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# 水热老化对不同方法制备的 Fe-ZSM-5 用于 NH<sub>3</sub>选择性 催化还原 NO<sub>x</sub> 的影响

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**摘要:**采用液体离子交换、等体积浸渍和固相离子交换制备了一系列 Fe-ZSM-5 催化剂,并将其用于 NH<sub>3</sub>选择性催化还原 NO<sub>x</sub> (NH<sub>3</sub>-SCR) 反应. 运用 X 射线衍射、紫外-可见漫反射吸收光谱和原位漫反射傅里叶变换红外光谱对催化剂进行了表征. 结果 表明, Fe-ZSM-5 催化剂表面 Fe 物种可分为孤立 Fe<sup>3+</sup>物种、低聚 Fe 氧化物团簇和 Fe<sub>2</sub>O<sub>3</sub>,各催化剂上 NH<sub>3</sub>-SCR 反应活性不同 的根本原因是其表面 Fe 物种分布不同.水热老化后, Fe-ZSM-5 催化剂上 400 °C 以下反应时 NO<sub>x</sub> 转化率降低,而高温活性略 有提高,各催化剂活性差异减小;同时 NH<sub>3</sub>氧化活性和 NO 氧化活性均明显降低.这可归因于水热老化使 Fe-ZSM-5 催化剂表 面的孤立 Fe<sup>3+</sup>物种相对浓度降低,低聚 Fe 氧化物团簇和 Fe<sub>2</sub>O<sub>3</sub> 相对浓度增加,以及催化剂表面 Brønsted 酸性位显著减少所致. **关键词**: 氮氧化物;选择性催化还原; 铁; ZSM-5 分子筛; 氨; 水热老化

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## Hydrothermal Deactivation of Fe-ZSM-5 Prepared by Different Methods for the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub>

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**Abstract:** A series of Fe/ZSM-5 catalysts were prepared by liquid ion exchange, incipient wetness impregnation, and solid-state ion exchange to investigate the selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR). The effect of hydrothermal deactivation of Fe-ZSM-5 catalysts prepared by different methods as a function of Fe loading was investigated. Freshly made and hydrothermal aged Fe-ZSM-5 catalysts were studied through NH<sub>3</sub>-SCR activity test and characterized using X-ray diffraction, UV-Vis diffuse reflectance spectroscopy, and in situ diffuse reflectance infrared Fourier transform spectroscopy. Iron species on the surface of Fe-ZSM-5 catalysts were assigned to isolated Fe<sup>3+</sup> species, oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters, and Fe<sub>2</sub>O<sub>3</sub> particles based on the UV-Vis spectra. The iron species distributions in the Fe-ZSM-5 catalysts prepared by these methods were quite different, which resulted in difference in SCR activity. The NH<sub>3</sub>-SCR activity of different Fe-ZSM-5 catalysts became very similar after aging, and the activity of NH<sub>3</sub> oxidation and NO oxidation decreased with the aged catalysts. Characterization results indicated that the activity change of the aged Fe-ZSM-5 catalysts was due to the change of iron species distribution in Fe-ZSM-5 catalysts after hydrothermal aging. The relative concentration of isolated Fe<sup>3+</sup> species was decreased, whereas the relative concentration of oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters and Fe<sub>2</sub>O<sub>3</sub> particles was increased in the aged catalysts. A considerable decrease in the Brønsted acidity of catalysts was observed for the aged Fe-ZSM-5 catalysts.

Key words: nitrogen oxide; selective catalytic reduction; iron; ZSM-5 zeolite; ammonia; hydrothermal aging

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柴油机排放的氮氧化物 (NO<sub>x</sub>) 和颗粒物 (PM) 严重地污染大气环境.NH<sub>3</sub>选择性催化还原 (NH<sub>3</sub>-SCR) 是净化富氧尾气中 NO<sub>x</sub> 的主流技术之 一.V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> 催化剂在 NH<sub>3</sub>-SCR 净化 NO<sub>x</sub> 中具有高活性和优良的抗硫性能,是最先得到商业 化应用的 SCR 催化剂,主要用于固定源烟气脱硝, 当用于柴油车尾气 NO<sub>x</sub> 净化时存在 V<sub>2</sub>O<sub>5</sub>毒性和催 化剂热稳定性的问题<sup>[1~3]</sup>,因此人们致力于研发新型 非钒基 NH<sub>3</sub>-SCR 催化剂.在众多催化剂体系中,过 渡金属交换的分子筛因具有比钒基催化剂更高的热 稳定性和更宽的活性温度窗口而受到重视,其中以 Fe-ZSM-5 最受关注<sup>[4,5]</sup>.

