

三维有序大孔结构脱硝催化剂制备及其抗重金属中毒机理

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摘 要: Cd、Pb、Zn 等重金属广泛存在于工业废气中, 会降低脱硝催化剂的活性。采用聚甲基丙烯酸甲酯(PMMA)模板制备得到具有三维有序大孔结构(3DOM)的 $\text{Ce}_{0.2}\text{Mn}_{0.2}/3\text{DOM TiO}_2$ (Fresh-CMT-3DOM), 作为对比, 制备普通结构 TiO_2 载体负载 Ce-Mn 得到 $\text{Ce}_{0.2}\text{Mn}_{0.2}/3\text{DOM}$ (Fresh-CMT)催化剂。活性测试结果表明: 相较于 Fresh-CMT, Fresh-CMT-3DOM 催化剂在 100~300 °C 时的 NO 转化率超过 85%, 且在 100~150 °C 低温下具有更高的脱硝活性。引入 Cd、Pb、Zn 后, Fresh-CMT-3DOM 催化剂仍保持较高活性, 在 175~300 °C 时的 NO 转化率均超过 85%; 而 Fresh-CMT 催化剂活性明显下降, 其中 Cd、Pb 中毒后催化剂的 NO 最高转化率分别不足 85%、100%。结果表明: 相较于 Fresh-CMT 催化剂, Fresh-CMT-3DOM 具有优异的 $\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ 及 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 氧化还原循环、更高的氧化还原能力及更多的酸性位点, 从而促进了 Fresh-CMT-3DOM 催化剂的低温脱硝活性及抗重金属性能。

关键词: 三维有序大孔; 催化剂; 低温氨选择性催化还原脱硝; 抗重金属中毒

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氨选择性催化还原($\text{NH}_3\text{-SCR}$)是治理 NO_x 污染的最常用的技术^[1-2]。目前使用最广泛的是 $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ 催化剂, 其在 300~400 °C 温度区间表现出高水平的脱硝活性^[3-4], 但存在着低温活性差、V 毒性高、易受重金属中毒等问题^[5-6]。因此迫切需要研发低温下重金属耐受能力更高的无钒催化剂。

由于 CeO_2 具备较高的释氧/储氧能力^[7-8], 被许多学者用作主活性组分来制备稀土基脱硝催化剂。锰氧化物(MnO_x)具有良好的低温催化活性, 常被用作改性组分来提高催化剂在低温下的脱硝活性^[9-10]。 TiO_2 的热稳定性较高、耐硫性较强, 其与活性组分存在较强的相互作用^[11]。然而, Ce-Mn/Ti 催化剂易受到烟气中有毒物质的毒害, 目前关于 SO_2 、 H_2O 等对 Ce-Mn/Ti 催化剂中毒的研究较多^[15-17], 但关于 Ce-Mn/Ti 催化剂重金属中毒的研究较少。

重金属包括 Cd、Pb、Zn 等广泛存在于固体废物焚烧废气、燃煤电厂烟气中。综合前人研究^[18-20],

Cd、Pb、Zn 其对催化剂的毒害作用体现在覆盖催化剂表面的活性位点、降低其氧化还原性、表面酸度、化学吸附氧等方面, 导致催化剂严重失活。因此, 增强催化剂的氧化还原能力、增加化学吸附氧和酸性位点能够提高催化剂的重金属耐受性。据文献[21-23]报道, 三维有序大孔结构(3DOM)结构催化剂具有优异的氧化还原性能、充足的化学吸附氧和适当的酸性位点, 从而促进其 $\text{NH}_3\text{-SCR}$ 脱硝反应。Wang 等^[21]合成了具有有序大孔结构的 3DOM ZSM-5 担载 Pr-Mn 催化剂, 其在协同脱除 NO 和烟尘方面具有优异的催化性能, 在 128~288 °C 时 NO 转化率超过 90%。Jiang 等^[22]制备的 3DOM Ce-W-Nb_{0.15} 催化剂 275~450 °C 时 NO 转化率超过 90%, 且具有较强的抗 $\text{SO}_2/\text{H}_2\text{O}$ 能力。Liu 等^[23]制备的 3DOM $\text{Ce}_{0.8}\text{Cu}_{0.1}\text{Zr}_{0.1}$ 催化剂在 150 °C 低温下 NO 转化率接近 60%, 且对 SO_2 和 H_2O 具有较强的耐受力, 3DOM 结构不仅提高了催化剂的氧化还原

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性能和表面活性位点, 而且由于金属离子和二氧化铈的强协同效应, 在催化剂中形成了更多的氧缺陷和 Ce^{3+} , 提高了复合氧化物催化剂的表面氧浓度, 进一步提高了催化活性。

本工作制备了具有三维有序大孔结构的 TiO_2 及普通结构 TiO_2 载体, 负载 Ce-Mn 复合氧化物得到 Fresh-CMT-3DOM 及 Fresh-CMT 催化剂, 对比研究 2 种催化剂的脱硝活性及抗重金属(Cd、Pb、Zn)性能。结合 SEM、BET、XRD、XPS、 H_2 -TPR 及 NH_3 -DRIFTS 等技术表征了催化剂的形貌特征、孔结构、晶相、价态变化、氧化还原性能、酸性位等表面性质, 研究 Fresh-CMT-3DOM 催化剂的抗重金属中毒机理。

1 实验

1.1 催化剂的制备

3DOM TiO_2 及普通结构 TiO_2 载体制备。依据参考文献[24]报道的方法制备了 3DOM TiO_2 材料。首先制备 TiO_2 前驱液。将 17 mL 钛酸四丁酯在剧烈搅拌下逐滴加入到 30 mL 无水乙醇中, 记为 A 液; 向去离子水(1.5 mL)与无水乙醇(10 mL)的混合溶液中滴加浓硝酸(65%, 质量分数), 溶液 pH 值调至 2~3, 记为 B 液。剧烈搅拌下将 B 液缓慢滴入 A 液中, 得到均匀透明的 TiO_2 溶液。接着将制备所得的聚甲基丙烯酸甲酯(PMMA)模板加入 TiO_2 前驱液中, 密封静置 12 h。然后采用真空抽滤法除去余量前驱液, 并于 50 °C 烘 24 h。最后样品在 300 °C 焙烧 2 h 后, 再加热至 500 °C 焙烧 5 h (升温速率均为 1 °C/min)。普通结构 TiO_2 载体制备过程同 3DOM TiO_2 , 其中不加 PMMA 模板。

$\text{Ce}_{0.2}\text{Mn}_{0.2}/3\text{DOM-TiO}_2$ (Fresh-CMT-3DOM) 及 $\text{Ce}_{0.2}\text{Mn}_{0.2}/3\text{DOM-TiO}_2$ (Fresh-CMT) 催化剂制备。按摩尔比配制 $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 和 $\text{Mn}(\text{NO}_3)_2$ 混合液, 分别浸渍 3DOM TiO_2 和普通 TiO_2 , 室温搅拌 4 h 后转移至油浴锅 80 °C 搅拌 6 h, 然后 80 °C 烘 24 h, 最后以 1 °C/min 升至 500 °C 并保持 5 h。所得样品分别记作 Fresh-CMT-3DOM、Fresh-CMT。

重金属(Cd、Pb、Zn)中毒催化剂制备。采用过量浸渍法, 按照金属离子与催化剂的质量比(10% Cd、10% Pb、5% Zn)配制硝酸镉、硝酸铅、醋酸锌溶液, 将 Fresh-CMT-3DOM 及 Fresh-CMT 催化剂分别加入上述重金属盐溶液, 对应的中毒催化剂分别记作 10% Cd-CMT-3DOM、10% Pb-CMT-3DOM、5% Zn-CMT-3DOM 和 10% Cd-CMT、10% Pb-CMT、5% Zn-CMT。

