Cu-SAPO-34/堇青石的原位制备及其催化丙烷还原 柴油机车尾气中 NO_x

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摘要: 采用原位水热法制备了 Cu-SAPO-34/堇青石整体式催化剂, 运用 X 射线衍射、扫描电镜和 N₂ 吸附-脱附等技术对其进行了表征, 并在固定床反应器上评价了其催化丙烷还原模拟柴油机车尾气中 NO_x 性能, 考察了丙烷和 O₂ 浓度以及水蒸气对催化剂性能的影响。结果表明, 所制整体式催化剂中 Cu-SAPO-34 涂层与载体结合牢固紧密, 经一次操作 Cu-SAPO-34 负载量大于 20%, 且其比表面积较载体显著增加。另外, Cu 的加入能显著提高催化剂上丙烷选择性催化还原 NO_x 的活性, 在 500~650 °C NO_x 浓度可降低 60% 以上。当原料气中添加 10% 水蒸气后, NO_x 转化率有所降低, 但停加水蒸气后, 催化剂活性可部分恢复。

关键词: 铜; SAPO-34 分子筛; 堇青石; 氮氧化物; 丙烷; 原位合成; 选择性催化还原; 柴油机车

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In Situ Synthesis of Cu-SAPO-34/Cordierite for the Catalytic Removal of NO_x From Diesel Vehicles by C₃H₈

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Abstract: A Cu-SAPO-34/cordierite catalyst was prepared by in situ hydrothermal synthesis. The morphology and structure of the Cu-SAPO-34/cordierite samples were characterized by X-ray diffraction, scanning electron microscopy, and physical adsorption-desorption analyzer. The removal of NO_x from simulated diesel vehicle exhaust gas was carried out using a fixed-bed reactor. The effects of C₃H₈, O₂ concentrations, and water vapor on the activity of the catalyst were studied. The results indicate that the Cu-SAPO-34 coatings obtained by the in situ synthesis are firm and compact, and the loading amount is found to be more than 20% after one synthesis operation. The surface areas of the Cu-SAPO-34/cordierite catalysts increase greatly compared with that of cordierite. The active Cu component prepared through in situ synthesis can significantly improve the activity of selective catalytic reduction of NO_x by C₃H₈. NO_x reduction over the Cu-SAPO-34/cordierite catalyst is more than 60% between 500 and 650 °C. The NO_x conversion decreases after the addition of 10% water vapor to the feed gas but the deactivation caused by water vapor is not permanent.

Key words: copper; SAPO-34; cordierite; NO_x; propane; in situ synthesis; selectivity catalytic reduction; diesel engines

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随着全球汽车工业的快速发展以及汽车拥有量的增加, 汽车尾气中 CO、碳氢化合物、NO_x 和微粒

物质的污染变得越来越严重,尤以 NO_x 危害备受关注。然而,由于柴油机尾气中富含氧,使传统三效催化剂很难有效脱除 NO_x。而 H₂、CO 或 NH₃ 对 NO_x 选择催化还原 (NO_x-SCR) 技术可有效脱除柴油机尾气中 NO_x^[1],所采用催化剂可分为金属氧化物催化剂、贵金属催化剂^[2]、分子筛催化剂^[3]和双功能催化剂^[4]。研究表明,有较高热稳定性的金属-SAPO-34 催化剂对 NO_x 的选择性还原有较高的活性^[5,6]。

众所周知,载体性质对负载型催化剂活性和寿命影响很大。堇青石 (2MgO·2Al₂O₃·5SiO₂) 因热稳定性好、热膨胀系数小和价格低廉^[7],而被广泛用作载体。堇青石蜂窝状催化剂一般由载体、涂层和活性组分组成。经传统涂覆技术制备的催化剂 (如 γ-Al₂O₃ 涂层的蜂窝状堇青石) 活性组分易流失,导致催化剂活性降低^[8];采用浸渍法负载活性组分,操作简单,但活性组分在载体上分散不均匀,易堵塞分子筛孔道,且活性组分流失将造成二次污染^[9]。然而,原位合成技术制备的蜂窝状堇青石分子筛涂层的比表面积较大,分子筛的内外表面可被完全利用,且其骨架结构或表面可含有高分散性金属,其中骨架中金属可很好用作氧化或还原反应活性中心^[10]。

本文采用一步水热法制备了 Cu-SAPO-34/堇青石催化剂,并运用 X 射线衍射 (XRD)、扫描电镜 (SEM) 和 N₂ 吸附-脱附等手段对催化剂性质进行了表征。将催化剂用于模拟柴油机车尾气中 NO_x 的脱除反应中,考察了还原气 C₃H₈ 和 O₂ 浓度以及水蒸气等对催化剂性能的影响。