大量研究表明<sup>[4]</sup>, 分子筛的 Si/Al 比、Fe 交换度 及其制备方法等均影响 Fe-ZSM-5 的 NH<sub>3</sub>-SCR 催 化活性.目前 Fe-ZSM-5 催化剂的制备方法主要有 液体离子交换 (IE)<sup>[6-8]</sup>, 等体积浸渍 (IWI)<sup>[7-10]</sup>, 化 学 气 相 沉 积 (CVD)<sup>[11-15]</sup> 以 及 固 相 离 子 交 换 (SSIE)<sup>[16-18]</sup>.

Fe-ZSM-5 催化剂的 NH<sub>3</sub>-SCR 活性与其表面 Fe 物种的分布相关. 用紫外-可见漫反射吸收光谱 (UV-Vis DRS)、穆斯堡尔光谱和电子顺磁共振的研 究结果认为, Fe-ZSM-5 表面存在孤立 Fe<sup>3+</sup>物种、低 聚 Fe 氧化物团簇以及 Fe<sub>2</sub>O<sub>3</sub> 颗粒等 Fe 物种<sup>[14,18-22]</sup>. 不同的 Fe 物种在 NH<sub>3</sub>-SCR 反应中的催化活性有所 差异. Schwidder 等<sup>[18,20]</sup> 认为, Fe-ZSM-5 表面孤立 Fe<sup>3+</sup>物种和低聚 Fe 氧化物团簇均参与 NH<sub>3</sub>-SCR 反 应; Iwasaki 等<sup>[14]</sup>发现 NH<sub>3</sub>-SCR 反应的本征活性仅 与 Fe-ZSM-5 催化剂表面孤立的 Fe<sup>3+</sup>物种相关; Brandenberger 等<sup>[19]</sup>研究表明, 低于 300 °C 反应时, 活性位主要是孤立 Fe<sup>3+</sup>物种; 随着反应温度的升 高, 低聚 Fe 氧化物团簇和 Fe 氧化物颗粒对 NH<sub>3</sub>-SCR 活性的贡献越来越大.

Fe-ZSM-5 在高温水热老化后失活是其在实际 应用中面临的重要问题<sup>[4,5]</sup>,尤其当催化剂置于柴油 机颗粒捕集器 (DPF) 之后以同时净化 NO<sub>x</sub> 和 PM 时, DPF 再生所引发的高温加上尾气中含有的大量 水分而形成高温水热环境,可能造成催化剂失活. Kröcher 等<sup>[22]</sup>将负载在董青石的 Fe-ZSM-5 催化剂 于 650 ℃ 用含 10% H<sub>2</sub>O 的空气热老化 50 h 后,低 温段的 NO<sub>x</sub> 转化效率约降低 5%~15%. Hensen 等<sup>[23]</sup> 对 CVD 法制备的 Fe-ZSM-5 经热处理和水热处理 的研究显示,在高温水热条件下,交换位上 Fe<sup>3+</sup>离子 发生迁移,导致 Fe 氧化物团簇和颗粒增长,同时分 子筛发生脱铝,催化活性下降.近期 Brandenberger 等<sup>[6]</sup>发现,水热老化使得 Fe-ZSM-5 催化剂中 Al-OH-Si 位上脱铝造成 Brønsted 酸位减少,双核 Fe 物种快速迁移和单核 Fe 物种的缓慢迁移,但研究对 象主要是液体离子交换法制备的 Fe-ZSM-5 催化剂,并未考察制备方法对催化剂水热老化结果的影响.

因此,本文对比研究了不同制备方法和 Fe 负载 量的 Fe-ZSM-5 催化剂,经相同水热老化条件处理 后,其催化 NH<sub>3</sub>-SCR 活性和表面 Fe 物种的变化,探 讨了水热老化影响 Fe-ZSM-5 催化活性的原因.

#### 1 实验部分

#### 1.1 催化剂的制备

Fe-ZSM-5 催化剂前驱体 H-ZSM-5 和 NH<sub>4</sub>-ZSM-5 的 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25 (南开大学催化剂厂).

IE 法<sup>[6]</sup>. 将 10.0 g NH₄-ZSM-5 加入 17.8 g/L FeCl₂·4H₂O 溶液中, 通入 100 ml/min N₂, 在 80 °C 水 浴中搅拌 24 h 进行离子交换, 交换完毕后抽滤、洗 涤, 在 110 °C 烘干后再于 550 °C 焙烧 6 h. 所得样 品记为 Fe(1.2)-IE, 其中括号内数字为 Fe 的百分含 量 (下同).

