低温等离子体处理对 NiO/Al₂O₃ 吸附 NO_x 的促进作用李秋荣^{1,2,*}, 武金宝¹, 郝吉明²¹燕山大学环境与化学工程学院, 河北秦皇岛 066004²清华大学环境科学与工程系, 北京 100084

摘要: 采用共沉淀法制备了不同 NiO 负载量的 NiO/Al₂O₃ 催化剂, 并用于 NO_x 储存还原技术去除 NO_x 反应中。结果表明, 当 Ni/Al 摩尔比为 0.3 时, NiO/Al₂O₃ 样品的 NO_x 吸附量最大; 随着 Ni 含量的增加, NiAl₂O₄ 晶相减少。沉淀物在高温煅烧前利用低温等离子体处理后, 所得催化剂吸附 NO_x 的能力明显增强, 当 Ni/Al 摩尔比为 0.3 的催化剂, NO_x 吸附量由未处理时的 345 μmol/g 增至经处理后的 477 μmol/g。研究发现, 经低温等离子体处理后, 催化剂上粒子更加分散, 比表面积增大。另外, 利用原位红外光谱分析了催化剂吸附 NO_x 的机理。结果表明, 吸附的 NO 首先在催化剂表面以桥式亚硝酸盐形式存在, 然后转变成不同形式的硝酸盐。

关键词: 氧化镍; 氧化铝; 氮氧化物; 低温等离子体; 吸附; 储存量; 稀燃发动机

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NO_x Storage Capacity Enhancement on NiO/Al₂O₃ Pretreated with a Non-thermal PlasmaLI Qiurong^{1,2,*}, WU Jinbao¹, HAO Jiming²¹College of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China²Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract: In the NO_x storage reduction (NSR) technology used to remove NO_x from lean burn engines, the NO_x storage material is crucial. For NiO/Al₂O₃ catalysts with different NiO loading prepared by coprecipitation, the maximum storage capacity for NO_x occurred at a Ni/Al molar ratio of 0.3 in the catalyst. The intensity of the NiAl₂O₄ diffraction peak decreased with increased nickel content. When the catalysts were pretreated by a non-thermal plasma (NTP) before calcination at high temperature, the adsorption capacities for NO_x increased, with an increase from 345 to 477 μmol/g on the NiO/Al₂O₃ catalyst with the Ni/Al molar ratio of 0.3. The metal dispersion was increased with the NTP treatment, which resulted in a high surface area. The NO_x storage mechanism was discussed on the basis of DRIFTS results, which indicated that NO was first adsorbed on the surface as bridged nitrites, and then the nitrites species was transformed into different kinds of NO₃⁻ adsorbed species.

Key words: nickel oxide; aluminum oxide; nitric oxides; non-thermal plasma; adsorption; storage capacity; lean burn engine

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十多年来, 氮氧化物 (NO_x) 储存还原 (NSR) 技术 一直应用于稀燃发动机的废气处理中。在常规 NSR

催化剂(如 Pt/BaO/Al₂O₃)中, 贵金属是催化剂的活性组分, 而碱土金属氧化物在 NO_x 储存方面起着重要作用^[1~7]. 由于在 200~500 °C 的较宽的温度范围内, NSR 催化剂在低温下应具有较大的 NO_x 储存能力^[8,9]. 考虑到贵金属催化剂的高成本, 人们一直尝试过渡金属氧化物(尤其是 NiO), 因具有良好的催化性能而被用于许多反应过程^[10~15], 另外, 低温等离子体(NTP)处理 Ni 基催化剂可极大改善其性能^[16,17]. 然而, 有关于 Ni 基催化剂的 NO_x 吸附性能的研究尚未见报道. 本文采用共沉淀法制备 NiO/Al₂O₃ 催化剂, 并在高温煅烧前用低温等离子体处理. 考察其低温储存 NO_x 的能力, 并探讨其储存 NO_x 的机理.

1 实验部分

1.1 催化剂的制备

采用共沉淀法制备 NiO/Al₂O₃ 催化剂. 先将 200 ml 0.6 mol/L 的 Al(NO₃)₃ 溶液和一定量聚乙二醇加入到 500 ml 三颈瓶中, 再加入沉淀剂 (NH₄)₂CO₃, 在 70 °C 搅拌 6 h 后, 分别按 Ni/Al 摩尔比为 0.15, 0.3, 0.45, 0.6, 和 1.0 加入硝酸镍溶液^[18]. 溶液 pH 值调为 9, 所得溶胶于 70 °C 老化, 过滤, 干燥后, 在 330 °C 煅烧 3 h, 然后升至 550 °C 煅烧 2.5 h, 所得催化剂分别记为 NiO/Al₂O₃-0.15(C), NiO/Al₂O₃-0.3(C), NiO/Al₂O₃-0.45(C), NiO/Al₂O₃-0.6(C) 和 NiO/Al₂O₃-1.0(C).

低温等离子体的装置参见文献[19]. 将上述所得不同 Ni/Al 摩尔比的溶胶经 330 °C 煅烧 3 h 后, 利用 NTP 处理(放电功率为 80 W) 30 min 后, 再在 550 °C 煅烧 2 h, 所得样品依次标记为 NiO/Al₂O₃-0.15(P), NiO/Al₂O₃-0.3(P), NiO/Al₂O₃-0.45(P), NiO/Al₂O₃-0.6(P) 和 NiO/Al₂O₃-1.0(P).

1.2 催化剂的表征

样品比表面积测定在 NOVA4000e 型比表面积分析仪上进行. 实验前样品于 300 °C 脱气 2 h, 以 N₂ 为吸附质于 -196 °C 下进行.

样品 X 射线衍射(XRD)实验采用 TTR-III 型粉末 XRD 仪, Cu 靶光源, 管电压 60 kV, 电流 300 mA, 扫描范围 10°~90°, 扫描速率为 4°/min.