1.2 表征

采用扫描电子显微镜(SEM, TESCAN MIRALMS, Czech)对催化剂的表面形貌和微观结构进行了分析。采用物理吸附仪(Micromeritics ASAP, USA)在液氮温度下测定氮气吸附等温线, 采用 BET (Brunauer-Emmet-Teller) 方程计算催化剂的比表面积, 介孔分布由 BJH (Barret-Joyner-Halenda) 法测定。采用 Cu-K_α (Bruker D8, 德国) 的 X 射线衍射仪(XRD) 分析了催化剂的晶相结构。在 X 射线光电子能谱(XPS) 光谱仪(Thermo Scientific K-alpha, USA) 上使用 Al-K_α 作为 X 射线源对催化剂元素价态进行分析。采用 FINESORB-3010 吸附仪(Finetechnics, Hangzhou, Zhejiang, China) 对催化剂的氧化还原性进行表征。称取催化剂 50 mg 在 300 °C、Ar 气氛下预处理 1 h, 温度恢复至 50 °C 后, 气体切换为 H_2 (5%, 体积分数)-Ar(95%) 混合气体(20 mL/min), 以 10 °C/min 升温至 800 °C, 利用热导池检测器(TCD) 记录信号, 得到催化剂的 H_2 -TPR(程序升温还原) 谱, 通过比较峰面积比较各催化剂的氧化还原性能。采用 Nicolet 6700 型仪器(ThermoFisherScientific, Waltham, Massachusetts, USA) 进行催化剂的氨气吸附实验, 来测定催化剂表面的酸类型。所有催化剂在 400 °C 和 N_2 气氛下预处理 1 h, 接着在 50 °C 通入 40 min 的 0.1%(体积分数) NH_3 , 然后断开 NH_3 并使用 N_2 吹扫 20 min, 最后扫描样品记录所有催化剂的红外光谱。

1.3 活性评价

在固定床石英反应器中进行催化剂的 NH_3 -SCR 脱硝活性测试, 气体组分为: 1 000 mg/L NO、1 000 mg/L NH_3 , 5%(体积分数) O_2 , N_2 为平衡气体。催化剂的反应空速为 30 000 h^{-1} , 采用烟气分析仪测定催化剂进出口的 NO 浓度, 按式(1) 计算催化剂的脱硝效率。

$$\eta_{\text{NO}} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

式中: η_{NO} 为 NO 转化率, %; $[\text{NO}]_{\text{in}}$ 、 $[\text{NO}_x]_{\text{out}}$ 分别为反应器进口 NO 及出口 NO、 NO_2 的含量。

2 结果与讨论

2.1 催化剂的活性测试及不同重金属(Cd、Pb、Zn)抗性

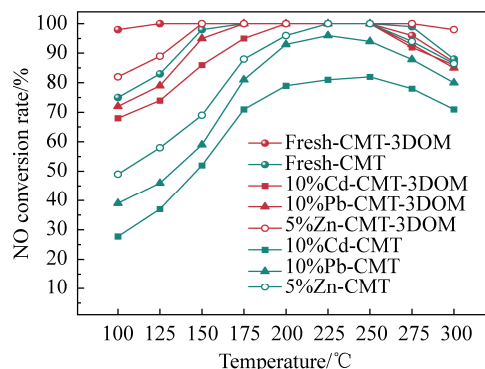
Mn 盐和 Ce 盐负载到 3DOM TiO_2 、普通 TiO_2 2 种不同结构的载体上, 得到的催化剂记作 Fresh-CMT 及 Fresh-CMT-3DOM, 图 1 为 Fresh-CMT 及

Fresh-CMT-3DOM 的活性及抗 Cd、Pb、Zn 重金属性能测试结果。在 175~300 °C 温度区间, Fresh-CMT-3DOM 及 Fresh-CMT 催化剂的 NO 转化率均超过 85%, 在 100~150 °C 的低温范围内, Fresh-CMT-3DOM 的 NO 转化率高于 Fresh-CMT, 尤其在 100 °C 时接近 100%, 这表明 Fresh-CMT-3DOM 具有更高的低温活性。当分别引入 Cd、Pb、Zn 3 种重金属后, 2 种催化剂表现出明显不同的抗性。由图 1 可知, 在 175~300 °C 温度区间, 10%Cd-CMT-3DOM、10%Pb-CMT-3DOM、5%Zn-CMT-3DOM 的 NO 转化率均超过 85%, 而在 100~150 °C 时脱硝活性出现不同程度的下降。同理, 比较 CMT 及 3 种金属中毒后的活性, 发现在 100~300 °C 时, 10%Cd-CMT 的 NO 最高转化率降至 85% 以下, 10%Pb-CMT 的 NO 最高转化率不足 100%, Zn 对 Fresh-CMT 的毒害相对较弱。3 种金属对 2 种催化剂的毒害程度排序从高到低均为: Cd、Pb、Zn。基于以上对比分析, 三维有序大孔结构一定程度上提高了 Fresh-CMT-3DOM 催化剂对 Cd、Pb、Zn 的耐受能力。

2.2 催化剂的形貌分析

图 2 为所有催化剂的 SEM 照片。由图 2a 可见,

3DOM TiO₂ 载体具有规整有序的三维有序大孔结构, 反应物分子通过窗口孔进入各层大孔孔道中, 大孔孔径范围在 200~250 nm, 窗口孔孔径范围在 (50±10) nm。而普通 TiO₂ 载体表面较致密, 无明显孔隙结构(见图 2b)。在担载 Mn、Ce 金属后(见图 2c), 催化剂大孔的有序性相较图 2a 有所降低, 这是因为大孔骨架上分布着活性组分, 活性金属颗粒在大孔



Reaction conditions: [NO]=[NH₃]=1 000 mg/L, [O₂]=5%(in volume), balance N₂, and GHSV about 30 000 h⁻¹.

图 1 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的 NO 转化率

Fig. 1 NO conversion of the Fresh-CMT-3DOM and Fresh-CMT catalysts and that after Cd, Pb, Zn doping

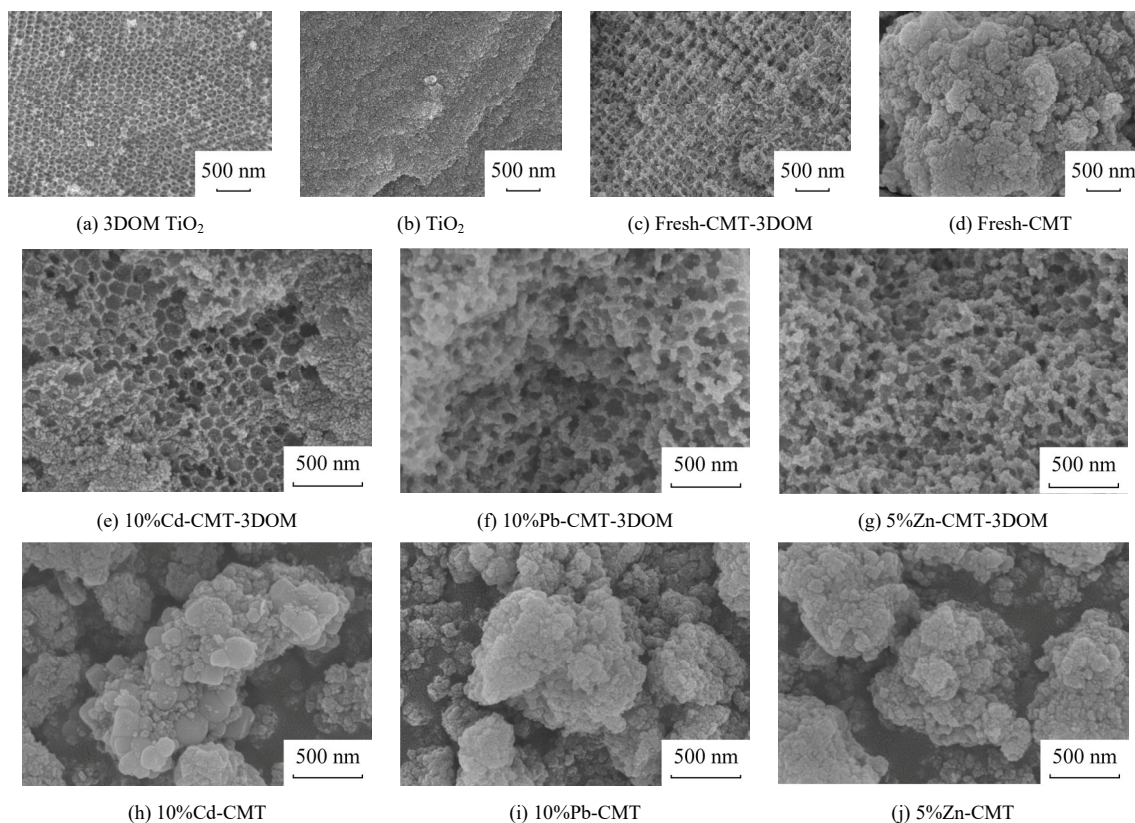


图 2 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的 SEM 照片

Fig. 2 SEM images of the Fresh-CMT-3DOM and Fresh-CMT catalysts and that after Cd, Pb, Zn doping

