Preparation of manganese containing HZSM-5 for the adsorptive removal of trace NO from a CO₂ stream

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Food-grade CO₂ is a kind of useful product, which is widely used as food additives and supercritical extraction solvent. A great challenge is to remove impurities, such as H₂S, SO₂, alkanes, alkenes, VOCs and NOx, in various CO₂ sources. Trace NO is one of the impurities contained in many CO₂ streams, which is hard to be removed before being oxidized to NO₂ at room temperature and ambient pressure. The concentration of NO or NO₂ regulated in food-grade CO₂ is no more than 2.5 ppm (ISBT).

It has been reported that porous carbon materials, activated carbon fibers (ACF), activated carbon (AC) and carbon nanotubes, are good adsorbents for NO adsorption and catalysts for NO oxidation [1-6]. However, they are not good for deep removal (< 1 ppm) of NO. Fe-Mn-Ti mixed oxide [7] has been found to be the best oxidative adsorbent at room temperature with a low regeneration temperature (no more than 640K), and but for NO adsorption in the present of CO₂ (10%), the breakthrough time (tₜ) decreased nearly by 50%, and the metal utilization percentage was also need to be improved for practical application. MnOx/Al₂O₃ has been reported as a good adsorbent for deep removal of NO in the absence of O₂, but the adsorptive capacity is poor [8]. Consequently, manganese species modified HZSM-5, which is a good catalyst for low-concentration NO oxidation in the present of O₂ [9], was considered to remove trace NO from CO₂ in the presence of O₂ for CO₂ applications.

HZSM-5(SiO₂/Al₂O₃=25) was modified by ion-exchange (at 353K, exchanged for 3 times), incipient wetness impregnation (IWI) and precipitation (KMnO₄ as the precipitator) method with Mn(CH₃COO)₂ solution. The prepared adsorbents were dried at 383K, calcined at 773K for 5 h, and then characterized by XRD, N₂ adsorption (77K), Laser Raman Spectroscopy (LSR) and UV–visible spectrophotometer. Hereafter the samples were abbreviated as Mn-HZ, Mn/HZ and MnOx/HZ respectively. The removal ability of the adsorbents for NO was tested in fixed bed flow system equipped with a U-type steel pipe (6 mm ID). The lowest outlet concentration of NO detected by a chemiluminescent NO/NOx analyzer (Thermo electron Inc., Model 42i LS) was no more than 0.02 ppm. Figure 1 and Table 1 shows that both the NO oxidation ability and adsorption capacity of the adsorbents increased in the sequence MnOx/HZ<Mn-HZ <Mn/HZ. The state of Mn species in HZSM-5(25) may their oxidation ability for NO. In XRD results (Figure 2), the bands of sample C at 2θ=33º and 55º indicated that Mn appeared as cubic Mn₂O₃ on the surface of MnOx/HZ. However, there is no signal of MnO₃ in the Raman spectroscopy. Raman results indicate that the bands at 657 and 372 cm⁻¹ of Mn/HZ could be attributed to Mn₃O₄ [10], and the low intensity is because of the low impregnation amount of Mn, which is not high enough to form monolayer Mn₃O₄. XPS and DTA-TG [11] also indicated that it is MnO₃ on Mn/HZ. The only band at 378 cm⁻¹ of Mn/HZ is the vibration of the five-member ring in HZSM-5. The UV–Vis DRS results could suggest the oxidation state of Mn. As is shown in Figure 4, the band at around 250 nm can be assigned to O₂⁻→Mn²⁺ charge transfer transition. The bands around 420 and 500 nm are assigned to the A₁g→A₂g and A₁g→T₂g crystal field transitions, respectively. The bands of MnO₃/HZ are at the same region of MnO₃ [12]. The simple absorption band of Mn/HZ can be assigned to Mn²⁺, and the bands of Mn/HZ at 250 and 340 nm are the similar as that of MnO₄ [13].

Results indicate that Mn/HZ prepared by IWI is the best adsorbent for NO removal from CO₂ in the presence of O₂ at room temperature and atmospheric pressure, and MnO₃ is the best active site for NO oxidation compared with Mn²⁺ and Mn₂O₃ in or into HZSM-5(25).

![Figure 1. Breakthrough curves of NO adsorption over Mn-modified HZSM-5(25). Adsorbent: 0.3g, 40-60 mesh; 185ppm NO in 10%CO₂, N₂ balance; temperature, 298 K; 7%O₂; W/F=0.15 g•s•m⁻³](image)

![Figure 2. XRD results of Mn-modified HZSM-5(25) adsorbents.](image)

Table 1. Correlation of NO oxidation and adsorption with the characteristics of Mn-modified HZSM-5(25)

<table>
<thead>
<tr>
<th>Method</th>
<th>Mn wt.%</th>
<th>BET/m²g⁻¹ NO to NO₂/% qₜ(NO/Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-exchange</td>
<td>2.01%</td>
<td>362</td>
</tr>
<tr>
<td>IWI</td>
<td>3.85%</td>
<td>355</td>
</tr>
<tr>
<td>precipitation</td>
<td>4.00%</td>
<td>352</td>
</tr>
</tbody>
</table>

Note: qₜ, molar ratios of adsorbed NO to Mn on the HZSM-5(25)
References