程序升温还原(H₂-TPR)测试在 Micromeritics ChemiSorb 2720 型自动装置上进行, 采用 U 形石英管反应器, 样品用量为 50 mg. 样品于 300 °C 通 N₂ 预处理 30 min, 冷却至室温. 切换为 10% H₂-90% Ar 混

合气, 控制混为 50 ml/min, 待记录仪基线平稳后, 以 10 °C/min 升温至 1000 °C. TCD 检测器检测耗 H₂ 量.

采用 JEOL 200CX 型透射电镜(TEM)观察样品形貌和粒径.

催化剂样品用 VG Scientific ESCALab220i-XL 型光电子能谱(XPS)仪分析. 激发源为 Mg K_α 射线, 功率为 300 W. 分析时基础真空为 3 × 10⁻⁷ Pa. 电子结合能用无定形碳的 C 1s (284.8 eV) 校正. 测定 C 1s, O 1s, Ni 2p 和 Al 2p 的结合能. 实验所得数据用 XPSPEAK 软件处理(Gaussian/Lorantzia 比为 90/10).

催化剂表面反应物吸附态及中间物种通过漫反射原位池和高灵敏度液氮冷却 MCT 检测器的 Nicolet Nexus 870-FTIR 型傅里叶红外光谱仪分析. 扫描范围 4000~400 cm⁻¹, 分辨率 4 cm⁻¹, 扫描数 100.

催化剂粉末试样直接置于原位池的样品台内并压实, 反应前于 500 °C 经 8% O₂-92% N₂ 混合气(400 ml/min)预处理 30 min 以除去表面杂质. 背景谱图是在指定温度下稳定 20 min 后采集, 样品谱图是在吸附开始后采集, 反应为 0.05% NO, 8% O₂, N₂ 平衡, 总流量为 100 ml/min. 吸附 30 min 后降温到 50 °C, 并用 100 ml/min 纯 N₂ 吹扫 1 h, 然后升温至各温度点进行脱附, 稳定 20 min 后采集图谱.

1.3 NO 吸附-脱附

称取 0.5 g 催化剂放入内径为 5 mm 的 U 形石英管中, 在 500 °C 经 8% O₂-92% N₂ 气流(400 ml/min)中预处理 30 min 后, 将反应器温度降到 100 °C, 通入总流量为 400 ml/min 的 0.05% NO + 8% O₂ + N₂ (平衡气) 吸附气体, 恒温吸附 30 min. 采用 NO-NO₂-NO_x 分析仪在线测量反应前后 NO_x 浓度. 程序升温脱附(TPD)测试实验装置和催化剂装量同上, 且在上述实验之后进行. 将催化剂吸附 0.05% NO + 8% O₂ + N₂ (平衡气) 30 min 后, 关闭 NO 和 O₂ 后, 用 N₂ (400 ml/min) 吹扫 1 h 以除去催化剂表面物理吸附的 NO_x, 然后以 10 °C/min 从常温升到 500 °C, 使用 NO-NO₂-NO_x 分析仪检测脱附气体中 NO、NO₂ 和 NO_x 浓度, 催化剂的 NO_x 储存量根据脱附峰面积计算.

2 结果与讨论

2.1 Ni 负载量和 NTP 处理对催化剂 NO_x 储存能力的影响

表 1 为不同 Ni 含量的 NiO/Al₂O₃ 催化剂的 NO_x

表 1 各 NiO/Al₂O₃ 催化剂在不同处理条件下的 NO_x 储存量和穿透时间

Table 1 NO_x storage capacity and break through time of different NiO/Al₂O₃ catalysts with different treatment conditions

Catalyst	Break through time (min)	NO _x storage capacity (μmol/g)
NiO/Al ₂ O ₃ -0.15(C)	5	283
NiO/Al ₂ O ₃ -0.15(P)	5.5	344
NiO/Al ₂ O ₃ -0.30(C)	5	345
NiO/Al ₂ O ₃ -0.30(P)	7	477
NiO/Al ₂ O ₃ -0.45(C)	5	330
NiO/Al ₂ O ₃ -0.45(P)	7	475
NiO/Al ₂ O ₃ -0.60(C)	5	316
NiO/Al ₂ O ₃ -0.60(P)	7	385
NiO/Al ₂ O ₃ -1.0(C)	4	268
NiO/Al ₂ O ₃ -1.0(P)	7	391

C—conventional method; P—plasma treatment method.

储存量和穿透时间. 由表可见, NiO/Al₂O₃-0.15(C), NiO/Al₂O₃-0.30(C), NiO/Al₂O₃-0.45(C) 和 NiO/Al₂O₃-0.60(C) 吸附穿透时间为 5 min, 而 NiO/Al₂O₃-1.0(C) 样品的为 4 min, 且当 Ni/Al 摩尔比为 0.3 时, 样品的 NO_x 储存能力达最大, 为 345 μmol/g. 催化剂经 NTP 处理后, 其吸附穿透时间明显延长. NiO/Al₂O₃-0.30(P), NiO/Al₂O₃-0.45(P), NiO/Al₂O₃-0.60(P) 和 NiO/Al₂O₃-1.0(P) 催化剂的吸附穿透时间为 7 min, 且 NiO/Al₂O₃-0.30(P) 样品的 NO_x 储存能力最大, 为 477 μmol/g, 比 NiO/Al₂O₃-0.30(C) 的提高了 38%. 吸附穿透后, 出口处 NO_x 浓度逐渐达到 0.07% 左右. 可见, 经 NTP 的催化剂需要较长时间达到吸附饱和. 由于 Ni/Al 摩尔比为 0.30 的 NiO/Al₂O₃ 催化剂的 NO_x 储存能力最高, 下文有关催化剂表征主要采用该催化剂.

图 1 催化剂的 NO_x-TPD 谱

Fig. 1. NO_x-TPD profiles of NiO/Al₂O₃-0.30(C) (1) and NiO/Al₂O₃-0.30(P) (2) catalysts.