骨架上聚集可能导致部分孔道堵塞、坍塌。同样地, 普通 TiO_2 载体担载活性金属后, Fresh-CMT 催化剂表面出现粒径不均一的金属颗粒(见图 2d)。图 2e~图 2g 分别为 Cd、Pb、Zn 负载到 Fresh-CMT-3DOM 后的催化剂 SEM 照片, 可以看出大孔有序性及完整度相较于 Fresh-CMT-3DOM 进一步降低, 催化剂孔道同样出现孔道堵塞、塌陷情况, 此外还出现了金属组分的覆盖现象, 这可能是由于重金属在负载过程中分散不均匀而团聚所致。同理, 分析 Cd、Pb、Zn 负载到 Fresh-CMT 催化剂后的表面形貌(见图 2h~图 2j), 可以看出催化剂表面出现较大的金属颗粒团聚现象。

2.3 催化剂的 BET 分析

图 3 为各催化剂的 N_2 吸附-脱附等温线及介孔分布情况, 表 1 为催化剂的比表面积、孔容和孔径结果。由图 3a 可见, Fresh-CMT-3DOM 和 Fresh-CMT 及其掺杂 Cd、Pb、Zn 后的 8 个催化剂均呈现典型

的 IV 型吸附等温线, 所有样品在 $0.4 < p/p_0 < 1.0$ 存在较明显的滞后环, 说明 8 个催化剂均存在介孔结构。由于 BET 测定的孔径范围受限, 而三维有序大孔结构的孔径尺寸在 $200 \sim 300 \text{ nm}$, 因此这里只分析催化剂的介孔分布。由图 3b 可见, 催化剂的介孔孔径大约在处于 $5 \sim 15 \text{ nm}$ 之间, 这与表 1 的结果相一致。由表 1 可知, Fresh-CMT-3DOM 比表面积及孔容 ($62.34 \text{ m}^2/\text{g}$, $0.15 \text{ cm}^3/\text{g}$) 低于 Fresh-CMT ($71.01 \text{ m}^2/\text{g}$, $0.19 \text{ cm}^3/\text{g}$), 这是因为大孔的存在降低了介孔及微孔的数量, 导致比表面积及孔容较低。在引入 Cd、Pb、Zn 后, Fresh-CMT-3DOM 及 Fresh-CMT 催化剂的比表面积及孔容均有所下降, 这可能是因为金属颗粒在催化剂的介孔及微孔孔道内堆积堵塞, 导致介孔及微孔数量减少。综合 BET 表征结果与图 1 中的活性测试结果分析, 催化剂的比表面积和孔容并不能解释 Fresh-CMT-3DOM 催化剂的抗重金属性优于 Fresh-CMT。

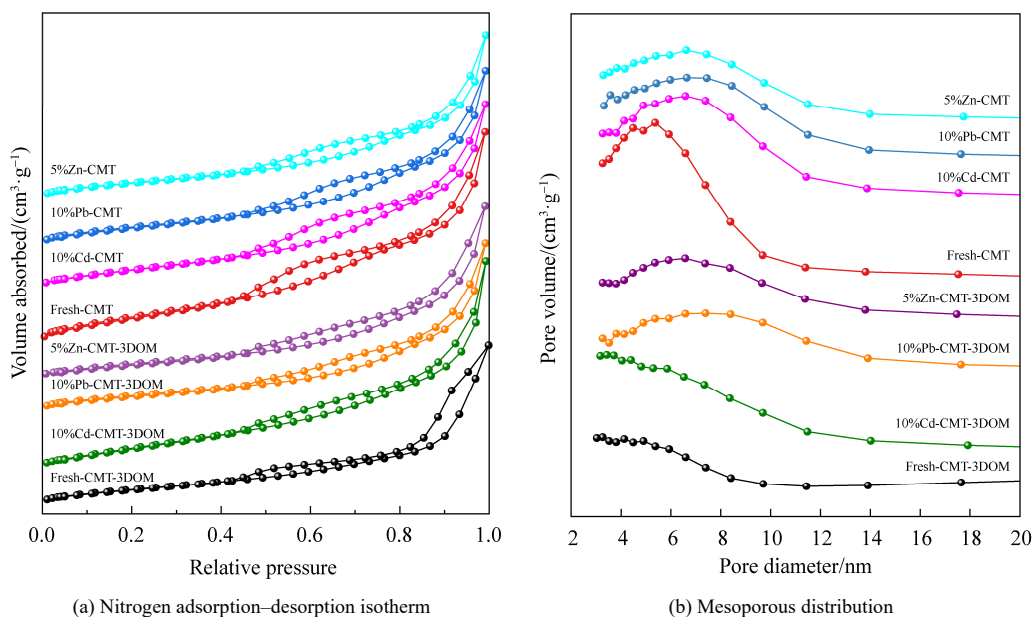


图 3 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的氮气吸附-脱附等温线及介孔分布图

Fig. 3 Nitrogen adsorption-desorption isotherm and mesoporous distribution of the Fresh-CMT-3DOM and Fresh-CMT catalysts and that after Cd, Pb, Zn doping

表 1 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的结构分析

Table 1 Textural properties of the Fresh-CMT-3DOM and Fresh-CMT catalysts and that after Cd, Pb, Zn doping

Catalyst	Surface area $A/(\text{m}^2 \cdot \text{g}^{-1})$	Pore volume $V/(\text{cm}^3 \cdot \text{g}^{-1})$	Average pore size d/nm
Fresh-CMT-3DOM	62.34	0.15	14.35
Fresh-CMT	71.01	0.19	7.79
10%Cd-CMT-3DOM	53.33	0.11	9.90
10%Pb-CMT-3DOM	40.92	0.12	10.75
5%Zn-CMT-3DOM	46.99	0.13	10.51
10%Cd-CMT	52.60	0.15	8.75
10%Pb-CMT	45.28	0.14	9.32
5%Zn-CMT	39.17	0.12	9.94

2.4 催化剂的 XRD 分析

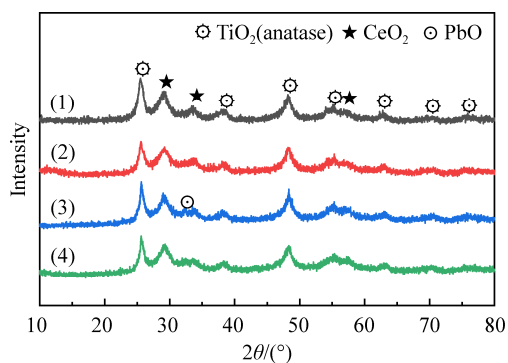
图 4 为 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的 XRD 谱。催化剂在 25.56°、38.42°、48.28°、54.22°、55.44°、62.97°、69.23° 和 75.27° 处出现了衍射峰，对应锐钛矿型 TiO_2 (JCPDS 21-1272) 的 (101)、(004)、(200)、(105)、(211)、(213)、(116)、(215) 晶面^[25]，位于 28.92°、33.37°、56.56°、70.45° 处的衍射峰属于萤石结构 CeO_2 (JCPDS 34-0394)，对应 (111)、(200)、(311)、(400) 晶面^[26]。没有检测到 MnO_x 的衍射特征峰，这表明 Mn 在 Fresh-CMT-3DOM 及 Fresh-CMT 催化剂上分散性良好。由图 4 可见，Fresh-CMT-3DOM 催化剂相较于 Fresh-CMT 的衍射峰较弱，推测是活性组分与载体间发生相互作用，在催化剂体系中形成了化学键 Ce-O-Ti，从而改变了材料的晶体形态，降低了 TiO_2 及 CeO_2 的结晶度，导致 Fresh-CMT-3DOM 催化剂衍射峰强度减弱，这表明 3DOM 结构更有利于活性组分的分散。两种催化剂添加 Cd、Pb、Zn 后，晶