SSIE 法. 称取一定量的 FeCl<sub>3</sub> 与 H-ZSM-5 在 球磨机内球磨 1 h, 将混合样品置于反应管中, 在 N<sub>2</sub> 气氛中于 600 °C 加热 2 h, 在此过程中, FeCl<sub>3</sub> 蒸气 与 分 子 筛 中 H<sup>+</sup> 发 生 反 应: FeCl<sub>3</sub>(g) + H<sup>+</sup><sub>zeol</sub> → [FeCl<sub>2</sub>]<sup>+</sup><sub>zeol</sub> + HCl(g) <sup>[14,18]</sup>, 产生的 HCl 气体用碱液 吸收. 反应结束后于 N<sub>2</sub> 中冷到室温取出, 样品抽 滤、洗涤, 在 110 °C 烘干后再于 550 °C 焙烧 6 h, 从 而 制 得 不 同 Fe 负 载 量 的 催 化 剂 Fe(1.1)-SSIE, Fe(3.5)-SSIE 和 Fe(6.6)-SSIE.

IWI 法<sup>[7]</sup>. 将 8 ml 一定浓度 FeCl<sub>2</sub>·4H<sub>2</sub>O 溶液加 到 10 g H-ZSM-5 中, 搅拌均匀后, 在隔绝空气条件 下老化 24 h, 于 60 ℃ 烘干后再于 550 ℃ 焙烧 6 h, 所得样品分别记为 Fe(1.2)-IWI 和 Fe(3.1)-IWI.

催化剂在含 10% H₂O 的空气中于 700 ℃ 水热

处理 8 h, 即得老化样品.

#### 1.2 催化剂的评价

NH<sub>3</sub>-SCR 反应中催化剂用量 50 mg (40~60 目). 原料气组成为: 0.05% NO, 0.05% NH<sub>3</sub>, 5% O<sub>2</sub>, N<sub>2</sub> 为 平衡气体, 气体总流量为 500 ml/min; 空速 GHSV 约 3.3 × 10<sup>5</sup> h<sup>-1</sup>. NO, NH<sub>3</sub>, N<sub>2</sub>O 和 NO<sub>2</sub> 浓度由配有 2 m 光程气体池的傅里叶变换红外光谱仪 (Nicolet Nexus 670) 测得.在整个反应过程中, 红外光谱上 未观察到其他含氮物种存在于气相反应物中, 因此 NO<sub>x</sub>转化率 X<sub>NOx</sub>用如下公式进行计算:

X<sub>NOx</sub> = (1-([NO] + [NO<sub>2</sub>])<sub>out</sub>/([NO] + [NO<sub>2</sub>])<sub>in</sub>)×100% 催化剂上 NO 氧化活性和 NH<sub>3</sub>氧化活性评价

实验分别在 0.05% NO-5% O<sub>2</sub> 和 0.05% NH<sub>3</sub>-5% O<sub>2</sub> 的气氛下进行, 其余同上.

#### 1.3 催化剂的表征

分子筛元素组成由美国 Perkin-Elmer 公司的 OPTIMA 2000 型 电感耦合等离子体光谱仪 (ICP-OES)进行分析. 将分子筛粉末 (50 mg) 加到 2 ml 混合浓酸溶液 (HNO<sub>3</sub>:HCl:HF = 5:1:1, v/v) 中,于 80 ℃ 水浴中消解 1 h,再加入 1 ml H<sub>3</sub>BO<sub>3</sub>饱和溶液, 并用超纯水定容为 25 ml 后进行分析.

催化剂的比表面积和孔体积在美国 Quanta-

chrome 公司 Autosorb(IQ) 型吸附仪上测定. 催化剂 粉末在 300 °C 下脱气预处理 5 h. 样品比表面积采 用 BET 公式计算的单点 BET 数值, 孔体积采用比 压最高点计算的总孔体积数值.

催化剂的 X 射线衍射 (XRD) 表征采用荷兰 Panalytical 型 X 射线衍射仪 (X'Pert PRO MPD), Cu *K*<sub>α</sub>射线, 扫描范围 2*θ* = 5°~60°, 扫描步长 0.02°.

样品 UV-Vis DRS 谱采用 Hitachi UV3010 型光 谱仪 (日本) 进行测定. 催化剂粉末样品以质量比为 1:4 与参比样品 BaSO<sub>4</sub> 混合后测试<sup>[18,21]</sup>. 谱图经 Kubelka-Munk (K-M) 函数变化后采用.

