolites in the absence and in the presence of ammonia, commonly injected in the flue gas of waste-to-energy units to reduce the release of NO_x (SNCR/SCR processes).

Materials and method

The faujasite type zeolite was used in protonic form (USHY, Si/Al = 5). The preparation of platinum catalyst was carried out by a cation exchange of zeolite from the Pt(NH₃)₄Cl₂ complex under the following conditions: the exchange was carried out at room temperature, at a pH between 6 and 7, which was controlled by addition of NH₄OH under moderate agitation (300 rpm) for 3 hours. The cation exchange was followed by calcination at 350°C (1°C/min) under dry air in dynamic system for 4h. Before oxidation reaction, the samples were pelletised, crushed and sieved to obtain a grain size between 0.2 and 0.4 mm then calcined under dry air at 500°C for 4 hours. The catalysts properties including the number of accessible platinum atoms (nPt) are given in table 1. The determination of the number of acid sites was performed by pyridine adsorption followed by infrared spectroscopy and the platinum dispersion was determined through carbon monoxide adsorption followed by infrared spectroscopy.

The oxidation of the 1-methylnaphthalene/1,2 dichlorobenzene mixture was carried out at a constant temperature in a fixed bed reactor containing 230 mg of catalyst. For each experiment, a new catalyst sample has been used and the reactions were monitored as a function of time. The mixture was composed of 240 ppm of 1-methylnaphthalene (1-MN), 305 ppm of 1,2 dichlorobenzene and 14 667 ppm of water for the standard reaction and with 100 ppm of NH₃ when reactions were carried out in the presence of ammonia. The space velocity (VVH) was 20 000 h⁻¹. The reaction products were analyzed on line by gas chromatography (Varian 3400) equipped with two detectors: a TCD detector for the analysis of carbon dioxide and a FID detector for the analysis of hydrocarbons.

Results and discussion

Oxidation of 1-MN / 1,2 dichlorobenzene mixture

Figure 1 shows the light off curves of the 1-MN and 1,2-dichlorobenzene oxidation on 0.8% PtUSHY catalyst. It is noticeable that 1-MN is the most easily degraded compound. Indeed, from 250°C 1-MN is completely destroyed when it is the only compound in the feed. In contrast, whatever the operating conditions, the 1,2-dichlorobenzene is completely destroyed at 400°C. However, the presence of 1-MN in the mixture seems to have no promoting effect on the conversion of 1,2-dichlorobenzene. Whatever the reaction temperature, the formation of chlorinated by-products was not observed during the reaction and no deactivation occurred in 7 hours reaction.

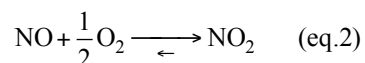
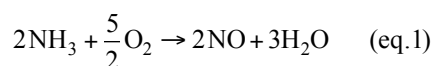
The 0.8%PtUSHY sample was characterized after 7 hours reaction at 400°C by pyridine (acidity) and carbon monoxide (Pt dispersion) adsorption followed by infrared spectroscopy (table 2). During the reaction, the platinum sintering is negligible and the number of Brønsted acid sites is almost constant. However we can observe a decrease of Lewis acid sites (-38%). This decrease can be attributed to a removing of extra framework aluminium species present in the parent zeolite. This phenomenon was due to the presence of steam and HCl in the feed, which led to the leaching of these aluminium species.

Oxidation of 1-MN / 1,2 dichlorobenzene mixture in the presence of ammonia

Besides POPs, ammonia as is also present in the municipal incinerator effluent in order to remove NO_x. It is important to know the effect of ammonia and the effect of the products of ammonia oxidation (nitrogen dioxide and monoxide) on the activity of the catalyst.

Whatever the conditions (presence and absence of NH₃) 1-MN is totally destroyed from 250°C. Figure 2 shows that in the presence of NH₃, the 1,2-dichlorobenzene is totally destroyed at 350°C against 400°C in the absence of NH₃. Furthermore the formation of carbon dioxide (caused by the mixture oxidation) increases when the reaction was carried out in the presence of NH₃.

In the presence of NH₃ at 250 and 300°C, we noticed the presence of by-products in small amounts. It is important to note that the presence of these products has not been observed at 350°C, the temperature of total destruction of 1,2-dichlorobenzene. These compounds identified by GC/MS coupling are mainly PhCl_x (x = 2 or 3). At 300°C, the sum of PhCl₂ concentration remains lower than 1.4 ppm and 25 ppm of PhCl₃ are also formed. The PhCl₃ production can be due to the rapid reduction of platinum atoms during the reaction [6]. The better destruction of 1,2-dichlorobenzene in mixture with 1-MN and in presence of NH₃ can be attributed to NO₂ production from NH₃ oxidation:



According to the work of Pesant and al. [7], it is possible to describe the oxidation reaction of the 1-MN / 1,2-dichlorobenzene mixture. The first step is nitrogen dioxide production from ammonia oxidation. It is well known in the literature that nitrogen dioxide is a stronger oxidant than oxygen and nitrogen monoxide [8, 9]. Two reactions can be proposed, the first is the classical oxidation with oxygen over Pt species and the second is the oxidation of the reactants by NO₂ formed from NH₃ (figure 3). In this reaction the Selective Catalytic Reduction (SCR process) can be envisaged and NO₂ can be reduced by 1-MN or/and 1,2-dichlorobenzene to produce nitrogen (N₂). The presence of NH₃ increases the oxidation rate of the reactants.