体相几乎没有变化，但衍射峰强度出现不同程度的变化。与 Fresh-CMT-3DOM 催化剂相比，10%Pb-CMT-3DOM 的衍射峰强度有所增加，在 32.22° 处出现了微弱 PbO 特征衍射峰^[27]，表明 Pb 的添加增大了催化剂的结晶度，这可能是 10%Pb-CMT-3DOM 催化剂活性下降的原因之一^[18–27]。此外，相较于 Fresh-CMT-3DOM 催化剂，10%Cd-CMT-3DOM 及 5%Zn-CMT-3DOM 的衍射特征峰强度略有下降，这表明 Cd、Zn 对 Fresh-CMT-3DOM 催化剂的结晶度影响较小。与 Fresh-CMT 催化剂相比，10%Pb-CMT 催化剂的衍射峰强度有所增加，且在 26.60°、32.01°、35.83° 处出现了 PbO 的衍射特征峰^[27]，这表明 Pb 的添加同样增加了 Fresh-CMT 催化剂的结晶度。随着 Cd、Zn 的加入，10%Cd-CMT、5%Zn-CMT 催化剂的结晶度出现了下降，这与 10%Cd-CMT-3DOM、5%Zn-CMT-3DOM 催化剂相似，表明 Cd、Zn 影响了 TiO_2 载体的结构特征。

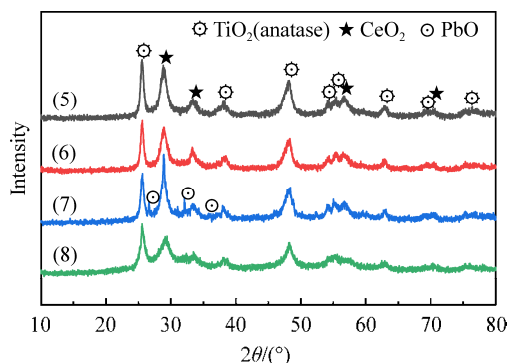
2.5 催化剂的 XPS 分析

图 5 为 Ce 3d 的 XPS 谱。Ce 3d 的 XPS 谱主要由 8 个峰组成 (见图 5a)，说明催化剂体系中同时存在 Ce^{3+} 和 Ce^{4+} 2 种价态。其中在 883.8~884.5 eV 及 903.2~903.9 eV 范围内粉色虚线标记的拟合峰属于 Ce^{3+} ，其他标记灰色虚线位置上的拟合峰属于 Ce^{4+} ^[28–29]。 Ce^{3+} 来源于铈缺陷，且总是伴随氧空位的形成^[30]。 Ce^{3+} 和氧空位的存在会产生电荷不平衡、不饱和的化学键，导致催化剂表面的化学吸附氧增加，从而促进 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 的氧化还原循环^[31]。通过计算 $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ 的峰面积比可得到 Ce^{3+} 的相对比值，如表 2 所示。从表 2 可看出 Fresh-CMT-3DOM 中 Ce^{3+} 的含量 (19.0%) 高于 Fresh-CMT (15.7%)，这可能是 CMT-3DOM 催化剂脱硝活性优异的原因之一。添加 Cd、Pb、Zn 后，Fresh-CMT-3DOM 催化剂中 Ce^{3+} 含量由 19.0% 分别降至 15.6%、16.7%、17.8%，而 Fresh-CMT 催化剂中 Ce^{3+} 含量由 15.7% 分别降至 11.2%、12.7%、14.3%，2 种催化剂中 Ce^{3+} 减少量受重金属影响程度从高到低排序为：Cd、Pb、Zn。与 Fresh-CMT 催化剂相比，Fresh-CMT-3DOM 催化剂中的 Ce^{3+} 含量受到重金属的影响较小，证明了 Fresh-CMT-3DOM 催化剂具有更高的抗重金属性能。

图 6 为 Mn 2p 的 XPS 谱。由图 6b 可见，Mn 2p_{3/2} 谱具有 3 个峰，结合能分别在 640.7~641.5、642.0~642.5 eV 和 643.3~644.9 eV 范围内，分别对应 Mn^{2+} 、 Mn^{3+} 和 Mn^{4+} ^[32]，这说明催化剂中的 Mn 离子具有多种价态，易形成 $\text{Mn}^{n+}/\text{Mn}^{(n+1)+}$ 氧化



(a) Fresh-CMT-3DOM and that after Cd, Pb, Zn doping

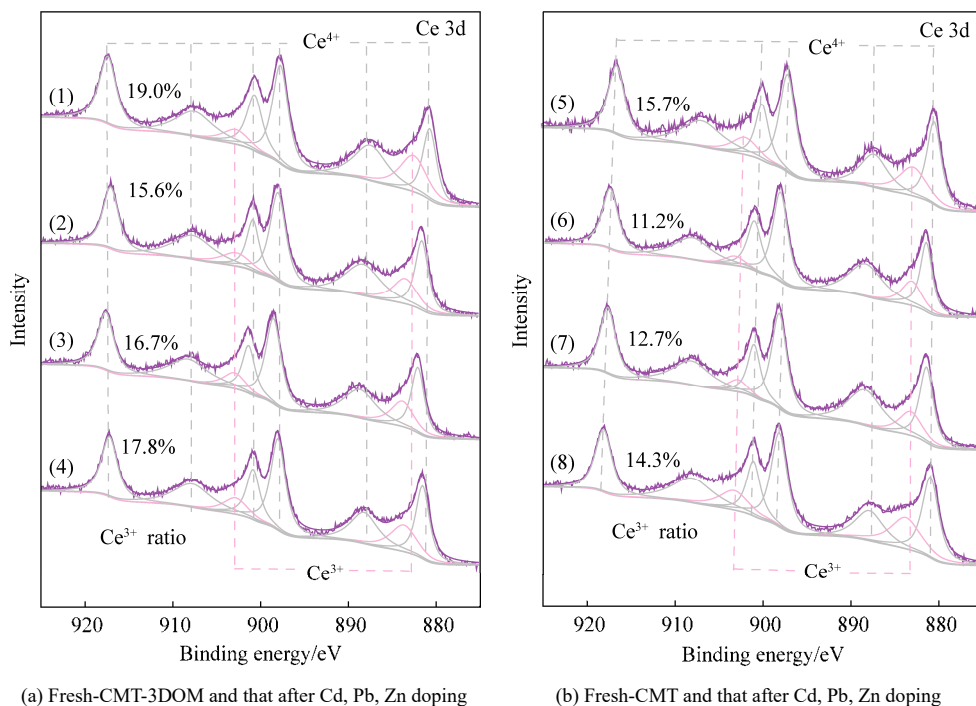


(b) Fresh-CMT and that after Cd, Pb, Zn doping

(1) Fresh-CMT-3DOM; (2) 10%Cd-CMT-3DOM; (3) 10%Pb-CMT-3DOM; (4) 5%Zn-CMT-3DOM; (5) Fresh-CMT; (6) 10%Cd-CMT; (7) 10%Pb-CMT; (8) 5%Zn-CMT.

图 4 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂的 XRD 谱

Fig. 4 Powder XRD patterns of Fresh-CMT-3DOM and Fresh-CMT and that after Cd, Pb, Zn doping



(a) Fresh-CMT-3DOM and that after Cd, Pb, Zn doping

(b) Fresh-CMT and that after Cd, Pb, Zn doping

Note: (1) Fresh-CMT-3DOM; (2) 10% Cd-CMT-3DOM; (3) 10% Pb-CMT-3DOM; (4) 5% Zn-CMT-3DOM; (5) Fresh-CMT; (6) 10% Cd-CMT; (7) 10% Pb-CMT; (8) 5% Zn-CMT.