1 实验部分

1.1 催化剂的制备

将蜂窝状堇青石切成 17 mm × 17 mm × 17 mm 大小的正方形块状,然后放入 15% 硝酸溶液中,80 °C 处理 2 h。用去离子水冲洗后,在 110 °C 干燥 2 h,再于 700 °C 焙烧 2 h,最后保存在干燥器中备用。

以吗啉为模板剂,分别以 CuO、磷酸、氢氧化铝和硅溶胶为活性金属源、磷源、铝源和硅源,晶化液按照 0.08 CuO:0.2 SiO₂:0.46 Al₂O₃:0.45 P₂O₅:1.25 C₄H₉NO:50 H₂O 的摩尔比配制。先将 CuO 添加到稀磷酸中,所得混合物在 80 °C 搅拌直至 CuO 被完全溶解;然后在搅拌下,于室温依次加入氢氧化铝、硅溶胶和吗啉,剧烈搅拌使之形成均匀溶胶;在 50

ml 高压釜的聚四氟乙烯的内衬底部支架上放置一块堇青石,并向其添加固定量的初始溶胶,密封;在 190 °C 和自身压力下静置晶化 7 d。晶化产物用去离子水冲洗,并在 110 °C 空气中干燥 3 h。随后,将制备的样品在含 O₂ 气氛中,于 700 °C 焙烧 5 h 以脱除模板剂^[11]。为了比较,同法制备 SAPO-34/堇青石。

1.2 催化剂的表征

通过称量负载前后堇青石质量,测得堇青石上 Cu-SAPO-34 的负载量。采用超声波发生器 (功率 200 W, 频率 20 kHz) 测试 Cu-SAPO-34/堇青石的机械强度及 Cu-SAPO-34 在堇青石上的附着程度。先用超声波发生器处理 Cu-SAPO-34/堇青石 60 min,再在 120 °C 干燥,根据下列方程式计算质量损失量: $\omega = (m_1 - m_0)/m_1 \times 100\%$, $\Delta\omega = (m_1 - m_2)/(m_1 - m_0) \times 100\%$ 。其中, ω 是 Cu-SAPO-34 的负载量, $\Delta\omega$ 是整体式催化剂质量损失, m_0 是初始堇青石质量, m_1 和 m_2 分别是超声处理前后 Cu-SAPO-34/堇青石质量。

催化剂的相结构在日本 Rigaku D/MAX2500 型 XRD 仪上表征, Cu K_α, $\lambda = 0.154056$ nm 辐射源,管电压 40 kV,管电流 100 mA,扫描速率 8°/min,扫描范围 5°~35°。样品形貌利用 Jeol Jsm-6700F 型 SEM 仪进行观察,为了增加样品的导电性,预先对样品表面喷金处理,加速电压为 10 kV。样品的比表面积在 Micromeritics 公司的 TriStar 3000 型物理吸附仪上测定,以液氮为吸附质。

1.3 催化剂的性能评价

在 C₃H₈ 气氛及常压下,于固定床反应器中考察 Cu-SAPO-34/堇青石催化剂上选择性催化还原 NO_x 的活性。装置由气路及其流量控制系统、固定床石英反应器 (内径 20 mm) 及其控温系统、检测系统组成。原料气组成为 0.05% NO_x, 0.05% C₃H₈ 和 0~10% O₂, 10% 水蒸气 (考察水蒸气影响的实验), N₂ 平衡气,总流量为 420 ml/min。通过加热使水汽化,并借助微量泵控制其流量。为考察空速的影响,放置 4 块 Cu-SAPO-34/堇青石 (平均直径为 18 mm,平均长度为 17 mm 的圆柱形) 在石英反应器中进行实验。采用烟气分析仪 (British, Kane-9106) 在线检测反应前后气体中 NO, NO₂, O₂ 和 C₃H₈ 的浓度。

为了确定原料气中 H₂O 对 NO_x 脱除性能的影响,在上述气体组成条件下,进行水的暂态响应实验。实验温度为 450 °C,使用 4 块催化剂,气体总流

表 1 整体式催化剂上 Cu-SAPO-34 的负载量及超声后的质量损失

Table 1 Cu-SAPO-34 loading and the mass loss of the samples

Sample	$\omega/\%$	$\Delta\omega/\%$
1	23.28	0.14
2	21.78	0.34
3	21.28	0.51

ω —the amount of Cu-SAPO-34 loading; $\Delta\omega$ —the mass loss of the monolithic catalyst.