原位漫反射傅里叶变换红外光谱 (DRIFTS) 在 Nicolet Nexus 670 型红外光谱仪上进行测定. 催化 剂表面吸附 NH<sub>3</sub> 后用于分析催化剂表面 Brønsted 酸性<sup>[25]</sup>. 催化剂在 550 °C 20%O<sub>2</sub>-80%N<sub>2</sub> 气氛中预 处理 20 min, 切换为 N<sub>2</sub> 吹扫 20 min 后降温至 150 °C, 通入 1% NH<sub>3</sub>-99% N<sub>2</sub>, 采集催化剂表面 NH<sub>3</sub> 吸 附达到饱和时的谱图.

#### 2 结果与讨论

#### 2.1 催化剂的活性

图 1 为各新鲜和老化的 Fe-ZSM-5 催化剂上



图 1 新鲜和水热老化的不同 Fe-ZSM-5 催化剂上 NH<sub>3</sub>-SCR 反应的 NO<sub>x</sub>转化率

**Fig. 1.** NO<sub>x</sub> conversion over H-ZSM-5 and Fe-ZSM-5 catalysts prepared by different methods. (a) Fresh catalysts; (b)–(d) Hydrothermal aged catalysts. Reaction conditions: 0.05% NO, 0.05% NH<sub>3</sub>, 5% O<sub>2</sub>, N<sub>2</sub> balance.

NH<sub>3</sub>-SCR 反应的 NO<sub>x</sub>转化率. 由图 1(a) 可见, 当 Fe 负载量约为 1.2% 时, 各 Fe-ZSM-5 催化剂的 SCR 活性有所差异, 各 Fe-ZSM-5 催化剂在 190~350 °C 反应时, 活性大小顺序为 Fe(1.2)- IE > Fe(1.1)-SSIE > Fe(1.2)-IWI, 而在 350~550 °C 反应时则呈相反趋 势, 低温段活性最低的 Fe(1.2)- IWI 表现出最高的 高温活性. Fe(3.5)-SSIE 与 Fe(3.1)-IWI 在不同温度 段的 NO<sub>x</sub>转化率也呈现相似规律, 即低温段活性较 高的催化剂, 在高温段活性则较低.

Iwasaki 等<sup>[14]</sup>认为,制备方法比 Fe 负载量对 SCR 活性的影响更大, 而制备方法相同时, 增加 Fe 负载量可提高催化剂活性. Qi 等<sup>[9]</sup>研究表明, Fe-ZSM-5 的 SCR 活性随着 Fe 负载量增加而增加, 但 Fe 负载量大于 2.5% 后,催化剂活性变化不大. 本文结果显示, 增加 Fe-ZSM-5 的 Fe 负载量可提高 其催化活性,如 Fe(3.5)-SSIE 和 Fe(3.1)-IWI 的 SCR 催化活性均明显优于 Fe(1.2)- SSIE 和 Fe(1.2)- IWI. Fe(6.6)- SSIE 与 Fe(3.5)- SSIE 相比, 其 SCR 活性在 整个反应温度区间略低. 由表 1 可见, 前者的孔体 积略低,可推测 Fe 负载量过高可能造成分子筛孔道 堵塞,使得部分负载的 Fe 物种不能参与催化反 应<sup>[17]</sup>. Brandenberger 等<sup>[19]</sup>发现, 当 Fe/Al≤0.45 时, Fe-ZSM-5 上 NO<sub>x</sub>转化率随着 Fe 负载量的增加而增 加,继续增加Fe负载量,样品活性下降.可见,对于 一定 Si/Al 比的分子筛而言, Fe 负载量存在一个最 佳范围.

表 1 Fe-ZSM-5 催化剂 Fe 负载量及其比表面积和孔体积 Table 1 Fe-loading, suface area and total pore volume of Fe-ZSM-5 catalysts

Catalyst	Fe content (%)	Fe/Al ratio	BET surface area (m <sup>2</sup> /g)		Total pore volume (cm <sup>3</sup> /g)	
			Fresh	Aged	Fresh	Aged
H-ZSM-5	_	_	325.3	_	0.189	_
Fe(1.2)-IE	1.2	0.21	301.1	288.7	0.177	0.177
Fe(1.1)-SSIE	1.1	0.19	286.8	282.9	0.184	0.178
Fe(3.5)-SSIE	3.5	0.61	283.4	276.4	0.176	0.177
Fe(6.6)-SSIE	6.6	1.37	280.1	263.0	0.169	0.168
Fe(1.2)-IWI	1.2	0.21	321.4	307.8	0.189	0.191
Fe(3.1)-IWI	3.1	0.58	304.9	296.4	0.180	0.182