图 5 Ce 3d 的 XPS 谱
Fig. 5 XPS spectra of Ce 3d

表 2 Fresh-CMT-3DOM 和 Fresh-CMT 及掺杂 Cd、Pb、Zn 后催化剂各元素价态占比
Table 2 Valence proportions calculated from fitted XPS spectra

x/%

Catalyst	$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$	$\text{Mn}^{4+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$	$\text{O}_\alpha/(\text{O}_\alpha+\text{O}_\beta)$
Fresh-CMT-3DOM	19.0	36.1	35.2
10% Cd-CMT-3DOM	15.6	22.0	24.4
10% Pb-CMT-3DOM	16.7	24.8	25.5
5% Zn-CMT-3DOM	17.8	31.1	27.9
Fresh-CMT	15.7	29.6	28.4
10% Cd-CMT	11.2	11.7	17.2
10% Pb-CMT	12.7	22.2	20.1
5% Zn-CMT	14.3	24.9	21.1

x is mole fraction.

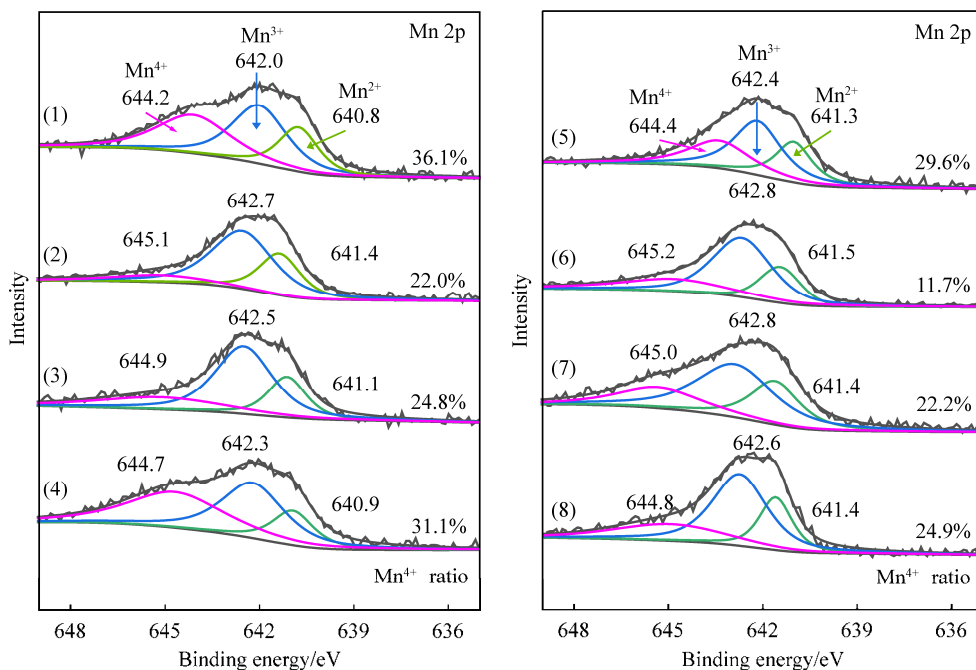
还原对, 有利于 $\text{NH}_3\text{-SCR}$ 反应的进行。其中, Mn^{4+} 具有高氧化还原能力, 可以促进 NO 氧化为 NO_2 , 从而促进“快速 $\text{NH}_3\text{-SCR}$ ”反应^[33]。如表 2 计算了 Mn^{4+} 的相对含量, 在 CMT-3DOM 催化剂中 Mn^{4+} 的占比(36.1%)高于 CMT(29.6%), 这与 Ce 3d 的 XPS 分析结论相符, 即 Fresh-CMT-3DOM 催化剂中的 Ce^{3+} 含量高于 Fresh-CMT 催化剂, 这是由于体系中的 Ce 与 Mn 之间的电子交换所致。 Mn^{2+} 及 Mn^{3+} 在催化剂体系中失去电子, 形成了 $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$ 的电子传递链^[34]。 Mn^{2+} 及 Mn^{3+} 失去的电子被 Ce^{4+} 获得而形成活性态 Ce^{3+} , 氧化还原循环会促进电子转移, 从而促进反应物的活化, 从而促

进了 Fresh-CMT-3DOM 催化剂的 $\text{NH}_3\text{-SCR}$ 低温脱硝性能^[35]。分别添加 Cd、Pb、Zn 后, Fresh-CMT-3DOM 及 Fresh-CMT 催化剂表面的 $\text{Mn}^{4+}/\text{Mn}^{n+}$ 比例有所下降, 这可能是由于重金属的添加, 不同程度地覆盖了部分 Mn^{4+} , 导致催化剂活性降低。与前面 Ce^{3+} 占比下降规律相似, Fresh-CMT-3DOM 及 Fresh-CMT 在 Cd 中毒后的 Mn^{4+} 相对含量下降最多(36.1%→22.0%; 29.6%→11.7%), Pb 中毒次之(36.1%→24.8%; 29.6%→22.2%), Zn 中毒对 Mn^{4+} 相对含量下降影响较小(36.1%→31.1%; 29.6%→24.9%)。根据表 2 结果可知, 3 种重金属中毒后的 Fresh-CMT-3DOM 表面的 Mn^{4+} 相对含量均高于对应的 Fresh-

CMT 催化剂, 说明 Fresh-CMT-3DOM 催化剂的 Mn^{4+} 含量受重金属中毒影响较小, 这有利于提高 Fresh-CMT-3DOM 催化剂的抗重金属性能。

图 7 为 O 1s 的 XPS 谱。529.7 eV 处的特征峰(标

记为 O_β)归属于晶格氧, 531.9 eV 处的特征峰(标记为 O_α)归属于化学吸附氧, 533.8 eV 处的特征峰(标记为 O_γ)归属于 H_2O 解离成的 OH 物种^[36–37]。综合前面对于 Ce 3d 和 Mn 2p 的特征峰分析, 化学吸附氧



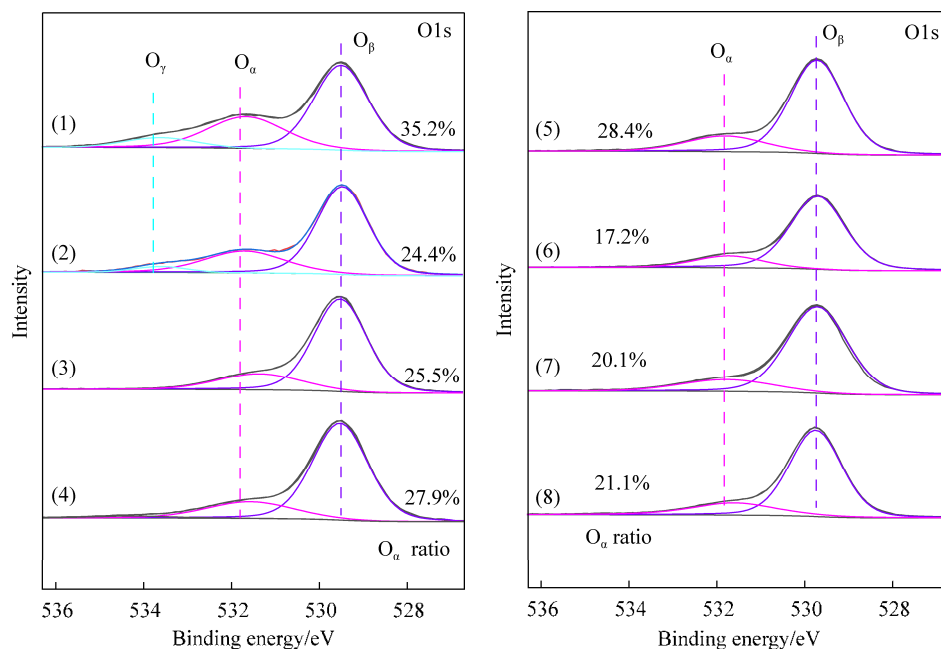
(a) Fresh-CMT-3DOM and that after Cd, Pb, Zn doping

(b) Fresh-CMT and that after Cd, Pb, Zn doping

(1) Fresh-CMT-3DOM; (2) 10%Cd-CMT-3DOM; (3) 10%Pb-CMT-3DOM; (4) 5%Zn-CMT-3DOM; (5) Fresh-CMT; (6) 10%Cd-CMT; (7) 10%Pb-CMT (8) 5%Zn-CMT.