2.2 NTP 处理对催化剂 NO_x 脱附的影响

由表 1 可见, 经 NTP 处理后, 催化剂的 NO_x 储存能力显著增加. 图 1 为 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 的 NO_x-TPD 谱. 可以看出, 这两个催化剂分别在 120, 200 和 430 °C 附近出现三个脱附峰. 但经 NTP 处理催化剂的 NO_x 脱附量在低温和高温区明显增加. 120 °C 处的脱附峰应与偏铝酸镍有关, 随着镍含量的增加, 偏铝酸镍的峰减弱, 偏铝酸镍可能是 NO_x 储存能力的一个重要因素^[18].

2.3 催化剂的表征

2.3.1 比表面积

表 2 为各催化剂的比表面积. 可以看出, 随着 Ni 负载量的增加, Ni 物种在载体表面发生聚集和堆积, 载体的一些孔道被堵塞, 导致 NiO 分散性变差, 因而催化剂的比表面积下降. 值得注意的是经 NTP 处理催化剂的比表面积明显增加, 这主要是由于 NTP 处理可以改善催化剂粒子的分散性.

表 2 经和未经 NTP 处理 NiO/Al₂O₃ 催化剂的比表面积

Table 2 Specific surface area of NiO/Al₂O₃ catalysts with and without the NTP treatment

Catalyst	<i>A</i> _{BET} /(m ² /g)
NiO/Al ₂ O ₃ -0.15(C)	201.6
NiO/Al ₂ O ₃ -0.15(P)	225.9
NiO/Al ₂ O ₃ -0.30(C)	193.3
NiO/Al ₂ O ₃ -0.30(P)	213.7
NiO/Al ₂ O ₃ -0.45(C)	189.2
NiO/Al ₂ O ₃ -0.45(P)	206.3
NiO/Al ₂ O ₃ -0.60(C)	175.6
NiO/Al ₂ O ₃ -0.60(P)	190.2
NiO/Al ₂ O ₃ -1.0(C)	146.8
NiO/Al ₂ O ₃ -1.0(P)	169.2

2.3.2 XRD 结果

图 2 为不同 NiO/Al₂O₃ 催化剂的 XRD 谱. 可以看出, Ni/Al 摩尔比为 0.15 和 0.30 时, NiO/Al₂O₃ 样品于 19°, 31°, 37°, 45° 和 65° 处出现 NiAl₂O₄ 衍射峰, 且经 NTP 处理后样品的稍弱, 这是由于 NTP 处理使得 NiAl₂O₄ 晶粒变小所致^[20], 但 NiO/Al₂O₃-0.30(P) 在 19° 的 NiAl₂O₄ 衍射峰则比 NiO/Al₂O₃-0.30(C) 的强.

经 NTP 处理后, Ni/Al 摩尔比为 0.60 和 1.0 的样品中 NiO 衍射峰强度增加, 且随着 Ni 含量增加, NiO 衍射峰增强. 这说明所得样品均具有良好的晶体结构. 另外, Ni/Al 摩尔比为 0.60 的 NiO/Al₂O₃ 样品的 NiAl₂O₄ 峰形比摩尔比为 0.30 的弥散, 而当摩尔比为

图 2 经和未经 NTP 处理 NiO/Al₂O₃ 催化剂的 XRD 谱

Fig. 2. XRD patterns of NiO/Al₂O₃ catalysts with and without the NTP treatment. (1) NiO/Al₂O₃-0.15(C); (2) NiO/Al₂O₃-0.15(P); (3) NiO/Al₂O₃-0.30(C); (4) NiO/Al₂O₃-0.30(P); (5) NiO/Al₂O₃-0.60(C); (6) NiO/Al₂O₃-0.60(P); (7) NiO/Al₂O₃-1.0(C); (8) NiO/Al₂O₃-1.0(P).

图 3 不同方法制备的 NiO/Al₂O₃ 催化剂的 H₂-TPR 谱

Fig. 3. H₂-TPR profiles of NiO/Al₂O₃ catalysts prepared by the different methods. (1) NiO/Al₂O₃-0.30(C); (2) NiO/Al₂O₃-0.30(P).

1.0 时基本消失. 结合样品的 NO_x 吸附量可知, Ni/Al 摩尔比为 0.3 样品的吸附性能最好, 故可推测 NiAl₂O₄ 可能是影响样品 NO_x 吸附性能的一个重要因素^[18].

2.3.3 H₂-TPR 结果

图 3 为 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 样品的 H₂-TPR 谱. 可以看出, 催化剂出现 2 个耗 H₂

峰: NiO/Al₂O₃-0.30(C) 的分别位于 318 和 639 °C, NiO/Al₂O₃-0.30(P) 的分别位于 308 和 612 °C. 低温还原峰应归属于 Ni₂O₃→NiO 的还原, 高温还原峰则对应于 NiO→Ni. 可以看出, 经 NTP 处理后, 催化剂还原温度降低, 峰形变宽, 说明催化剂经 NTP 处理后更易于被还原, 更有利于 NO 的氧化.

2.3.4 TEM 结果

图 4 为 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 样品的 TEM 照片. 由图可见, NiO/Al₂O₃-0.30(C) 样品上的粒子分散不是非常均匀, NiO 团聚现象比较严重. 与 NiO/Al₂O₃-0.30(C) 相比, NiO/Al₂O₃-0.30(P) 的团聚现象则不是太明显, 粒子分布比较均匀. 利用等离子体物理和凝聚态物理研究低温等离子体处理催化剂的特性^[21], 等离子体处理后催化剂的活性显著提高.

图 4 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 样品的 TEM 照片

Fig. 4. TEM images of NiO/Al₂O₃-0.30(C) (a) and NiO/Al₂O₃-0.30(P) (b) samples.

2.3.5 XPS 结果

不同方法制备的催化剂的 Ni 2p_{3/2} 结合能见图 5. 由图可见, NiO/Al₂O₃-0.30(C) 的 Ni 2p_{3/2} 主峰在 853.8 eV 处, 卫星峰在 859.9 eV, 自旋轨道耦合能间隙

图 5 不同方法制备的 NiO/Al₂O₃ 催化剂的 Ni 2p XPS 谱
Fig. 5. Ni 2p XPS spectra of NiO/Al₂O₃ catalysts prepared by the different methods. (1) NiO/Al₂O₃-0.30(C); (2) NiO/Al₂O₃-0.30(P).