由图 1(b)~(d) 可以看出,水热老化后 Fe(1.2)-IE 和 Fe(1.1)-SSIE 的活性略高于 Fe(1.2)-IWI. 各 SSIE 催化剂经水热老化后,低温段活性接近,可见,增加

Fe 负载量并不能提高催化剂的水热稳定性.水热老 化的各催化剂在 400 ℃ 以下反应时 NO<sub>x</sub>转化率均 下降,而 IE 和 SSIE 催化剂经水热老化后高温段的 NO<sub>x</sub>转化率提高. Brandenberger 等<sup>[6]</sup>也发现水热老 化后的 Fe-ZSM-5 催化剂在高温段 (>500 ℃) 的 SCR 活性提高.可见,水热老化减少了有利于低温 段 SCR 反应 的 Fe 物种,而增加了有利于高温段反 应的 Fe 物种.

图 2 为 SSIE 法制备的系列 Fe-ZSM-5 催化剂 水热老化前后的 NO 氧化和 NH<sub>3</sub> 氧化活性.可以看 出,经水热老化后,各催化剂上 NH<sub>3</sub> 氧化活性和 NO 氧化活性均明显下降.有人认为,在 Fe-ZSM-5 上进 行 NH<sub>3</sub>-SCR 反应时, Fe<sup>3+</sup>位上 NO 氧化为 NO<sub>2</sub> 是低 温段的慢速步骤<sup>[14,15,24]</sup>,因此,水热处理后催化剂的 NO 氧化能力下降,可能是导致催化剂低温活性下 降的原因之一.在 NH<sub>3</sub>-SCR 反应的较高温度段发 生还原剂 NH<sub>3</sub> 的氧化会降低 NO<sub>x</sub>转化率,水热老化



图 2 水热老化对 Fe-ZSM-5 催化剂 NH<sub>3</sub> 和 NO 氧化活性 的影响

Fig. 2. Effect of hydrothermal aging on  $NH_3$  oxidation and NO oxidation activity of Fe-ZSM-5 cataltysts. Reaction conditions: (a) 0.05%  $NH_3$ , 5%  $O_2$ ,  $N_2$  balance; (b) 0.05% NO, 5%  $O_2$ ,  $N_2$  balance.

后 Fe-ZSM-5 催化剂的 NH<sub>3</sub>氧化能力降低,提高了 高温段的 NO<sub>x</sub>转化率.

#### 2.2 催化剂表征结果

#### 2.2.1 比表面积和孔体积

由表 1 可见, 负载 Fe 后, H-ZSM-5 比表面积和 孔体积均降低, 尤以 Fe(6.6)-SSIE 为甚. 对于制备方 法相同的催化剂, 随着 Fe 负载量的增加, 比表面积 和孔体积随着 Fe 负载量的增加而降低. 另外, 水热 老化处理对 Fe-ZSM-5 的孔体积基本无影响, 而比 表面积略有降低.

#### 2.2.2 XRD 结果

各 Fe-ZSM-5 催化剂的 XRD 谱见图 3, 图中同 时给出了 H-ZSM-5 和 5%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 混合样品的谱图. 典型的  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 衍射峰出现在  $2\theta = 33.1^{\circ}$ , 35.6°, 40.9°和 49.5°<sup>[9,14,15]</sup>.可以看出, Fe(6.6)-SSIE 与 Fe(3.1)-IWI 样品出现明显的  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 衍射峰, 说明 催化剂存在粒径大于 3~5 nm 的  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 相<sup>[9,14,15]</sup>. 而负载量与 Fe(3.1)-IWI 接近的 Fe(3.5)-SSIE 样品 上几乎观察不到  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 衍射峰, 表明 IWI 法制备 的 Fe-ZSM-5 比 SSIE 法的更易形成 Fe<sub>2</sub>O<sub>3</sub>. Qi 等<sup>[9]</sup> 和 Iwasaki 等<sup>[14]</sup>也观察到高负载量的 Fe-ZSM-5 催 化剂存在  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 而浸渍法制备的 Fe-ZSM-5 催化 剂的  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 衍射峰强度高于化学气相沉积法<sup>[14]</sup>. 水热老化后样品的 XRD 谱未发生明显变化 (未示 出). 通过对 Fe(6.6)-SSIE 和 Fe(3.1)-IWI 样品在 2 $\theta$ 



#### 图 3 各 Fe-ZSM-5 催化剂的 XRD 谱

**Fig. 3.** XRD patterns of fresh Fe-ZSM-5 catalysts. (1) H-ZSM-5; (2) Fe(1.2)-IE; (3) Fe(1.1)-SSIE; (4) Fe(3.5)-SSIE; (5) Fe(6.6)-SSIE; (6) Fe(1.2)-IWI; (7) Fe(3.1)-IWI; (8) 5% Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5.

