Catalytic Conversion of 1,2-Dichlorobenzene Over Mesoporous Materials from Zeolite

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In this study, 1,2-dichlorobenzene (DCB), an important precursor of PCDDs and PCDFs, was chosen as a suitable model compound for the catalyzed deep oxidation of dioxin. The recently developed mesoporous materials from zeolites (MMZ) were used for the first time as a support for an oxidation catalyst. The catalytic oxidation of 1,2-dichlorobenzene over Pt/MMZ was carried out, and the catalytic activity was compared with that of Pt/γ-Al₂O₃, Pt/Al-MCM-41 and Pt/Beta catalysts. Pt/MMZ showed the highest catalytic activity among the catalysts tested. Interestingly, the catalytic activity of Pt/MMZ was maintained (~40%) at low temperatures (250 °C) at which the other catalysts showed extremely low activity (~5%). The high catalytic activity of Pt/MMZ was attributed to both the sufficient acidity and mesoporosity of the MMZ support.

Keywords: Mesoporous Material from Zeolite (MMZ), Oxidation, 1,2-Dichlorobenzene.

1. INTRODUCTION

Dioxins are persistent organic pollutants (POPs) that are produced as by-products in industrial processes and solid waste incinerators through incomplete combustion. Highly toxic polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are well-known sources of dioxins in municipal incinerators. Such chemicals have been considered as suspects for human carcinogens for decades.¹ ² Therefore, considerable effort has been made to decompose toxic chlorinated compounds. For example, catalytic oxidation,³ ⁴ catalytic hydrodechlorination,⁵ UV irradiation,⁶ ozonation,⁷ pyrolysis,⁸ and electron beam treatment⁹ have been used for the decomposition of chlorinated compounds. Among these studies, catalytic oxidation using metal oxides or supported noble metals (platinum or palladium) is considered to be one of the most promising approaches for removing organic compounds from waste gas.

Zeolites, which possess micropores and strong acid sites based on aluminum species, are considered to be effective supports for noble metal and metal oxide catalysts. However, the application of zeolites is limited because of its small pore size (<1 nm), which limits molecular diffusion for oxidative destruction. Zeolites show a high level of activity but only for small molecules, such as 1,2-dichloromethane and trichloroethylene.¹⁰ In this regard, mesoporous materials¹¹ ¹² have been considered for the catalytic decomposition of chlorinated compounds with a larger molecular diameter. Recently, we reported the synthesis and application of mesoporous materials from commercially available zeolites (designated as MMZ) for the catalytic pyrolysis of biomass.¹³ ¹⁴

In this study, mesoporous materials synthesized from zeolite beta (hereafter, MMZ.beta) were used for catalytic oxidation for the first time. This study examined the catalytic performance of a platinum catalyst, which has attracted most attention for the destruction of organic pollutants,⁴ supported on this new MMZ.beta in the gas phase catalytic oxidation of 1,2-dichlorobenzene (DCB). The results were compared with those from Pt/γ-Al₂O₃, Pt/Al-MCM-41, and Pt/Beta catalysts. 1,2-dichlorobenzene was chosen as the model compound of dioxins because
it is structurally similar to the most toxic of polychlorinated dibenzo-\(p\)-dioxins (2,3,7,8-tetrachlorodibenzo-\(p\)-dioxin) and dibenzofurans, and is one of the most hazardous organic compounds.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of MMZ\(_{\text{beta}}\) and Al-MCM-41

MMZ\(_{\text{beta}}\) and Al-MCM-41 were synthesized using the method reported elsewhere,\(^{13,15}\) respectively.

Briefly, MMZ\(_{\text{beta}}\) was synthesized using proton exchanged zeolite beta with a Si/Al ratio of 75 after first being dissolved in a NaOH (NaOH/Si molar ratio = 2.0) solution. Cetyltrimethylammonium bromide (CTAB) and a dissolved zeolite solution were used as the structure directing agent and precursor, respectively. In a typical synthesis, 2.25 g of zeolite beta was dissolved in a NaOH solution (1.5 g of NaOH in 5.0 g of H\(_2\)O) and diluted with 2.5 g of H\(_2\)O. This zeolite solution was added to an aqueous CTAB solution (4.6 g of CTAB in 70 g of H\(_2\)O) with vigorous stirring at 25 °C. The reaction mixture was stirred for 1 day and kept in a 100 °C oven for another day. The mixture was titrated to pH 10 using acetic acid and kept at 100 °C for another day. The MMZ\(_{\text{beta}}\) was obtained after filtration, surfactant extraction and calcination. Al-MCM-41 (Si/Al = 30) was obtained using a post alumination method.\(^{15}\) γ-Al\(_2\)O\(_3\) and zeolite beta were purchased from Aldrich and Zeolyst international, respectively.