量为 420 ml/min. 原料气和尾气中 NO_x 的浓度也由烟气分析仪在线测定. NO_x (NO 和 NO_2) 的转化率 X 由下式计算: $X = (c_1 - c_0)/c_1 \times 100\%$, 其中, c_1 和 c_0 分别是反应前后 NO_x 的浓度.

2 结果与讨论

2.1 Cu-SAPO-34 的负载量

活性组分的负载量和牢固度是影响整体式催化剂活性的重要因素, Cu-SAPO-34 的负载量及超声后的质量损失见表 1. 可以看出, 相同条件下, 由 3 个水热反应釜制备的 Cu-SAPO-34 的负载量分别是 23.28%, 21.78% 和 21.28%. 由此可见, 1 次操作后 Cu-SAPO-34 的负载量就可达 20% 以上, 而且实验的重复性较好. 60 min 超声振荡处理后, 质量损失分别为 0.14%, 0.34% 和 0.51%, 可见 Cu-SAPO-34/堇青石有着很好的牢固度, 由此可推断, 所制备的 Cu-SAPO-34/堇青石整体式催化剂在复杂条件下用于 NO_x 的还原时, 活性组分的流失小、机械性能好.

图 1 空白堇青石、Cu-SAPO-34 和 Cu-SAPO-34/堇青石的 XRD 谱

Fig. 1. XRD patterns of black cordierite (1), Cu-SAPO-34 (2), and Cu-SAPO-34/cordierite (3).

2.2 XRD 和 SEM 结果

图 1 为空白堇青石、Cu-SAPO-34 和 Cu-SAPO-34/堇青石的 XRD 谱. 可以看出, Cu-SAPO-34/堇青石在 $2\theta = 9.5^\circ, 15.96^\circ, 17.92^\circ, 20.05^\circ, 25.82^\circ, 30.92^\circ$ 和 31.2° 处出现的衍射峰, 归属为 SAPO-34, 表明 SAPO-34 已负载于堇青石基上. 同时样品中还出现少量其他物相的衍射峰, 但未出现 Cu 物种的衍射峰. 这可能是由于 Cu 含量低且分散均匀, 或者在合成过程中大部分 Cu 进入了催化剂的骨架^[12].

图 2 为堇青石和 Cu-SAPO-34/堇青石样品的 SEM 照片. 由图可见, 堇青石载体的表面结构不规

图 2 空白堇青石、Cu-SAPO-34 和 Cu-SAPO-34/堇青石的 SEM 照片

Fig. 2. SEM images of the surface of blank cordierite (a), Cu-SAPO-34/cordierite powder (b), external surface (c), and internal surface (d) of Cu-SAPO-34/cordierite.

图3 SAPO-34/堇青石及 Cu-SAPO-34/堇青石上 NO_x 转化率和 NO_2 选择性

Fig. 3. NO_x conversion (a) and NO_2 selectivity (b) of SAPO-34/cordierite (1) and Cu-SAPO-34/cordierite (2). Experimental conditions: 0.05% NO_x , 0.05% C_3H_8 , 7% O_2 , and SV = 6000 h^{-1} .

整; 而 Cu-SAPO-34/堇青石样品中既含有具有规整结构的颗粒, 又有无定形物质, 这与 XRD 结果一致。另外, 在 Cu-SAPO-34/堇青石样品中, 载体的内外表面负载的组分形貌不同^[13], 其中在载体外表面上 Cu-SAPO-34 趋向于形成更小的晶体, 呈空心状且表面有裂缝; 而在载体内表面的 Cu-SAPO-34 为均匀的矩形或正方形, 长度约为 20 μm , 且排列紧凑。

蜂窝状堇青石拥有不规整的多孔结构, 其比表面积仅为 1 m^2/g , 而负载 Cu-SAPO-34 后, 整体催化剂的比表面积显著增至 30 m^2/g 。催化剂比表面积的增加为化学吸附和催化反应提供了更多的位点, 从而有利于反应的进行^[14]。