表 3 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 催化剂表面元素的相对含量

Table 3 Relative amounts of the elements on NiO/Al₂O₃-0.30(C) and NiO/Al₂O₃-0.30(P) surface

Catalyst	Relative amounts (%)		
	O	Al	Ni
NiO/Al ₂ O ₃ -0.30(C)	69.59	22.45	7.96
NiO/Al ₂ O ₃ -0.30(P)	70.11	21.61	8.28

为 17.8 eV, 而 NiO/Al₂O₃-0.30(P) 样品的以上各峰分别出现在 854.4, 860 和 16.9 eV. NiO 和 NiAl₂O₄ 的 Ni 2p_{3/2} 结合能分别为 854.5 和 856 eV. 由上可见, NiO/Al₂O₃-0.30(P) 的 Ni 2p_{3/2} 结合能比 NiO/Al₂O₃-0.30(C) 的稍高, 这是由于它们表面元素含量差异所致^[22]. 表 3 为这 2 个样品表面元素的相对含量. 可以看出, 经 NTP 处理后, 催化剂表面 O 和 Ni 的相对含量有所增加, 且其中偏铝酸镍的含量也略高, 所以 NiO/Al₂O₃-0.30(P) 的 Ni 2p_{3/2} 结合能比 NiO/Al₂O₃-0.30(C) 的高, 这与 NO_x-TPD 的结果一致.

2.4 FT-IR 结果

2.4.1 NO_x 吸附

图 6 为 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 催化剂在 100 °C 吸附 NO 随时间变化的 DRIFT 谱. 可以看出, 催化剂表面吸附物种的吸收峰集中在 1000~1800 cm⁻¹, 其中 1040 cm⁻¹ 可归属于 *cis*-(N₂O₂)²⁻ 吸附物种, 1205 cm⁻¹ 附近为桥式亚硝酸盐, 1260, 1400 和 1560 cm⁻¹ 为不同形式的硝酸盐物

种, 1620 cm⁻¹ 可归属为气态 NO₂ 的物理吸附^[23,24].

对于 NiO/Al₂O₃-0.30(C) 样品, 吸附刚开始时, 在催化剂表面主要有桥式亚硝酸盐 (1215 cm⁻¹) 和弱 NO₂ 吸附物种 (1624 cm⁻¹)^[25], 至 3 min 时, NO₂ 的吸收峰比较明显, 并出现桥式硝酸盐 (1560 cm⁻¹) 物种. 吸附 5 min 时, 硝酸盐物种吸收峰明显增强. 至 7 min 时, 吸附物种转变为桥式亚硝酸盐 (1263 cm⁻¹), 单齿硝酸盐 (1296 cm⁻¹), 桥式硝酸盐和 NO₂ 吸附物种. 至 10 min 时, *cis*-(N₂O₂)²⁻ (1040 cm⁻¹) 吸附物种以及桥式亚硝酸盐, 单齿硝酸盐, 桥式硝酸盐和 NO₂ 吸附物种吸收峰增强. 继续吸附至 30 min 时, 各吸附峰变化不大^[26~29]. 对于 NiO/Al₂O₃-0.30(P) 样品, 吸附刚开始时, 催化剂表面主要以桥式亚硝酸盐 (1199~1223 cm⁻¹) 为主, 吸附 10 min 后, 吸附物种主要是桥式亚硝酸盐 (1269 cm⁻¹), 单齿硝酸盐 (1299 cm⁻¹), 桥式硝酸盐 (1542 cm⁻¹) 和少量气态 NO₂ 物理吸附, 没有出现 *cis*-(N₂O₂)²⁻ 的吸附物种. 另外, NiO/Al₂O₃-0.30(P) 样品的各吸收峰比 NiO/Al₂O₃-0.30(C) 的较宽.

2.4.2 NO_x 的脱附

NO_x 在 0.3 NiO/Al₂O₃(C) 和 0.3 NiO/Al₂O₃(P) 催化剂表面吸附 30 min 后, 停止 NO + O₂ 进气, 改以相同气量 N₂ 吹扫, 然后程序升温并采集 DRIFTS 谱, 结果见图 7. 对于 NiO/Al₂O₃-0.30(C) 样品, 200 °C 时仍存在 NO₂ 的物理吸收峰, 1294 和 1251 cm⁻¹ 处的吸收带逐渐减弱, 并在 400 °C 完全消失. 当温度升到 400 °C 时, 弱 *cis*-(N₂O₂)²⁻ 吸收物种消失. 桥式硝酸盐的吸

图 6 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 的 DRIFTS 谱

Fig. 6. DRIFTS spectra of NiO/Al₂O₃-0.30(C) (a) and NiO/Al₂O₃-0.30(P) (b).

图 7 NiO/Al₂O₃-0.30(C) 和 NiO/Al₂O₃-0.30(P) 的 NO_x 脱附红外光谱

Fig. 7. DRIFTS spectra of NO_x thermal desorption of the catalyst with and without NTP treatment. (a) NiO/Al₂O₃-0.30(C); (b) NiO/Al₂O₃-0.30(P).

收峰强度在 400 °C 开始减弱, 至 500 °C 时完全消失.

对于 NiO/Al₂O₃-0.30(P) 样品, NO₂ 物理吸附峰在 300 °C 以下仍稳定存在, 至 400 °C 时完全消失; 其他吸收峰在 500 °C 时完全消失, 这与 NiO/Al₂O₃-0.30(C) 的相同, 而且 NiO/Al₂O₃-0.30(P) 的脱附峰更宽.

比较图 1 和图 7, 可以发现, 经 NTP 处理后, 催化剂上各物种吸收峰和脱附峰面积较大, 说明催化剂表面吸附物种的量增加. 然而, 目前关于低温等离子体处理催化剂的吸附机理还不十分清楚.