2.2. Platinum Loading

The platinum-loaded catalysts (0.5 wt%) were prepared by the incipient wetness impregnation of supports with an appropriate amount of an aqueous H\(_2\)PtCl\(_6\) solution. Al-MCM-41, MMZ\(_{\text{beta}}\), zeolite beta and γ-Al\(_2\)O\(_3\) were used as the supports. All Pt loaded catalysts were calcined under air at 500 °C for 4 h.

2.3. Catalytic Oxidation of DCB

The oxidation of 1,2-dichlorobenzene was carried out in a fixed bed reactor of 1/4" O.D., which was loaded with 75 mg of the catalyst. 1,2-dichlorobenzene was injected by air saturation at 50 ml/min at 20 °C. The products were analyzed by gas chromatography equipped with a FID and a 10% OV-101 on chromosorb W-HP 80/100 column for the analysis of 1,2-dichlorobenzene and with a methanizer/FID and a carbosphere 80/100 column for the analysis of CO and CO\(_2\).

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of γ-Al\(_2\)O\(_3\), Al-MCM-41, MMZ\(_{\text{beta}}\), and zeolite beta in the low and high angle region. The XRD patterns of the Al-MCM-41 and MMZ\(_{\text{beta}}\) showed 3 diffraction peaks corresponding to the 100, 110, and 200 Bragg reflections of typical 2D-hexagonal mesostructures (Fig. 1(a)). The γ-Al\(_2\)O\(_3\), Al-MCM-41, MMZ\(_{\text{beta}}\) and zeolite beta phases...
Fig. 2. Nitrogen sorption isotherms (A) and pore size distributions (B) of γ-Al₂O₃ (a), zeolite beta (b), Al-MCM-41 (c) and MMZ beta (d).

were identified from XRD patterns in the high angle region (Fig. 1(b)). Al-MCM-41 has no crystalline framework, while zeolite beta and γ-Al₂O₃ have a highly crystalline framework. MMZ beta showed a somewhat similar XRD pattern to Al-MCM-41 in both the low and high angle regions, which is consistent with our previous result.

The nitrogen adsorption–desorption isotherms show the porosity of the samples (Fig. 2). The isotherm curves of Al-MCM-41 and MMZ beta showed a typical type IV with steep sorption in the range of \(P/P_0\) 0.3∼0.4, while that of zeolite beta exhibited no steep sorption in this range due to the lack of mesoporosity. γ-Al₂O₃ exhibited a type IV isotherm with an adsorptive increase in the wide range of \(P/P_0\) 0.6∼0.9. The pore size distribution curves were obtained from the isotherm curves using the BJH (Barret–Joyner–Halenda) method (Fig. 2(b)). As expected from the isotherms, Al-MCM-41 and MMZ beta develop mesoporosity with a narrow distribution, while zeolite beta and γ-Al₂O₃ have a very small portion of mesoporosity. As summarized in Table I, the mesopore size of Al-MCM-41 and MMZ beta was 2.6 nm. The mesopore size of γ-Al₂O₃ was 8 nm. However, its porosity was not well developed and the pore size distribution was very wide.

Table I. Physicochemical properties of zeolite beta, MMZ beta, Al-MCM-41, and γ-Al₂O₃.

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m²/g)</th>
<th>(V_p) (cc/g)</th>
<th>(D_p) (nm)</th>
<th>(a_0)</th>
<th>Wall thickness (nm)</th>
<th>Si/Al⁴</th>
</tr>
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<tbody>
<tr>
<td>Zeolite beta</td>
<td>598</td>
<td>0.28</td>
<td>-2.00</td>
<td>—</td>
<td>—</td>
<td>64</td>
</tr>
<tr>
<td>MMZ beta</td>
<td>965</td>
<td>0.75</td>
<td>2.60</td>
<td>4.60</td>
<td>2.00</td>
<td>62</td>
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<tr>
<td>Al-MCM-41</td>
<td>1062</td>
<td>1.01</td>
<td>2.65</td>
<td>4.20</td>
<td>1.55</td>
<td>43</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>197</td>
<td>0.42</td>
<td>5.15</td>
<td>—</td>
<td>—</td>
<td>∞</td>
</tr>
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</table>

⁴ICP measurement.

A temperature programmed desorption (TPD) technique was used to characterize the acid sites in the samples. Figure 3 shows the TPD curves of the four samples. Zeolite beta showed the largest level of acidity consisting of weak and strong acid sites in the temperature regions.
MOMZ_{beta} exhibits excellent catalytic activity because the catalytic activity is related to the amount and strength of the acid sites.\textsuperscript{13} However, zeolite beta did not have very high activity, probably because diffusion was limited by the small micropores. MOMZ_{beta} has both well developed mesoporosity and strong acidity, which are essential for the catalytic oxidation of DCB.

4. CONCLUSION

MOMZ_{beta} was synthesized using conventional zeolite beta as a platinum catalyst support for the catalytic oxidation of dichlorinated benzene. MOMZ_{beta} which possesses both a sufficient number of acid sites and well developed mesoporosity, was found to be an excellent support for the platinum catalyst, and showed much higher conversion than the other supports over wide temperature range.

References and Notes