2.3 整体式催化剂的 NO_x -SCR 活性

在 0.05% NO_x , 0.05% C_3H_8 , 7% O_2 的原料气组成, 空速 6000 h^{-1} 及 200~650 $^{\circ}\text{C}$ 条件下, 研究了 SAPO-34/堇青石及 Cu-SAPO-34/堇青石的 SCR- NO_x 活性, 结果见图 3。可以看出, Cu 的加入显著提高了整体式催化剂的活性, 这和 Iwamoto 等^[15]的研究结果类似: 在 560~585 $^{\circ}\text{C}$ 反应时, SAPO-34/堇青石上 NO_x 的最高转化率为 10%; 而在 500~650 $^{\circ}\text{C}$, Cu-SAPO-34/堇青石上 NO_x 的最高转化率达 30%。还可以看出, 在 300~400 $^{\circ}\text{C}$ 时, 这两种催化剂上

图4 C_3H_8 浓度对 Cu-SAPO-34/堇青石的 SCR- NO_x 活性的影响

Fig. 4. Effect of $\text{C}_3\text{H}_8/\text{NO}_x$ ratio on the NO_x -SCR activity of Cu-SAPO-34/cordierite. Experimental conditions: 0.05% NO_x , 7% O_2 , $\text{C}_3\text{H}_8/\text{NO}_x = 1:2, 1:1$ or $2:1$, and SV = 3000 h^{-1} .

NO_2 的选择性较大, 但在 NO_x 转化率较高的温度区间 560~585 $^{\circ}\text{C}$, NO_2 选择性较小, 分别仅有 5.6% 和 3.9%。

2.4 反应条件对 NO_x -SCR 反应活性的影响

柴油机是典型的贫燃型发动机, 它在富氧条件下工作。因此, 本文考察了贫燃气氛下空速、还原剂和 O_2 浓度对 Cu-SAPO-34/堇青石上 NO_x 的 SCR 活性的影响。

随着柴油机工作条件的不同, 碳氢化合物浓度也会发生很大的变化, 从而对选择性催化还原 NO_x 活性产生明显的影响。图 4 为在 0.05% NO_x , 7% O_2 和 SV = 3000 h^{-1} 条件下, 还原剂 C_3H_8 的浓度对整体式催化剂上 NO_x 和 C_3H_8 转化率的影响。由图可见, 当 $\text{C}_3\text{H}_8/\text{NO}_x$ 由 1:2 增加到 2:1 时, NO_x 转化率由 50.2% 增加到 80.2%; 当 $\text{C}_3\text{H}_8/\text{NO}_x$ 为 2:1 时, 在 480~680 $^{\circ}\text{C}$ NO_x 转化率在 60% 以上, 说明 C_3H_8 的增加有利于反应的进行。另外, C_3H_8 转化率随反应温度的升高而增加, 低于 600 $^{\circ}\text{C}$ 时 C_3H_8 转化的变化趋势与 NO_x 一致; 当达 600 $^{\circ}\text{C}$ 时, C_3H_8 基本上被完全氧化, 但当 $\text{C}_3\text{H}_8/\text{NO}_x$ 由 1:2 增加到 2:1 时, C_3H_8 催化氧化不受影响。

图 5 O_2 浓度对 Cu-SAPO-34/堇青石 NO_x -SCR 活性的影响

Fig. 5. Effect of O_2 concentration on the NO_x -SCR activity of Cu-SAPO-34/cordierite. O_2 concentration: (1) 2%; (2) 5%; (3) 7%; (4) 10%. Experimental conditions: 0.05% NO_x , 0.05% C_3H_8 , and $SV = 3000\ h^{-1}$.

图 5 为 O_2 浓度对 Cu-SAPO-34/堇青石催化剂的 SCR 活性的影响。由图可见, 随着 O_2 浓度的增加, NO_x 转化率逐渐降低。当 O_2 浓度为 2% 时, 在 500~650 $^{\circ}C$ NO_x 转化率能达到 78.0%, 而当 O_2 浓度为 10% 时, NO_x 转化率低于 50%。这表明在较高 O_2 浓度下, 氧化反应的存在抑制了 NO_x 的 SCR 反应的进行。

尾气净化催化剂所使用空速的变化非常大, 因此本文考察了空速对 Cu-SAPO-34/堇青石上 NO_x -SCR 活性的影响, 结果见图 6。可以看出, 在一个较宽的空速范围内, NO_x 转化率保持较高的水平;

图 6 空速对 Cu-SAPO-34/堇青石的 NO_x -SCR 活性的影响

Fig. 6. Effect of space velocity on the NO_x -SCR activity of Cu-SAPO-34/cordierite. Space velocity: (1) $3000\ h^{-1}$; (2) $4000\ h^{-1}$; (3) $6000\ h^{-1}$; (4) $12000\ h^{-1}$. Reaction conditions: 0.05% NO_x , 0.05% C_3H_8 , and 7% O_2 .