3 结论

NiO 负载量是影响 NiO/Al₂O₃ 催化剂的 NO_x 储存能力的一个因素, 当 Ni:Al 摩尔比为 0.3 时, 催化剂的 NO_x 储存量最大. NiO 负载量明显影响粒子的分散性, 随着 Ni 含量的增加, 催化剂比表面积减小, NiAl₂O₄ 晶粒变小, 它对样品 NO_x 储存能力的影响较大. 经等离子体活化后, 催化剂的 NO_x 储存量增加, 当 Ni:Al 摩尔比为 1.0 时, 经等离子体处理催化剂的 NO_x 储存量是未经等离子体处理的 1.46 倍. 在 NO_x 的吸附过程中, NO 首先以桥式亚硝酸盐形式吸附在催化剂表面, 然后变成不同形式的硝酸盐物种.

参 考 文 献

- 1 Takahashi N, Shinjoh H, Iijima T, Suzuki T, Yamazaki K, Yokota K, Suzuki H, Miyoshi N, Matsumoto S I, Tanizawa T, Tanaka T, Tateishi S S, Kasahara K. *Catal Today*, 1996, **27**: 63
- 2 Li J H, Goh W H, Yang X C, Yang R T. *Appl Catal B*, 2009, **90**: 360
- 3 Wei L S, Li J H, Tang X F. *Catal Lett*, 2009, **127**: 107
- 4 Li J H, Li W, Yang R T. *Catal Lett*, 2009, **129**: 104
- 5 Cheng W H, Wu K C, Lo M Y, Lee C H. *Catal Today*, 2004, **97**: 145
- 6 Zhou G, Luo T, Gorte R J. *Appl Catal B*, 2006, **64**: 88
- 7 Xu J, Harold M P, Balakotaiah V. *Appl Catal B*, 2009, **89**: 73
- 8 Nova I, Lietti L, Castoldi L, Tronconi E, Forzatti P. *J Catal*, 2006, **239**: 244
- 9 Frola F, Prinetto F, Ghiotti G, Castoldi L, Nova I, Lietti L, Forzatti P. *Catal Today*, 2007, **126**: 81
- 10 Opoku-Gyamfi K, Adesina A A. *Appl Catal A*, 1999, **180**: 113
- 11 Seo Y S, Kang S K, Han M H, Baek Y S. *Catal Today*, 1999, **47**: 421
- 12 Radwan N R E, El-Shobaky G A, Fahmy Y M. *Appl Catal A*, 2004, **274**: 87
- 13 Lee K M, Lee W Y. *Catal Lett*, 2002, **83**: 65
- 14 李翠平, 赵瑞红, 郭奋, 陈建峰. 物理化学学报 (Li C P, Zhao R H, Guo F, Chen J F. *Acta Phys-Chim Sin*), 2007, **23**: 157
- 15 李翠平, 赵瑞红, 郭奋, 陈建峰. 北京化工大学学报 (Li C P, Zhao R H, Guo F, Chen J F. *J Beijing Univ Chem Technol*), 2007, **34**: 358
- 16 Wang J G, Liu C J, Zhang Y P, Yu K, Zhu X L, He F. *Catal Today*, 2004, **89**: 183
- 17 Cheng D G, Zhu X L, Ben Y H, He F, Cui L, Liu C J. *Catal Today*, 2006, **115**: 205
- 18 李秋荣, 李俊华, 贺君, 刘遥, 郝吉明. 环境化学 (Li Q R, Li J H, He J, Liu Y, Hao J M. *Environ Chem*), 2010, **29**: 721

- 19 Liu C J, Yu K L, Zhang Y P, Zhu X L, He F, Eliasson B. *Appl Catal B*, 2004, **47**: 95
- 20 Zou J J, Liu C J, Zhang Y P. *Langmuir*, 2006, **22**: 2334
- 21 Clayton R D, Harold M P, Balakotaiah V, Wan C Z. *Appl Catal B*, 2009, **90**: 662
- 22 Lenglet M, Hochu F, Dürr J, Tuilier M H. *Solid State Commun*, 1997, **104**: 793
- 23 Fanson P T, Horton M R, Delgass W N, Lauterbach J. *Appl Catal B*, 2003, **46**: 393
- 24 Su Y, Amiridis M D. *Catal Today*, 2004, **96**: 31
- 25 Westerberg B, Fridell E. *J Mol Catal A*, 2001, **165**: 249
- 26 Chen L, Li J H, Ge M F. *J Phys Chem C*, 2009, **113**: 21177
- 27 Chen L, Li J H, Ge M F, Zhu R H. *Catal Today*, 2010, **153**: 77
- 28 Li J H, Zhu R H, Cheng Y S, Lambert C K, Yang R T. *Environ Sci Technol*, 2010, **44**: 1799
- 29 Muncief R L, Khanna P, Kabin K S, Harold M P. *Catal Today*, 2004, **98**: 393

英 译 文

English Text

NO_x storage-reduction (NSR) technology for lean burn exhaust treatment has been much studied in the past decade. In the conventional NSR catalysts such as Pt/BaO/Al₂O₃, the noble metal is the active component. The alkaline earth oxides also play a key role in NO_x storage [1–7]. NSR catalysts should have a large NO_x adsorption capacity at low temperature because of the wide temperature range it must be used in, which range from 200 to 500 °C [8–9]. Due to the high cost of precious metals, transition metal oxides have been much investigated, especially, catalysts with NiO as the active component that have been used in many chemical reactions for their performance [10–15]. The application of a non-thermal plasma (NTP) during the preparation of a Ni-based catalyst can improve the catalyst performance [16,17]. The NO_x adsorption capability of Ni-based catalysts have not yet been reported. In this work, NiO/Al₂O₃ catalysts were prepared by coprecipitation, and the catalysts that were treated with NTP before calcination at high temperature were compared with those without a NTP treatment before calcination. The adsorption capacity of NO_x at low temperature on NiO/Al₂O₃ with a NTP treatment was investigated. A promotional mechanism was proposed on the basis of characterization results.