图 6 Mn 2p 的 XPS 谱

Fig. 6 XPS spectra of Mn 2p



(a) Fresh-CMT-3DOM and that after Cd, Pb, Zn doping

(b) Fresh-CMT and that after Cd, Pb, Zn doping

图 7 O 1s 的 XPS 谱

Fig. 7 XPS spectra of O 1s

可以填补氧缺陷, 从而加速 $\text{Mn}^{2+}/\text{Mn}^{4+}$ 及 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 的氧化还原循环。根据图 7 中各峰的峰面积, 计算的得到 O_α 的相对含量结果如表 3 所示, Fresh-CMT-3DOM 催化剂的化学吸附氧(35.2%)高于 Fresh-CMT。当分别添加 Cd、Pb、Zn 3 种重金属后, 5%Zn-CMT-3DOM 的 O_α 相对含量(27.9%)比 10%Cd-CMT-3DOM(24.4%)、10%Pb-CMT-3DOM (25.5%)更多。此外, 10%Zn-CMT 催化剂中 O_α (21.1%)相较于 10%Cd-CMT (17.2%)、10%Pb-CMT (20.1%)损失较小。这些催化剂中的 O_α 、 Ce^{3+} 及 Mn^{4+} 的相对含量变化规律相似, 这与图 1 中催化剂的 NH_3 -SCR 活性结果相一致, 进一步说明三维有序大孔结构能够有效

保护催化剂的活性物种。

图 8 为 Ti 2p 的 XPS 谱。由图 8b 可见, 存在 2 个 Ti 2p 特征峰, 结合能分别为 458.4~458.9、464.1~464.7 eV。与催化剂 Fresh-CMT 相比, 催化剂 Fresh-CMT-3DOM 的特征峰出现偏差, 其曲线的峰值位置向结合能较低的一侧偏移。推测这是因为三维有序大孔 TiO_2 载体从 Ce 中吸收了更多电子, 从而促进了 Ce^{3+} 的生成, 进而促进了 Fresh-CMT-3DOM 催化剂的氧化还原反应。此外, 当添加 Cd、Pb、Zn 后, Fresh-CMT-3DOM 及 Fresh-CMT 催化剂的特征峰向高结合能方向移动, 这说明重金属的添加一定程度上促进了催化剂体系中电荷向 Ti 的转移。

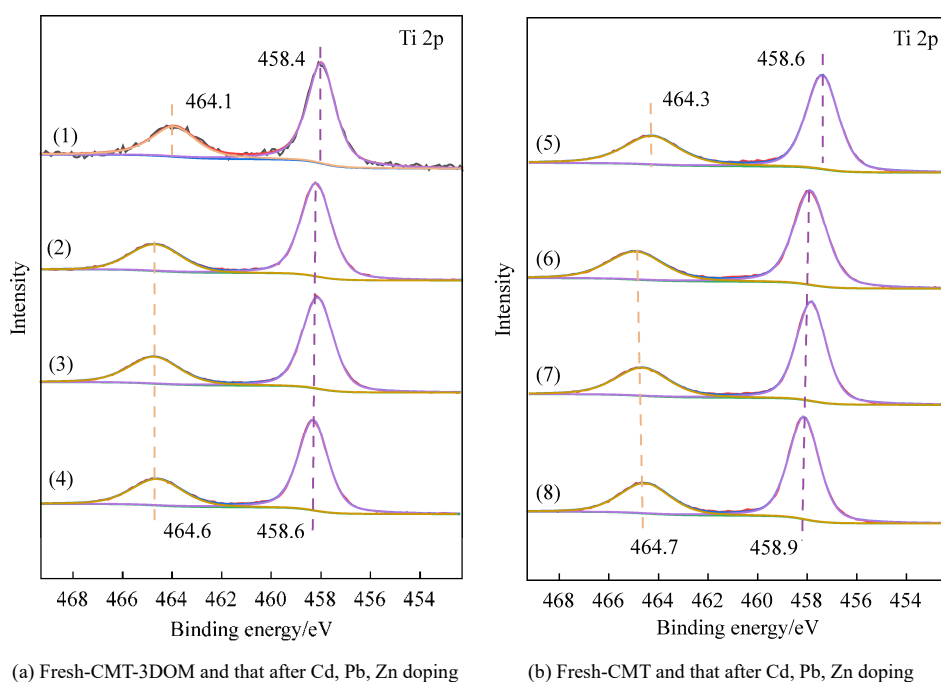


图 8 Ti 2p 的 XPS 谱
Fig. 8 XPS spectra of Ti 2p

2.6 催化剂的 H_2 -TPR 分析

图 9 为通过 H_2 -TPR 表征技术对所有催化剂的氧化还原性能进行研究。Fresh-CMT-3DOM 催化剂的 H_2 -TPR 还原曲线在 301、370 $^{\circ}\text{C}$ 处出现的还原峰归属于 $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ ^[38-40], 而在 Fresh-CMT 催化剂的还原曲线上表现为在 379 $^{\circ}\text{C}$ 处的大包峰, 可以看出 Fresh-CMT-3DOM 催化剂还原峰向更低温度方向移动。催化剂 Fresh-CMT-3DOM 及 Fresh-CMT 分别在 465、493 $^{\circ}\text{C}$ 处出现还原峰, 这是由 $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ 和 $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ 共同引起^[41]。与 XPS 分析结果相一致, 可以看出, Fresh-CMT-3DOM 催化剂的还原峰温度更低。计算峰面积大小来反映催化剂的氧化还原能力相对强弱。由图 9c 可见, 与

CMT-3DOM 相比, Fresh-CMT-3DOM 的相对峰面积更高, 这说明 3DOM 结构更有利于催化剂的氧化还原反应。当添加 Cd、Pb、Zn 之后, 2 种催化剂的还原峰均向高温方向移动, 表明重金属与催化剂的活性物种结合。其中, 10%Cd-CMT-3DOM 及 10%Cd-CMT 催化剂分别在 227、238 $^{\circ}\text{C}$ 处的峰由 CdO 的还原所致^[42]。通过计算得到所有催化剂还原峰的相对峰面积, 根据计算结果可知 3 种重金属对 Fresh-CMT-3DOM 催化剂的氧化还原性能的降低程度从高到低排序为: Cd、Pb、Zn。同样地, 重金属对 Fresh-CMT 催化剂氧化还原性能的影响程度规律相似。Cd、Pb、Zn 对催化剂氧化还原性能的影响与 SCR 脱硝性能测试结果相符, 说明催化剂的氧化

还原能力是影响 SCR 脱硝活性及抗重金属性能的关键因素。

2.7 催化剂的 NH_3 -DRIFTS 分析

图 10 为所有催化剂在 50 °C 的 NH_3 吸附原位红外谱, 在 1080~1250、1580~1730 cm^{-1} 处归属于 Lewis 酸性位点的 NH_3 ^[43-44], 而在 1280~1530 cm^{-1} 处归属于 Brønsted 酸性位点上的 NH_4^+ ^[45-46]。从图 10 可以看出, Lewis 酸是 Fresh-CMT-3DOM 及 Fresh-

CMT 催化剂的主要酸类型, 且 Fresh-CMT-3DOM 催化剂的 Lewis 酸位点比 Fresh-CMT 更多。对于 Fresh-CMT-3DOM 催化剂, 在分别添加 Cd、Pb、Zn 后, 10%Cd-CMT-3DOM、10%Pb-CMT-3DOM 及 5%Zn-CMT-3DOM 催化剂的 Lewis 酸位有所减少, 损失程度从高到低排序为: Cd、Pb、Zn。10%Cd-CMT-3DOM、10%Pb-CMT-3DOM 及 5%Zn-CMT-3DOM 催化剂的 Brønsted 酸性位损失程度从