图 7 水蒸气对 Cu-SAPO-34/堇青石的 NO_x -SCR 活性的影响

Fig. 7. Effect of water vapor on the NO_x -SCR activity of Cu-SAPO-34/cordierite. (1) Before adding water; (2) Adding water; (3) Stop adding water. Experimental conditions: 0.05% NO_x , 0.05% C_3H_8 , 7% O_2 , and $SV = 3000\ h^{-1}$.

随着空速的增加, NO_x 转化率有所降低。当空速为 $3000\ h^{-1}$ 时, NO_x 转化率能达到 60%。在较低的空速下, 反应气体的接触时间延长, 从而导致 NO_x 的 SCR 活性增加^[16]。

在上述实验基础上, 考察了 10% 水蒸气对 Cu-SAPO-34/堇青石催化剂上 NO_x -SCR 活性的影响, 结果见图 7。可以看出, 当原料气中引入水后, NO_x 最高转化率由无水时的 60.2% 下降至有水时的 38.8%, 当停止引入水后, NO_x 转化率可恢复至 45%。

为了进一步揭示 H_2O 对 NO_x -SCR 活性的影响, 进行了 H_2O 的暂态响应实验: 在一定时间将 10% 的 H_2O 添加到原料气中或从原料气中去除, 然后当出口气体中 NO_x 浓度不再改变时停止添加, 结果见

图 8 Cu-SAPO-34/堇青石作用下 H_2O 对尾气中 NO_x 浓度的影响

Fig. 8. Effect of H_2O on the NO_x concentration of the effluent in Cu-SAPO-34/cordierite. Reaction conditions: 0.05% NO_x , 0.05% C_3H_8 , 7% O_2 , 10% H_2O (when used), $SV = 3000\ h^{-1}$, and 500 $^{\circ}C$.

图 8. 可以看出, 加入水后, 尾气中 NO_x 浓度明显下降; 当停加水后, NO_x 浓度上升到一稳定值, 由此推测由水蒸气引起的失活是部分可逆的. Shelef 研究表明^[17], 在催化剂表面上 NO_2 的形成是 SCR 反应的速率控制步骤. 在催化剂表面上的 H_2O 分子和 NO_2 分子的竞争吸附引起了催化剂活性的降低. 但是将水去除后, 此竞争反应随之停止, 所以反应活性可以部分恢复.

3 结论

采用原位水热法制备了 Cu-SAPO-34/堇青石整体式催化剂, 经 1 次合成就可使 Cu-SAPO-34 的负载量超过 20%, 而且它和堇青石具有很高的牢固度, 整体式催化剂的比表面积也显著增加至 $30 \text{ m}^2/\text{g}$. 制备的整体式催化剂对柴油机车尾气表现出高的脱硝活性, 在 $500\sim 650^\circ\text{C}$ 范围内 NO_x 的脱除率在 60% 以上. 适当增加 C_3H_8 浓度, 或降低 O_2 浓度或空速都有利于 NO_x -SCR 活性的提高. 在原料气中添加 10% 的水后, NO_x 转化率降低, 但停加水蒸气后, 催化剂活性可部分恢复.

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英 译 文

English Text

Along with the rapid development of the global automotive industry and the increase in automobile ownership, pollution by carbon monoxide, hydrocarbons, NO_x , and particulate matter in the exhaust gases of cars has become more serious. Pollution by NO_x has especially received plenty of attention. However, the removal of NO_x is difficult using the conventional three-way catalyst because of the high oxygen content in diesel engine exhaust gas. The selective catalytic reduction (SCR) of NO_x under an oxidizing atmosphere by hydrogen, hydrocarbons or NH_3 has been used for the catalytic removal of NO_x in diesel engine exhaust gases [1]. The catalyst can generally be divided into four categories: metal oxide catalysts, noble metal catalysts [2], molecular sieve catalysts [3], and bifunctional catalysts [4]. The metal-SAPO-34 has been reported to be highly active for the selective reduction of NO_x with high thermal stability [5,6].

The carrier properties greatly affect the supported catalyst's activity and service-life. Cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) monoliths are widely used because of their superior hydrothermal stability, low thermal expansivity, plasticity and low price [7]. Honeycomb catalysts are generally composed of a carrier, a coating and active components. Catalysts prepared by traditional coating technology such as the $\gamma\text{-Al}_2\text{O}_3$ coating honeycomb cordierite easily lose active components resulting in the reduction of catalytic efficiency [8]. The impregnation method for the loading of active components is simple but their distribution on the carrier is inhomogeneous and the pores of the molecular sieve are easily blocked. Furthermore, the loss of active components leads to secondary pollution [9]. However, the molecular sieve coatings of the honeycomb cordierite catalysts that were prepared by in situ synthesis have a larger surface area and the internal and external surfaces of the molecular sieve may be fully used. These direct methods provide materials with good metal dispersion in the structure and the metal of the skeleton are good activity centers for oxidation or reduction [10].