1 Experimental

1.1 Preparation of catalyst

The catalysts were prepared by coprecipitation. The Al(NO₃)₃ (200 ml 0.6 mol/L) solution and a required quantity

of polyoxyethylene glycol were mixed in a 500 ml three-necked flask. Then the precipitating agent (NH₄)₂CO₃ was slowly added with high speed stirring at 70 °C for 6 h. The appropriate amount of nickel nitrate solution was added to give molar ratios of Ni/Al of 0.15, 0.3, 0.45, 0.6, and 1.0 [18]. The pH of the solution was adjusted to 9 and the inorganic colloidal sol was aged at 70 °C. After filtration and drying, the catalysts were calcined at 330 °C for 3 h and then at 550 °C for 2.5 h. This was for the preparation without a NTP treatment. The products were denoted as NiO/Al₂O₃-0.15(C), NiO/Al₂O₃-0.30(C), NiO/Al₂O₃-0.45(C), NiO/Al₂O₃-0.60(C), and NiO/Al₂O₃-1.0(C).

The setup for the NTP treatment has been described elsewhere [19]. When the non-thermal plasma treatment was used, the samples prepared as above were treated by NTP in air before calcination at 550 °C with a discharge power of 80 W for 30 min. After the NTP treatment, the catalysts were calcined at 550 °C for 2 h. These samples were denoted as NiO/Al₂O₃-0.15(P), NiO/Al₂O₃-0.30(P), NiO/Al₂O₃-0.45(P), NiO/Al₂O₃-0.60(P), and NiO/Al₂O₃-1.0(P).

1.2 Characterizations of the catalysts

The BET surface areas were measured by N₂ adsorption at –196 °C using a NOVA4000e instrument. Prior to the measurement, the samples were degassed at 300 °C for 2 h.

Phase identification was performed by an X-ray diffractometer (XRD, TTR-III) operated at 60 kV voltage and 300 mA current.

H₂ temperature-programmed reduction (H₂-TPR) experiments were performed on a Micromeritics ChemiSorb 2720 using 50 mg samples. After pretreatment in N₂ at 300 °C for 1 h, the samples were cooled down to room temperature. The reducing gas, a mixture of 10% H₂-90% Ar, at a flow rate of 50 ml/min, was used to reduce the catalysts from room temperature to 1000 °C with a temperature ramp of 10 °C/min.

Transmission electron microscope (TEM) images to determine the particle size were obtained using a JEOL 200CX microscope operated at 200 kV.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K_α radiation. The base pressure was 3 × 10^{–7} Pa. The binding energies were referenced to the C 1s line from adventitious carbon at 284.8 eV. Binding energies (*E_b*) were measured for C 1s, O 1s, Ni 2p, and Al 2p. The spectra were deconvoluted using the XPSPEAK program by curve fitting with a Gaussian/Lorentian ratio of 90/10 after smoothing and subtraction of the Shirley-type background.

All spectra were measured with 4 cm^{–1} resolution between 4000–400 cm^{–1} and 100 scans using a liquid nitrogen cooled

MCT detector on a Nicolet Nexus 870-FTIR.

The in situ DRIFTS measurements were carried out in a high temperature cell fitted with ZnSe windows. The samples were finely ground, placed in a ceramic crucible and manually pressed. The feed gas was flowed into the cell at a total flow rate of 100 ml/min. Prior to measurement, the samples were pretreated at 500 °C in a mixture of N₂ and 8% O₂ for 30 min. Background spectra were collected after dwelling for 20 min at a given temperature. Sample spectra were collected after dwelling for 30 min in the mixture gas of 0.05% NO, 8% O₂, and balanced by N₂ at 100 ml/min.

1.3 NO adsorption-desorption

NO adsorption experiments were carried out in a U-shaped quartz reactor with an inner diameter of 5 mm under atmospheric pressure. The amount of catalysts was 0.5 g for each run. The samples were pretreated in 8% O₂-92% N₂ at a total flow rate of 400 ml/min at 500 °C for 30 min, and then cooled to 100 °C in N₂ for adsorption. When the temperature stabilized at 100 °C, a mixture gas comprising 0.05% NO, 8% O₂, and balanced with N₂ at 400 ml/min was passed through the samples. At this stage, the concentrations of NO, NO₂, and NO_x in the outlet stream were recorded by an online Chemiluminescence NO_x analyzer (42C High Level, Thermo Electron Corporation). After adsorption for 30 min, NO and O₂ were removed and pure N₂ (400 ml/min) was introduced for 1 h to remove weakly adsorbed species on the surface of catalysts. Then temperature-programmed desorption (TPD) experiments were performed by ramping the temperature from room temperature to 500 °C at 10 °C/min with 400 ml/min N₂. The concentration of NO, NO₂, and NO_x in the outlet stream were also measured by the NO_x analyzer. The NO_x storage capacity (NSC) was calculated from the integral area of the desorption profile.

2 Results and Discussion

2.1 Influence of NiO loading and NTP treatment on NSC of the catalysts

The NO_x storage capacity and break through time of the catalysts with different Ni contents are listed in Table 1. No NO_x was detected in the effluent in the initial 5 min for NiO/Al₂O₃-0.15(C), NiO/Al₂O₃-0.30(C), NiO/Al₂O₃-0.45(C), and NiO/Al₂O₃-0.60(C), and in the initial 4 min for NiO/Al₂O₃-1.0(C). When the molar ratio of Ni and aluminum was 0.3, the NO_x storage capacity reached the maximum value of 345 μmol/g on NiO/Al₂O₃-0.30(C). When the NiO loading was higher or lower than that of NiO/Al₂O₃-0.30(C), the NSC of the catalyst was lower than that of NiO/Al₂O₃-0.30(C). For the catalysts that were first treated

by the NTP in the preparation, the time of breakthrough clearly increased, and it was 7 min for NiO/Al₂O₃-0.30(P), NiO/Al₂O₃-0.45(P), NiO/Al₂O₃-0.60(P), and NiO/Al₂O₃-1.0(P). The maximum NSC of 477 μmol/g was obtained on NiO/Al₂O₃-0.30(P), which was increased by 38% compared to the NSC of NiO/Al₂O₃-0.30(C). After breakthrough, the NO_x concentration in the outlet stream gradually increased to 0.07%. The results showed that it took a longer time to reach adsorption saturation on the catalysts subjected to the NTP treatment. Hereafter, the characterization was mainly with the NiO/Al₂O₃ catalyst with a Ni/Al molar ratio of 0.30 because of its higher NO_x storage capacity.