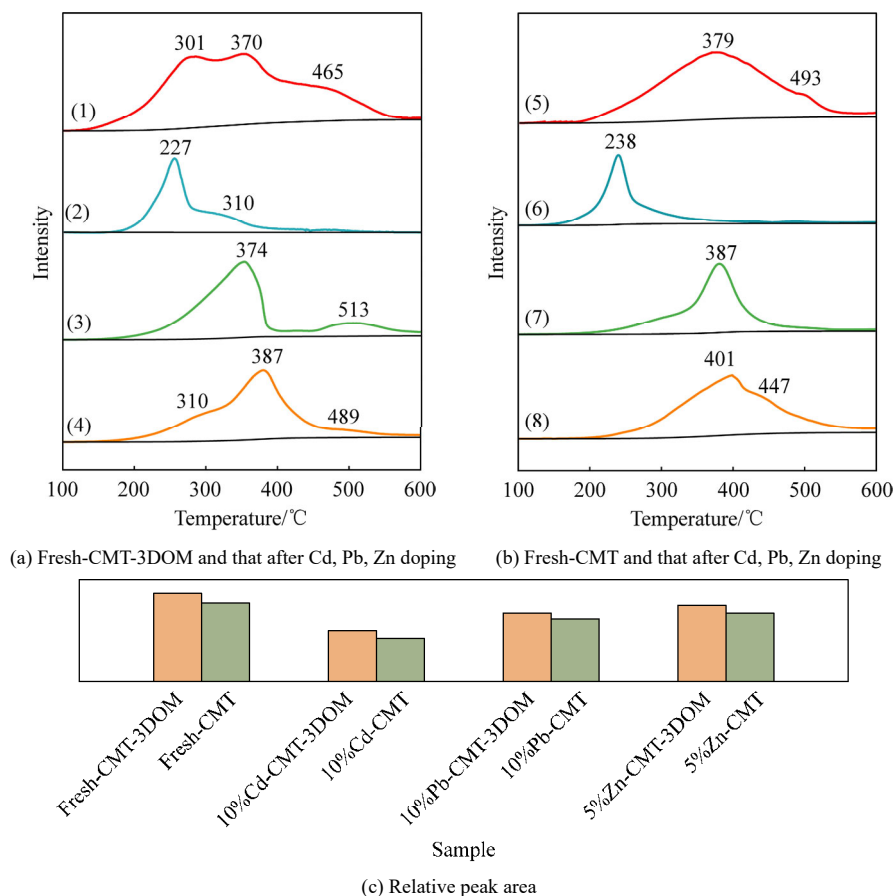


图 9 H_2 -TPR 及相对峰面积对比图

Fig. 9 H_2 -TPR (Temperature programmed reduction) plot and relative peak area

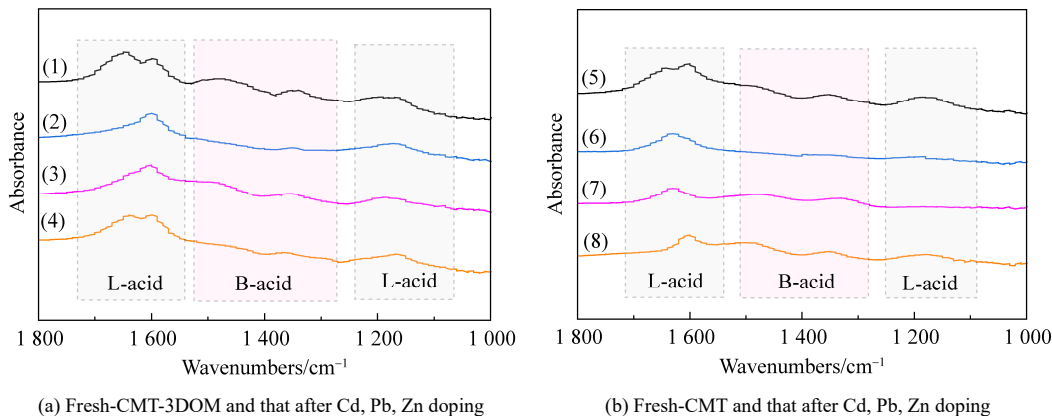


图 10 氨气吸附原位红外谱

Fig. 10 *In situ* infrared spectra of ammonia adsorption

高到低排序为: Cd、Pb、Zn, 其中, 损失最大的 10%Cd-CMT-3DOM 催化剂的 Brønsted 酸性位近乎消失, 这可能是 10%Cd-CMT-3DOM 活性最差的原因之一。重金属中毒后的 Fresh-CMT 催化剂的酸性位损失与 Fresh-CMT-3DOM 变化规律相似, 其 Brønsted 酸性位变化情况与催化剂活性测试结果相一致。此外可观察到, 相较于 Fresh-CMT 催化剂, Fresh-CMT-3DOM 具有更多 Brønsted 酸性位, 且重金属对其酸性位点影响较小。综上分析, Fresh-CMT-3DOM 催化剂具有更多酸性位, 这可能导致其具有更高的抗重金属性能。

3 结论

利用 PMMA 模板制备了具有三维有序大孔结构的 TiO₂ 载体, 担载 Ce、Mn 后得到 Fresh-CMT-3DOM 催化剂, 研究其与具有普通 TiO₂ 载体结构 Fresh-CMT 催化剂的活性和抗重金属性能。结果表明, Fresh-CMT-3DOM 催化剂具有较宽的温度区间, 在 100~300 °C 时的 NO 转化率超过 85%, 且在 100~150 °C 时的低温活性明显高于 Fresh-CMT。当引入 Cd、Pb、Zn 后, Fresh-CMT-3DOM 在 175~300 °C 时的 NO 转化率仍保持在 85% 以上; 而 Cd、Pb、Zn 中毒后的 Fresh-CMT 活性出现明显下降趋势, 其中对应 Cd、Pb 中毒后的催化剂的 NO 最高转化率均不足 85% 及 100%。Fresh-CMT-3DOM 及 Fresh-CMT 催化剂具有相似的晶相, 但 Fresh-CMT-3DOM 的衍射峰强度更弱, 其活性组分更为分散。相较于 Fresh-CMT 催化剂, Fresh-CMT-3DOM 催化剂具有优异的 Mn⁴⁺/Mn³⁺/Mn²⁺ 及 Ce⁴⁺/Ce³⁺ 氧化还原循环、更高的氧化还原能力及更多的酸性位点, 从而提高 Fresh-CMT-3DOM 的抗重金属性能。

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Heavy Metal Poisoning Tolerance of Three-Dimensional Ordered Macroporous Denitration Catalyst

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Extended Abstract

Introduction Ammonia selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is an effective technology for NO_x removal. As a catalyst, V₂O₅-WO₃ (MoO₃) /TiO₂ has a high denitrification activity, but suffers from the problems of poor low-temperature activity, high V-toxicity, and susceptibility to heavy metal toxicity at 300–400 °C. Heavy metals such as Cd, Pb, Zn, etc. widely present in the flue gas of solid waste incineration and coal-fired power plants. The toxic effects on catalysts are manifested via covering the active sites on the catalyst surface, reducing the redox properties, acidifying the surface and chemically adsorbing oxygen, leading to severe catalyst deactivation. CeO₂ as an effective catalyst has a higher oxygen release/storage capacity, which is characterized by a higher oxygen release/storage capacity, compared to the conventional catalysts. CeO₂ is used as a main active component in the preparation of rare-earth-based denitrification catalysts due to its high oxygen release/storage capacity. Manganese oxide (*i.e.*, MnO_x) exhibits a good low-temperature catalytic activity, which is often used as a modified component to improve the low-temperature denitrification activity of catalysts. TiO₂ interacts with the active component and has a higher thermal stability and a sulphur resistance. However, Ce-Mn/Ti catalysts are susceptible to poisoning by toxic substances in the flue gas, and there are more studies on the poisoning of Ce-Mn/Ti catalysts by SO₂, H₂O, etc.. However, a few studies on the poisoning of Ce-Mn/Ti catalysts by heavy metals are reported. Catalysts with three-dimensional ordered macroporous structures have superior redox properties, sufficient chemisorbed oxygen and suitable acid sites to promote its NH₃-SCR denitrification reaction. In this paper, Ce-Mn/Ti catalysts with three-dimensional ordered macro-porous structures were thus prepared to increase the redox properties and acidic sites and promote the denitrification activity.