In this paper, we report on the preparation of a Cu-SAPO-34/cordierite catalyst by a one-step hydrothermal procedure. The characteristics of the Cu-SAPO-34/cordierite

samples were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and physical adsorption-desorption analyzer. The removal of NO_x from simulated diesel vehicle exhaust gas was carried out. The effects of C_3H_8 , oxygen concentration, and water vapor on catalyst activity were investigated.

1 Experimental

1.1 Catalyst preparation

Cordierite honeycomb was cut into square-shaped samples with dimensions of 17 mm $\times$ 17 mm $\times$ 17 mm. The samples were treated with a 15% nitric acid solution at 80 °C for 2 h, washed with deionized water, dried at 110 °C for 2 h, calcined at 700 °C for 2 h and then stored in a drier for future use.

We used morpholine as a template, copper oxide as the source of the active metal, phosphoric acid, aluminum hydroxide and silica gel as the phosphorus source, aluminum source and silicon source, respectively. The molar ratio used was 0.08CuO:0.2SiO₂:0.46Al₂O₃:0.45P₂O₅:1.25 C₄H₉NO:50 H₂O in the crystallization solution. The Cu-SAPO-34/cordierite sample was synthesized as follows: CuO was added to the dilute solution of orthophosphoric acid. The mixture was stirred at 80 °C until the CuO was completely dissolved. Al(OH)₃ was then added at room temperature to form a homogeneous gel by stirring. Subsequently, SiO₂ and morpholine were added to the gel under stirring. A piece of cordierite was placed in the bottom of the PTFE liner of a 50 ml autoclave and the certain amount initial gel was put into, sealed. At 190 °C and under an autogenous pressure, the gel was statically crystallized for 7 d. The crystalline product was washed with distilled water and dried in air for 3 h. The synthesized samples were calcined under an oxygen atmosphere at 700 °C for 5 h to remove the template [11]. For comparison, SAPO-34/cordierite was also prepared according to the above-mentioned methods.

1.2 Catalyst characterization

The loading mass was calculated by weighing the cordierite before and after the loading. The mechanical intensity of the Cu-SAPO-34/cordierite and the degree of adhesion of Cu-SAPO-34 onto cordierite was evaluated using an ultrasonic generator (power 200 W, frequency 20 kHz). Cu-SAPO-34/cordierite monoliths were treated for 60 min by ultrasonic vibration. The samples were dried at 120 °C and then the mass losses were calculated based on the formulae $\omega = (m_1 - m_0)/m_1 \times 100\%$ and $\Delta\omega = (m_1 - m_2)/(m_1 - m_0) \times 100\%$, where ω is the amount of Cu-SAPO-34 loading, $\Delta\omega$ is

the mass loss of the monolithic catalyst, m_0 is the weight of raw cordierite, m_1 and m_2 are the weights of Cu-SAPO-34/cordierite before and after ultrasonic treatment, respectively.

The catalyst phase structures were examined by (Rigaku D/max2500 diffractometer) with a graphite monochromator and Cu K_α radiation sources ($\lambda = 0.154056$ nm), a tube voltage of 40 kV and a tube current of 100 mA. The scan rate was 8°/min and the 2θ value ranged from 5° to 35°. The morphology of the samples was examined by SEM (JEOL Jsm-6700F). The samples were covered with a thin gold layer and the accelerating voltage was 10 kV. The surface area of the samples was determined by BET analysis (TriStar 3000, Micromeritics Instrument Corporation) using liquid nitrogen adsorption.

1.3 Catalyst evaluation

The activities of the Cu-SAPO-34/cordierite catalyst for the SCR reaction of NO_x by C_3H_8 at atmospheric pressure were determined using a fixed-bed flow microreactor. The devices were composed of a gas-way equipped with a flow controller, fixed bed quartz reactors (inner radii 20 mm), a temperature controller, and a detection system. A total flow rate of 420 ml/min was used for the catalytic activity runs. The feed gas consisted of 0.05% NO_x , 0.05% C_3H_8 , 0–10% O_2 , with or without 10% H_2O , and N_2 was used as the balance gas. The water was gasified by heating and the amount was controlled using a trace pump. Four pieces of Cu-SAPO-34/cordierite (cylindrical shape with an average diameter of 18 mm and an average length of 17 mm) were put into the quartz reactor for each run except for the evaluation of the influence of space velocity. NO , NO_2 , O_2 , and C_3H_8 in the gases before and after the catalytic reaction were analyzed simultaneously on-line by flue gas analysis (British, Kane-9106).