2.2 Influence of NTP treatment on NO_x desorption

It can be seen from Table 1 that the NSC of the catalysts were increased by the NTP treatment. Figure 1 shows the TPD profiles of NO+O₂ adsorption over NiO/Al₂O₃-0.30(C) and NiO/Al₂O₃-0.30(P). Three NO_x desorption peaks at 120, 200, and 430 °C were observed on the catalysts with and without the NTP treatment.

The NSCs of NiO/Al₂O₃-0.30(P) were larger than those of NiO/Al₂O₃-0.30(C) at both low and high temperatures. NO_x desorption amounts of the catalysts with the NTP treatment were clearly enhanced in both the low and high temperature regions. The NO_x desorption peak observed at 120 °C was related to nickel meta-aluminate (NiAl₂O₄). The reason is that the intensity of nickel meta-aluminate peak weakened with an increase of Ni content. The presence of nickel meta-aluminate is an important factor in NO_x storage capacity [18].

2.3 Characterization of the catalysts

2.3.1 Specific surface area

The specific surface areas are summarized in Table 2. It can be seen that the specific surface area of the catalysts decreased with increasing Ni loading. The reason is that nickel oxides supported on the carrier agglomerated so that some pores of the carrier were clogged. It is significant that the specific surface area of the catalysts with the NTP treatment increased. The probable reason is that the NTP treatment improved the dispersion of the particles.

2.3.2 XRD characterization

The XRD patterns of NiO/Al₂O₃-0.30(C) and NiO/Al₂O₃-0.30(P) are shown in Fig. 2. Two phase structures were observed: one was assigned to NiO, and the other was attributed to NiAl₂O₄. Fig. 2(1) and (4) show the main peaks of NiAl₂O₄. The peaks of NiAl₂O₄ in NiO/Al₂O₃ catalysts

with Ni/Al molar ratio of 0.15 and 0.30 are very distinct at 19°, 31°, 37°, 45°, and 65°. The intensities of NiO/Al₂O₃ catalysts with the NTP treatment were weaker than those without the NTP treatment. The intensities of some peaks decrease as a result of the breakup of crystalline granules by the plasma treatment [20], but the peak intensity of NiAl₂O₄ in NiO/Al₂O₃-0.30(P) at 19° was stronger than that of NiO/Al₂O₃-0.30(C).

Figure 2(5)–(8) are the XRD patterns of NiO/Al₂O₃ catalysts with Ni/Al molar ratio of 0.6 and 1.0. However, the diffraction intensities of the catalysts with the NTP treatment were strengthened. With increasing Ni content, the intensities of the NiO diffraction peaks were enhanced. These results revealed that the catalysts had good crystalline structure. The peaks of NiAl₂O₄ in NiO/Al₂O₃ with Ni/Al molar ratio of 0.6 were more diffuse than those of NiO/Al₂O₃ with Ni/Al molar ratio of 0.3. The peaks of NiAl₂O₄ in NiO/Al₂O₃ with Ni/Al molar ratio of 1.0 had basically disappeared. The adsorption capacity of NiO/Al₂O₃ with Ni/Al molar ratio of 0.3 was the largest among the catalysts, which indicated NiAl₂O₄ had an obvious effect in the crystalline complex.

2.3.3 H₂-TPR characterization

H₂-TPR experiments were carried out to investigate the reducibility of the catalysts. The results are shown in Fig. 3. The NiO/Al₂O₃-0.30(C) catalyst showed one reduction peak at 318 °C, while it was at 308 °C for NiO/Al₂O₃-0.30(P), which was attributed to the reduction of Ni₂O₃ into NiO. The NiO/Al₂O₃-0.30(C) catalyst showed another reduction peak at 639 °C, which was at 612 °C for NiO/Al₂O₃-0.30(P), which can be described to the reduction of NiO into Ni.

The reduction temperature of the catalyst with the NTP treatment was lower than that of the catalyst without the NTP treatment. The peak temperature of the catalyst with the NTP treatment decreased and the peak became wider. The catalysts with the NTP treatment were easier to reduce, which would be advantageous for NO oxidation.

2.3.4 TEM characterization

TEM images of NiO/Al₂O₃ with Ni/Al molar ratio of 0.3 are shown in Fig. 4. The results showed that NiO/Al₂O₃-0.30(C) did not have good particle dispersion, and the agglomeration phenomenon of nickel oxide on the surface of catalyst was very serious. In comparison with NiO/Al₂O₃-0.30(C), agglomeration of the particles on NiO/Al₂O₃-0.30(P) was not obvious. Many particles had a highly discrete distribution in Fig. 4(b), and the particle distribution of NiO/Al₂O₃-0.30(P) was very uniform. The characteristics of the highly efficient catalysts prepared from using a NTP treatment had been studied by plasma physics

and cluster physics [21], which showed that the activity of the loaded metal was greatly modified by the NTP treatment.