= 33.1°的 α-Fe<sub>2</sub>O<sub>3</sub> 衍射峰进行粒径计算可知,水热 处理后上述样品的 Fe<sub>2</sub>O<sub>3</sub> 粒径分别增加了 10% 和 6%.

#### 2.2.3 UV-Vis DRS 结果

UV-Vis DRS 是分析 Fe-ZSM-5 表面 Fe 物种的 常用手段,尽管无法区分单核 Fe 物种和双核 Fe 物 种,但仍可将 UV-Vis DRS 谱中位于 $\lambda < 300$  nm 的 谱峰归属为孤立 Fe<sup>3+</sup>位, 300~400 nm 之间归属为低 聚 Fe 氧化物团簇, 400 nm 以上归属为 Fe<sub>2</sub>O<sub>3</sub>颗 粒<sup>[14,17,21]</sup>. Brandenberger 等<sup>[19]</sup>提出, 催化剂上不同 的 Fe 物种在不同温度区间对 NH<sub>3</sub>-SCR 活性的贡献 程度不同: 当反应温度低于 300 ℃时, 活性位主要 是单核 Fe 物种; 300~400, 400~500 和高于 500 ℃ 时, 双核 Fe 物种、低聚 Fe 氧化物和 Fe<sub>2</sub>O<sub>3</sub>颗粒分别 起到较重要的作用. 图 4 为新鲜和水热老化后各 Fe-ZSM-5 催化剂的 UV-Vis 谱经 K-M 变化后的结 果. 可以看出,水热老化后所有样品位于 λ < 300 nm 的谱峰强度减弱, λ > 400 nm 的谱峰强度均增强. 表 2 为上述谱图经去卷积分峰计算后, $\lambda \leq 295$  nm, 300~400 nm 和 > 400 nm 范围内峰面积所占的百分 比 I1, I2 和 I3<sup>[17,21]</sup>. 结果显示, 水热处理后 I1 减少, I2 和 I3有所增大. 可见, 水热老化造成了 Fe-ZSM-5 上 孤立 Fe<sup>3+</sup>物种的减少, 而低聚 Fe 氧化物团簇和 Fe<sub>2</sub>O<sub>3</sub>增加. 水热老化后催化剂的 UV-Vis DRS 结 果与 Brandenberger 等<sup>[6]</sup>对 Fe-ZSM-5 水热老化失活 途径的推测吻合,即水热老化可造成孤立 Fe<sup>3+</sup>物种 的迁移,并逐渐形成 Fe 氧化物颗粒.

由图 4 和表 2 可见, 当 Fe 负载量相近时, SSIE 法制备的 Fe-ZSM-5 表面孤立 Fe<sup>3+</sup>物种较多,  $I_1$ 较 高; IWI 法制备的催化剂中低聚 Fe 氧化物团簇和 Fe<sub>2</sub>O<sub>3</sub>颗粒较多,  $I_2$ 和  $I_3$ 较高.可见 Fe 负载量相近 时,制备方法可导致相应 Fe-ZSM-5 表面 Fe 物种分 布不同,从而影响催化活性.对于相同方法制备的 Fe-ZSM-5 催化剂,  $I_1$ 随着 Fe 负载量的增加而减小, 而 Fe(3.5)-SSIE 和 Fe(3.1)-IWI 的 NO<sub>x</sub>转化率明显 高 于 Fe(1.1)-SSIE 和 Fe(1.2)-IWI. Brandenberger 等<sup>[19]</sup>指出,对 Fe/Al 低于 0.45 的 IE 法制备的 Fe-ZSM-5 样品,低温段 NO<sub>x</sub>转化率的高低与单核 Fe 活性位的多少一致.可见,要获得较高的 SCR 活 性,在尽量形成较多孤立 Fe<sup>3+</sup>物种的同时,还应该提 高 Fe 负载量.