PtUSHY catalyst is a very interesting and promising catalyst to remove POPs formed in combustion and thermal processes, including waste-to-energy incineration. PtUSHY is able to destroy a mixture representative of HAP/dioxins (1MN/1,2-dichlorobenzene mixture). 1-MN can be removed from 250°C and 1,2-dichlorobenzene the more difficult product to destroy, near 400°C. The presence of ammonia in the mixture have a promoting effect on the destruction of these molecules and increases the selectivity in carbon dioxide at low temperature.

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Table 1: Characterization of fresh catalysts

Catalysts	Number of acids sites ($\mu\text{mol.g}^{-1}$)		Pt dispersion (%)	nPt ($\times 10^{18}$ atoms.g $^{-1}$)
	Brønsted	Lewis		
USHY	537	165	/	/
0.8%PtUSHY	460	138	15	4

Table 2: Characterization of catalysts after 7hours reaction with 1-MN/ 1,2-dichlorobenzene at 400°C

Catalysts	Number of acids sites ($\mu\text{mol.g}^{-1}$)		Pt dispersion (%)	nPt ($\times 10^{18}$ atoms.g $^{-1}$)
	Brønsted	Lewis		
0.8%PtUSHY ^a	460	138	15	4
0.8%PtUSHY ^b	475	85	14	4

a: fresh catalyst

b: after 7h reaction at 400°C

Figure 1: Conversion over 0.8%PtUSHY catalyst of 1-methylnaphthalene (◆) and 1,2-dichlorobenzene (■) in the mixture and 1,2-dichlorobenzene alone (▲) taken after 7h reaction as function of the temperature

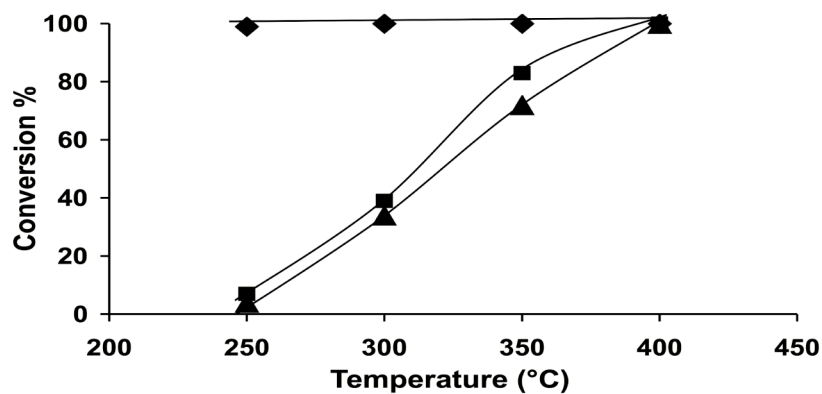


Figure 2: Conversion over 0.8%PtUSHY catalyst of 1,2-dichlorobenzene (■) in the mixture with NH₃ and (◆) in the mixture without NH₃ taken after 7h reaction as function of the temperature

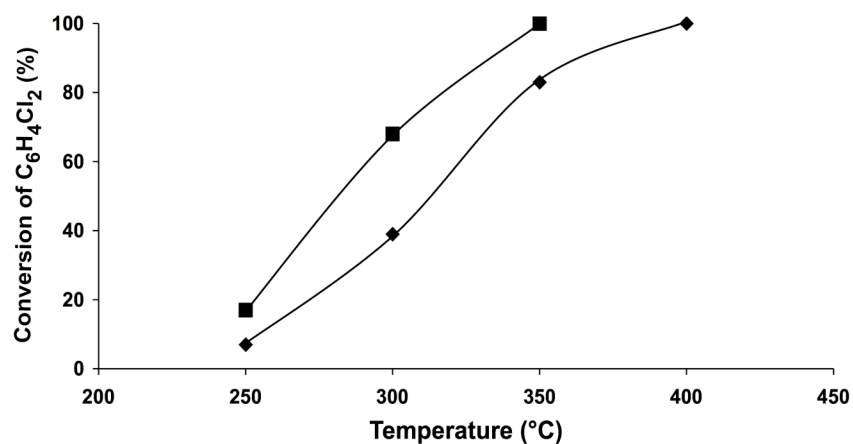


Figure 3: Catalytic oxidation of 1-MN (C₁₁H₁₀)/1,2-dichlorobenzene (C₆H₄Cl₂) using NO₂ as oxidant.