2.3.5 XPS characterization

The Ni 2p_{3/2} binding energy of the catalysts by the different treatment methods are shown in Fig. 5. The NiO/Al₂O₃-0.30(C) exhibited the Ni 2p_{3/2} main peak at 853.8 eV with satellites around 859.9 eV and a spin-orbit coupling energy gap of 17.8 eV. The NiO/Al₂O₃-0.30(P) exhibited the Ni 2p_{3/2} main peak at 854.4 eV with satellites around 860 eV and a spin-orbit coupling energy gap of 16.9 eV. The Ni 2p_{3/2} E_B of pure NiO is 854.5 eV while for NiAl₂O₄ spinel, it appears at 856 eV. The Ni 2p_{3/2} E_B of NiO/Al₂O₃-0.30(P) was slightly higher than that of NiO/Al₂O₃-0.30(C), which reflected the different surface elements present [22]. Table 3 shows the relative amounts of surface nickel and oxygen. The amounts of nickel and oxygen on the surface of the catalyst increased after the NTP treatment. The amount of NiAl₂O₄ on the surface of the catalyst treated by NTP was more than that of the catalyst without the NTP treatment, so the Ni 2p_{3/2} E_B of NiO/Al₂O₃-0.30(P) was higher than that of NiO/Al₂O₃-0.30(C). This was consistent with the NO_x-TPD results.

2.4 FT-IR spectra

2.4.1 NO_x adsorption

In situ DRIFTS of NiO/Al₂O₃-0.30(C) and NiO/Al₂O₃-0.30(P) during adsorption of 0.05% NO in the presence of 8% O₂ at 100 °C are shown in Fig. 6. The adsorption peaks of the species on the surface of the catalysts were between 1000–1800 cm⁻¹. The peak at 1040 cm⁻¹ can be assigned to *cis*-(N₂O₂)²⁻, that at 1205 cm⁻¹ nearby can be assigned to bridging nitrite, and those at 1260, 1400, and 1560 cm⁻¹ were assigned to different nitrates. The peak at 1620 cm⁻¹ nearby can be assigned to physical adsorbed NO₂ [23,24].

When adsorption began on the surface of the catalysts, there were mainly bridging nitrite (1215 cm⁻¹) and weakly adsorbed NO₂ species (1624 cm⁻¹) [25]. After 3 min, the adsorption peak at 1624 cm⁻¹ became obvious and bridging nitrate (1560 cm⁻¹) species appeared. After 5 min, the adsorbing peak of nitrate adsorbed species became obvious. After 7 min, the adsorption species changed into bridging nitrite (1263 cm⁻¹), monodentate nitrate (1296 cm⁻¹), bridging nitrate (1560 cm⁻¹), and NO₂ adsorbed species (1624 cm⁻¹). After 10 min, the adsorbed species intensity of *cis*-(N₂O₂)²⁻ (1040 cm⁻¹) increased, and simultaneously, bridging nitrite (1263 cm⁻¹), monodentate nitrate (1296 cm⁻¹), bridging nitrate (1560 cm⁻¹), and NO₂ adsorbed spe-

cies (1624 cm⁻¹) existed on the surface of catalysts. The adsorption peaks at 15 and 30 min were the same as those at 10 min [26–29]. The DRIFTS spectrum of NiO/Al₂O₃-0.30(P) is shown in Fig. 6(b). When adsorption began on surface of the catalyst, there was mainly bridging nitrite (1199–1223 cm⁻¹). After 10 min, the adsorbed species were mainly bridging nitrite (1269 cm⁻¹), monodentate nitrate (1299 cm⁻¹), bridging nitrate (1542 cm⁻¹), and a small amount of NO₂ physically adsorbed (1624 cm⁻¹). There were no adsorbed species of *cis*-(N₂O₂)²⁻ (1040 cm⁻¹) on the catalyst surface. The adsorption peak bands of NiO/Al₂O₃-0.30(P) were broader than those of NiO/Al₂O₃-0.30(C).

2.4.2 Thermal desorption of NO_x species

Further information on the nature of the surface species observed in the NO/O₂ adsorption experiments were gained from thermal desorption studies. Figure 7 shows the results of NO_x desorption from NiO/Al₂O₃-0.30(C) and NiO/Al₂O₃-0.30(P). In Fig. 7(a), it can be seen that the physically adsorbed NO₂ with its characteristic band at 1620 cm⁻¹ was stable to 200 °C. The bands at 1294 and 1251 cm⁻¹ decreased gradually and vanished at 400 °C. As the temperature increased to 400 °C, the weakly adsorbed species at 1040 cm⁻¹ vanished. The intensity of bridging nitrate (1570 cm⁻¹) bands started to decrease at 400 °C and had completely disappeared by 500 °C. In Fig. 7(b), physically adsorbed NO₂ with its characteristic band at 1621 cm⁻¹ was stable to 300 °C and it disappeared at 400 °C. The other peaks of NiO/Al₂O₃-0.30(P) had completely vanished at 500 °C, which was the same result as that of NiO/Al₂O₃-0.30(C). The desorption peak bands of NiO/Al₂O₃-0.30(P) also became broad.

On comparing the desorption temperature in the NO_x-TPD spectra (Fig. 1) and the DRIFTS spectra of the thermal desorption experiment (Fig. 7), the NO_x-TPD spectra indicated that the areas of the adsorption peaks and desorption peaks on catalysts with the NTP treatment became larger. This indicated that the amounts of adsorbed species on the catalysts with the NTP treatment were larger than that on the catalysts without the NTP treatment. However, the adsorption mechanism on the catalysts with the NTP treatment is not yet known.

3 Conclusions

NiO loading was one factor that influenced the NO_x storage capacity of NiO/Al₂O₃ catalysts. The optimum NiO loading was 30% molar ratio. The NiO loading affected the dispersion, and with increased Ni loading, the specific surface area of the catalyst decreased. The nickel meta-aluminate diffraction peaks weakened with increased Ni loading, and nickel meta-aluminate could be a key phase for NO_x storage capacity. The storage capacities of NO_x on the catalysts prepared with a NTP were higher than those on the catalysts without the NTP treatment. The NO_x storage capacity of NiO/Al₂O₃ with the NTP treatment was 1.46 times larger than that of NiO/Al₂O₃ (molar ratio of 1 for Ni and Al) without the NTP treatment. The DRIFTS results indicated that during NO_x adsorption on the catalysts, NO was first adsorbed on the surface as bridging nitrites, and then the nitrite species transformed into different kinds of NO₃⁻ adsorbed species.

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