表 2 图 4 中 UV-Vis DRS 谱图分峰结果 Table 2 Percentage of the area of subbands derived by deconvolution of the UV-Vis DRS spectra in Fig. 4

Catalyst	Fresh (%)			Hydrothermal aged (%)			
	$I_1^{a}$	$I_2^{b}$	$I_3^{c}$	$I_1^{a}$	$I_2^{b}$	$I_3^{\rm c}$	
Fe(1.2)-IE	59.2	30.1	10	52.1	26.4	21.4	
Fe(1.1)-SSIE	68.6	27.1	4.3	58.7	26.9	14.4	
Fe(3.5)-SSIE	38.9	33.6	27.5	26.4	38.4	35.5	
Fe(6.6)-SSIE	29.7	30.2	40.6	18.3	33	48.6	
Fe(1.2)-IWI	38.2	34.5	27.3	27.7	38.5	33.8	
Fe(3.1)-IWI	30.9	35.2	34.0	26.8	37.9	35.1	
<sup>a</sup> Subbands at $\lambda$	< 295 r	um <sup>b</sup> Subl	hands at	300 nm < .	d < 400 m	nm <sup>c</sup> Sub-	

Subbands at  $\lambda \le 295$  nm. Subbands at 500 nm <  $\lambda < 400$  nm. Subbands at  $\lambda > 400$  nm.

#### 2.2.4 DRIFTS 结果

Fe-ZSM-5 吸附 NH<sub>3</sub>时由于其表面羟基的消耗 会在其吸收波数位置产生倒峰. 图 5(a) 为各 Fe-ZSM-5 催化剂在吸附 NH<sub>3</sub>饱和时,在 3750~3450 cm<sup>-1</sup> 范围内出现的 DRIFTS 消耗峰. 位于 3610 cm<sup>-1</sup>的谱峰归属为 Fe-ZSM-5 催化剂表面 Brønsted 酸位的 OH 振动, 3660 cm<sup>-1</sup> 处峰归属为非骨架 Al 相联的羟基原子团,其中前者的谱峰面积可反映催 化剂表面 Brønsted 酸性位的相对浓度<sup>[6]</sup>. 由图可见, 负载 Fe 后, H-ZSM-5 位于 3610 cm<sup>-1</sup> 处的谱峰强度 下降,制备方法相同时,样品中该谱峰强度随着 Fe 负载量的增加而降低,其中 Fe(6.6)-SSIE 的最弱.水 热处理后所有催化剂在 NH3 吸附实验中均观测不 到 3610 cm<sup>-1</sup> 谱峰 (水热处理后样品的红外光谱与 新鲜 Fe(6.6)-SSIE 对比, 见图 5(b)). 可见, 水热老化 造成了各催化剂表面 Brønsted 酸浓度大幅度降低, 与 Brandenberger 等<sup>[6,25]</sup>结果相同, 他们认为, Brønsted 酸性位并非是 Fe-ZSM-5 具有较好低温活 性的关键因素; Schwidder 等<sup>[26]</sup>也发现, NH<sub>3</sub>-SCR 反应可以在 Fe-ZSM-5 没有酸性位的情况下进行, 但认为在低温段催化剂表面 NH4NO2 的分解是 SCR



图 5 Fe-ZSM-5 催化剂吸附 NH3 的原位 DRIFTS 谱

Fig. 5. In situ DRIFTS spectra for fresh Fe-ZSM-5 catalysts after  $NH_3$  adsorption (a) and comparing hyrothermal aged catalysts with fresh Fe(6.6)-SSIE (b).

反应的决速步骤,而 Brønsted 酸性位的存在促进了 低聚 Fe 氧化物团簇上 NH<sub>4</sub>NO<sub>2</sub>的分解,有利于实现 高 SCR 催化活性.本文结果显示,尽管水热老化使 得催化剂 Brønsted 酸位显著减少,但其在较高温度 段仍表现出高 NH<sub>3</sub>-SCR 活性.表明在高温段 NH<sub>3</sub>-SCR 活性与催化剂表面 Brønsted 酸位无关.

#### 3 结论

700 °C 时用含 10%H<sub>2</sub>O 的空气水热老化 8h 后, Fe-ZSM-5 催化剂上 NH<sub>3</sub>-SCR 低温活性显著降低, 但 400 °C 以上反应时活性有所提高. IWI 法制备的 催化剂中孤立 Fe<sup>3+</sup>物种相对浓度低,且易生成大颗 粒 Fe<sub>2</sub>O<sub>3</sub>,因此低温活性低而高温活性高; SSIE 法 制备催化剂时增加 Fe 负载量,可使催化剂生成较多 的孤立 Fe<sup>3+</sup>物种,但 Fe 负载量不宜过高.水热老化 使得不同方法制备的以及相同方法制备的不同 Fe 负载量的各 Fe-ZSM-5 催化剂在整个反应温度区间 活性差异减小,但初始活性较高的催化剂经水热老 化后,其活性仍较高.水热老化后催化剂的 NH<sub>3</sub>氧 化和 NO 氧化性能均下降.水热处理略降低了催化 剂的比表面积,孔体积基本不变,但造成了催化剂的 孤立  $Fe^{3+}$ 物种减少, 低聚 Fe 氧化物团簇和  $Fe_2O_3$  增加, 未形成粒径较大的  $Fe_2O_3$ 颗粒; 同时样品表面 Brønsted 酸位显著减少.