To identify the influence of H_2O in the feed gas on NO_x removal, H_2O -response experiments were performed using the fixed bed reactor and the above-mentioned typical feed gas. These experiments were carried out at 450 °C with four pieces of catalyst and a total flow of 420 ml/min. The NO_x concentration of the feed and effluent gases was also measured on-line by the flue gas analyzer.

NO_x (NO and NO_2) conversion was calculated using the following equation $X = (c_1 - c_0)/c_1 \times 100\%$, where X is the conversion of NO_x , c_1 and c_0 are the concentration of NO_x before and after the reaction, respectively.

2 Results and discussion

2.1 Cu-SAPO-34 loading

The amount of loading and the degree of active component adhesion are important factors for the activity of the mono-

lithic catalyst. The amount of Cu-SAPO-34 loading and the mass losses after ultrasonic treatment are shown in Table 1.

The loading of Cu-SAPO-34 from the three different autoclaves under the same conditions were 23.28%, 21.78%, 21.28%, respectively. Cu-SAPO-34 loading was found to be more than 20% after one synthesis operation and the repeatability of the experiment was very good. The mass losses after 60 min of ultrasonic oscillations were found to be 0.14%, 0.34%, and 0.51%, respectively. These results indicate that Cu-SAPO-34/cordierite has a good degree of adhesion and that it can be used under complex conditions for the reduction of NO_x .

2.2 XRD and SEM results

The XRD patterns of blank cordierite, Cu-SAPO-34, and Cu-SAPO-34/cordierite are shown in Fig. 1. The characteristic diffraction peaks at $2\theta = 9.5^\circ, 15.96^\circ, 17.92^\circ, 20.05^\circ, 25.82^\circ, 30.92^\circ$, and 31.2° for Cu-SAPO-34/cordierite correspond to the characteristic peaks of SAPO-34, which suggests that the SAPO-34 crystallites are loaded onto the cordierite substrate. Meanwhile, a few diffraction peaks are also present in Fig. 1. It should be noted that no characteristic peaks of Cu species are present in the Cu-SAPO-34/cordierite spectrum. This is attributed to a very even Cu distribution on the surface or to the transfer of a majority of the Cu to the skeleton of the catalyst during the synthesis process [12].

The SEM images of the cordierite and Cu-SAPO-34/cordierite samples are given in Fig. 2. It is shown that the cordierite supports have an irregular structure, however, there are many grains with a regular structure and some amorphous material in Cu-SAPO-34/cordierite samples. The results from SEM are consistent with the XRD spectra of the samples. However, it is interesting that some differences exist in the feature of the component loaded on the internal and external surfaces of the carriers [13], as shown in Fig. 2. We conclude that Cu-SAPO-34 tends to form smaller crystalloids on the external surfaces than on the internal surfaces of the support, moreover, the Cu-SAPO-34 crystalloids that are loaded onto the external surface of cordierite appear to be blocked crystalloids and cracks are present on the outer surface; however, the Cu-SAPO-34 loaded on the inner surface of cordierite show uniform rectangles crystalloids of about 20 μm in length.

The cordierite substrate has an irregular macroporous structure and its specific surface area was only 1 m^2/g . The specific surface areas of the monolithic catalyst after loading Cu-SAPO-34 increase greatly to 30 m^2/g . This increase in specific surface area is essential for the catalytic reaction and it provides more sites for chemical adsorption and catalytic reactions so that it is good for the reactions [14].

2.3 NO_x -SCR activity of the monolithic catalysts

The NO_x -SCR activity of SAPO-34/cordierite and Cu-SAPO-34/cordierite under dry conditions (0.05% NO_x , 7% O_2 , $\text{SV} = 6000 \text{ h}^{-1}$) from 200 to 650 $^\circ\text{C}$ was investigated and the results are shown in Fig. 3. The highest conversion rate of NO_x on the SAPO-34/cordierite was around 10% between 560 and 585 $^\circ\text{C}$. The conversion rate of NO_x on the Cu-SAPO-34/cordierite was 30% between 500 and 650 $^\circ\text{C}$. This result suggests that the addition of copper significantly improves the monolithic catalyst activity, which is the same as the results of Iwamoto et al. [15]. Figure 3 also shows that NO_2 selectivity over both the catalysts was high from 300 to 400 $^\circ\text{C}$. However, from 560 to 585 $^\circ\text{C}$ where NO_x conversions were high, the NO_2 selectivities were only about 5.6% and 3.9% for SAPO-34/cordierite and Cu-SAPO-34/cordierite, respectively.