Methods 17 mL of tetrabutyl titanate was added drop by drop into 30 mL of anhydrous ethanol under vigorous stirring, which was recorded as liquid A. Concentrated nitric acid (65%, in mass fraction) was added dropwise into the mixed solution of deionized water (1.5 mL) and anhydrous ethanol (10 mL) at pH values of 2–3, which was recorded as liquid B. The solution was then mixed into a mixture of deionized water (1.5 mL) and anhydrous ethanol (10 mL). Liquid B was slowly mixed into liquid A under vigorous stirring to obtain a homogeneous and transparent TiO₂ solution. A certain amount of PMMA template was added to the TiO₂ precursor solution, sealed and stayed for 12 h. The remaining precursor solution was removed by vacuum filtration and baked at 50 °C for 24 h. Finally, the samples were baked at 300 °C for 2 h, and then heated at a heating rate of 1 °C/min at 500 °C for 5 h. The ordinary structure TiO₂ carriers were prepared in the same process as 3DOM TiO₂ without PMMA template. After the preparation of TiO₂ carriers, Ce(NO₃)₃·6H₂O and Mn(NO₃)₂ mixtures were prepared at different molar ratios, and impregnated with 3DOM TiO₂ and normal TiO₂, respectively, and stirred at room temperature for 4 h. Afterwards, the catalysts were transferred to an oil bath and stirred at 80 °C for 6 h. They were baked at 80 °C for 24 h, and finally, the catalysts were heated at 1 °C/min at 500 °C for 5 h. The obtained samples were recorded as fresh-CMT-3DOM (*i.e.*, fresh-CMT). The catalyst with heavy metals (*i.e.*, Cd, Pb, Zn) were prepared by an excess impregnation method. A certain amount of cadmium nitrate, lead nitrate, and zinc acetate solution was prepared at different mass ratios of metal ions to catalyst (10% Cd, 10% Pb and 5% Zn), and fresh-CMT-3DOM and fresh-CMT catalysts were added to the heavy metal salt solutions, respectively.

The morphology structure was detected by a scanning electron microscope (SEM, TESCAN MIRALMS Co., Czech Republic). The specific surface area and pore size were determined by specific surface area intrusion based on BET (Micromeritics Co., USA). The crystalline phase structure of the catalysts was analyzed by an X-ray diffractometer (XRD, Bruker Co., Germany). The elemental valence states of the catalysts were analyzed by an X-ray photoelectron spectroscopy (XPS, Thermo Scientific Co., USA) using Al K_α as X-ray sources. The redox properties of the catalysts were characterized using a FINESORB-3010 adsorption apparatus (Finetec Instruments Co., China). The ammonia adsorption experiments of the catalysts were carried out by a Nicolet 6700 instrument (Thermo Fisher Scientific Co., USA) to determine the type of acid on the catalyst surface. The NH₃-SCR denitrification activity was analyzed in a fixed bed quartz reactor at 1 000 mg/L NO, 1 000 mg/L NH₃, 5% (v/v) O₂ and N₂ as ab equilibrium gas. The denitrification efficiency of the catalyst was calculated according to the results that were determined by a flue gas analyzer.

Results and discussion The NO conversion for 10% Cd-CMT-3DOM, 10% Pb-CMT-3DOM, and 5% Zn-CMT-3DOM exceeds 85% at 175–300 °C. However, the denitrification activity decreases at 100–150 °C. Compared to the activity of CMT and the three metals after poisoning, the maximum NO conversion of 10% Cd-CMT decreases to less than 85% at 100–300 °C. The maximum NO conversion of 10% Pb-CMT is less than 100%, and fresh CMT is weakly poisoned by Zn. The three-dimensional ordered macro-porous structure enhances the CMT-3DOM catalyst's tolerance to Cd, Pb, and Zn to some extent.

The ratio of Ce^{3+} can be determined *via* calculating the peak area ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$. The proportion of Ce^{3+} in fresh-CMT-3DOM (19.0%) is greater than that in fresh-CMT (15.7%), accounting for the favorable denitrification activity of CMT-3DOM catalyst. After adding Cd, Pb and Zn, the content of Ce^{3+} in the fresh-CMT-3DOM catalyst shows a better resistance to heavy metals, compared to the fresh-CMT catalyst. This indicates that the fresh-CMT-3DOM catalyst is more resistant to heavy metals. Based on the calculation results of Mn^{4+} content, which decreases similarly to Ce^{3+} content, fresh-CMT-3DOM and fresh-CMT display the greatest reduction in Mn^{4+} content after Cd poisoning, followed by Pb poisoning. Zn poisoning has a smaller impact on the Mn^{4+} content reduction. The Mn^{4+} content on the surface of fresh-CMT-3DOM is relatively higher after three heavy metals poisoning rather than that on the corresponding fresh surface. Also, the relative contents are higher than those of the corresponding fresh-CMT catalysts. This indicates that the Mn^{4+} content of fresh-CMT-3DOM catalysts is less affected by heavy metal poisoning, which is beneficial to improving the anti-heavy metal performance of fresh-CMT-3DOM catalysts. The relative content of O_α in the catalysts is obtained *via* the calculation. The amount of chemisorbed oxygen in fresh-CMT-3DOM catalysts (*i.e.*, 35.2%) is greater than that of fresh-CMT. The relative content of O_α , Ce^{3+} and Mn^{4+} depict a consistent pattern of variation in these catalysts, which coincide with the outcomes of the NH_3 -SCR activity. This further shows the safeguarding ability of the catalysts active species through the three-dimensionally ordered macropore structure. Based on the H_2 -TPR reduction peak results, the reduction peaks of fresh-CMT-3DOM move to lower temperatures, compared to those of fresh-CMT catalysts. The relative peak areas of fresh-CMT-3DOM are greater, indicating that the 3DOM structure is more favorable for the redox reaction of the catalysts. When Cd, Pb, and Zn are introduced, the reduction peaks of both catalysts shift towards at higher temperatures, indicating that the heavy metals form bonds with the active species of the catalysts. The reduction peaks of all catalysts are analyzed to determine the relative peak areas. The influence of Cd, Pb, and Zn on the catalytic redox activity aligns with SCR denitrification performance. This indicated that the catalysts ability to undergo redox reactions is a crucial factor affecting their heavy metal resistance and SCR denitrification activity. The NH_3 -DRIFTS characterization results indicate that the Lewis acid is a primary acid type in both fresh-CMT-3DOM and fresh-CMT catalysts. Moreover, fresh-CMT-3DOM catalysts have a higher concentration of the Lewis acid sites rather than fresh-CMT. Fresh-CMT-3DOM after the heavy metal poisoning has the more Brønsted acid sites, compared to fresh-CMT catalysts, and the influence of heavy metals on its acid sites is reduced. Fresh-CMT-3DOM catalysts possess a larger number of acidic sites, resulting in a greater resistance to heavy metals.

Conclusions TiO_2 carrier with a three-dimensional ordered macro-porous structure was prepared using PMMA template, and fresh-CMT-3DOM catalysts were obtained after loading with Ce and Mn. The activity and heavy metal resistance performance were investigated. The experimental results showed that the fresh-CMT-3DOM catalyst had the excellent activity with the NO conversion rate of more than 85% at 100–300 °C. The low-temperature activity was higher than that of fresh-CMT, which still remained at 85% at 100–150 °C. When Cd, Pb and Zn were introduced, NO conversion rate of fresh-CMT-3DOM at 175–300 °C, while the fresh-CMT activity after Cd, Pb and Zn poisoning decreased, in which the maximum NO conversions of the catalysts corresponding to Cd and Pb poisoning were less than 85% and 100%, respectively. The characterization results indicated that the NO conversions of the catalysts corresponding to Cd, Pb and Zn poisoning were higher than those of fresh-CMT-3DOM and fresh-CMT-3DOM. 3DOM and fresh-CMT catalysts had the similar crystalline phases, but the diffraction peaks of fresh-CMT-3DOM were weaker in intensity and its active components were more dispersive. Compared with fresh-CMT catalysts, fresh-CMT-3DOM catalysts had excellent $\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycling, higher redox capacity and more acidic sites, thus improving the anti-heavy metal performance of fresh-CMT-3DOM.

Keywords three-dimensional ordered macroporous; catalyst; low-temperature selective catalytic reduction of NO_x with NH_3 (NH_3 -SCR); heavy metal poisons resistance