2.4 Effect of reaction conditions on NO_x -SCR activity

The diesel engine, as a true lean-burn engine, works under excess oxygen conditions. Moreover, the SCR activity of NO_x over Cu-SAPO-34/cordierite in lean mixture environments was investigated. The factors that influence the SCR activity of NO_x are mainly the space velocity, the reducing agent, and the O_2 concentration.

The concentration of hydrocarbon in a diesel engine changes greatly under different conditions so that the SCR activity of NO_x is greatly influenced by the reducing agent's concentration. Figure 4 shows the effect of the reducing agent C_3H_8 concentration on the NO_x -SCR over the monolithic catalyst at 0.05% NO_x , 7% O_2 , and a SV of 3000 h^{-1} . The NO_x conversion rate increases from 50.2% to 80.2% when the $\text{C}_3\text{H}_8/\text{NO}_x$ ratio increases from 1:2 to 2:1. At a $\text{C}_3\text{H}_8/\text{NO}_x$ ratio of 2, the conversion rate of NO_x is more than 60% between 480 and 680 $^\circ\text{C}$. This suggests that a moderate increase in hydrocarbon favors NO_x -SCR activity.

Figure 4(b) shows that C_3H_8 was completely oxidized at a reaction temperature of 600 $^\circ\text{C}$ and the results show that C_3H_8 is activated with difficulty on the catalyst. An increase in the hydrocarbon concentration does not affect the C_3H_8 oxidation process.

The NO_x -SCR activity of the catalysts was investigated using different O_2 concentrations and the results are shown in Fig. 5. The NO_x conversion decreases gradually with an increase in the O_2 concentration. At an O_2 concentration of 2%, NO_x conversion is 78.0% between 500 and 650 $^\circ\text{C}$, however, at an O_2 concentration of 10%, NO_x conversion lower than 50%. This means that the SCR process of NO_x will be inhibited because of the oxidative reaction at the high O_2 concentration.

The catalysts used in exhaust gas purification operate

under complex conditions such as fast changes in gas flow. Therefore, the effect of space velocity on the NO_x -SCR activity of Cu-SAPO-34/cordierite was investigated and the results are shown in Fig. 6. We found that NO_x conversion remains high over a broader range of space velocity and it decreases with an increase in space velocity. When the space velocity is 3000 h^{-1} , NO_x conversion reaches 60%. The contact time of the reaction gas is long at a low space velocity, which leads to high NO_x -SCR activity [16].

The effect of 10% water vapor on the NO_x -SCR activity of Cu-SAPO-34/cordierite is shown in Fig. 7. NO_x conversion decreases obviously from 60.2% without water to 38.8% with water. When water addition was stopped the highest NO_x conversion was still 45%.

To differentiate the effect of H_2O on the NO_x -SCR activity, H_2O -response experiments were carried out. In this experiment, H_2O was added to the feed gas at specific times and then removed when the NO_x concentration in the effluent did not change. The results are shown in Fig. 8. It can be seen that the NO_x concentration of the exhaust decreased obviously after H_2O addition, and the NO_x concentration rose to a stable value after H_2O removal. The deactivation caused by water vapor is not permanent. Shelef [17] found that the

formation of NO_2 on the catalyst surface is rate controlled during the SCR reaction. Competitive adsorption between H_2O molecules and NO_2 molecules on the surface of the catalyst resulted in a decrease in catalyst activity.

3 Conclusions

The Cu-SAPO-34/cordierite monolithic catalyst was prepared by in situ hydrothermal synthesis. The amount of Cu-SAPO-34 loading on cordierite is more than 20% after one synthesis operation and its degree of adhesion is high. The specific surface area of the monolithic catalyst significantly increases to $30 \text{ m}^2/\text{g}$. The prepared monolithic catalyst shows high activity for the de- NO_x reaction with more than 60% conversion between 500 and 650°C . A higher amount of C_3H_8 , a lower oxygen concentration or a lower space velocity favors NO_x -SCR activity. NO_x conversion decreases after the addition of 10% water to the feed gas and the deactivation trend caused by water vapor is abated when it is removed.

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