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### 英译文 English Text

Nitrogen oxides  $(NO_x)$  and particulate matter (PM) emitted from diesel vehicles are major sources of atmospheric pollutants. Selective catalytic reduction of NO by NH<sub>3</sub> (NH<sub>3</sub>-SCR) is one of the most efficient technologies used for removing NO<sub>x</sub>. V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> is the first commercialized catalyst system due to its high activity and sulfur resistance, and it has been widely used for deNO<sub>x</sub> from stationary sources. However, toxicity of vanadium pentoxide and the thermal stability of TiO<sub>2</sub> when the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst system is applied for diesel vehicles make this catalyst inefficient [1–3]. Hence, efforts are being devoted to the development of new SCR catalysts. Fe-loaded zeolites, especially Fe-ZSM-5, have received much attention in recent years because of their much higher thermal stability and wider temperature range than vanadia-based catalysts [4,5].

The activity of Fe-ZSM-5 for NH<sub>3</sub>-SCR can be affected by many parameters, including the Si/Al ratio of the zeolite, the ion-exchange degree as well as preparation methods, etc [4]. For a given parent zeolite, the activity of Fe-ZSM-5 for NH<sub>3</sub>-SCR depended strongly on the preparation method. Among various methods for Fe-ZSM-5 preparation, liquid ion exchange (IE) [6–8], incipient wetness impregnation (IWI) [7–10], chemical vapor deposition (CVD) [11–15], and solid state ion exchange (SSIE) [16–18] are well known.

The performance of Fe-ZSM-5 in the NH<sub>3</sub>-SCR reaction is related to the Fe species distributions on the catalyst. According to the results of UV-Vis diffuse reflectance spectroscopy (DRS), Mössauber, and electron paramagnetic resonance (EPR) spectroscopy, the Fe species coexisting on Fe-ZSM-5 in some studies of the application of Fe-ZSM-5 in  $NH_3$ -SCR are generally distinguished as isolated Fe<sup>3+</sup>, oligometric Fe<sub>x</sub>O<sub>y</sub> cluster, and Fe<sub>2</sub>O<sub>3</sub> particles [14,18–22]. Thus, different Fe species showed different catalytic performance in the NH<sub>3</sub>-SCR reaction. Schwidder et al. [18,20] suggested that both isolated and oligometric Fe oxo sites can participate in the standard SCR reaction. Also, Iwasaki et al. [14] proposed that the ion-exchanged oxo-Fe<sup>3+</sup> should be the active sites and can determine the turnover frequency for the NH<sub>3</sub>-SCR reaction. Brandenberger et al. [19] indicated that the contribution of different Fe species on Fe-ZSM-5 to SCR activity strongly depended on temperature. At temperatures below 300 °C, monomeric iron is the most active site for the SCR reaction while at higher temperatures, the contribution of dimeric iron species, oligomeric species, and Fe<sub>2</sub>O<sub>3</sub> particles become important [19].

One of the challenges for the practical application of Fe-ZSM-5 catalysts is their limited hydrothermal stability at high temperatures [4,5]. Furthermore, the SCR system may

be installed at the downstream of diesel particulate filters (DPF) in order to reduce  $NO_x$  and PM simultaneously [5]. Because of the thermal regeneration of DPF, temperatures of the exhaust which contains about 10% water are increased and result in the formation of a high temperature hydrothermal condition, which can lead to deactivation of the SCR catalyst. Kröcher et al. [22] investigated the hydrothermal stability of a Fe-ZSM-5 catalyst coated on cordierite and observed 5%–15% loss in the deNO<sub>x</sub> activity of the catalyst after hydrothermal aging at 650 °C in 10% H<sub>2</sub>O for 50 h. Hensen et al. [23] studied the effects of thermal and hydrothermal treatment on Fe/ZSM-5 prepared by the CVD method for N2O decomposition. They found that after severe hydrothermal aging the activity of the catalyst observed decreased, and the Fe<sup>3+</sup> migrated out of the ion exchange sites as well, followed by the iron oxide aggregated and Al removed from framework positions. Recently, Brandenberger et al. [6] concluded that three parallel processes were responsible for the hydrothermal breakdown of Fe-ZSM-5, and these included the rapid dealumination of Al-OH-Si sites, the rapid depletion of dimeric iron species, and the slow migration of isolated iron ions followed by the dealumination of these Al sites. However, in their study, only a series of Fe-ZSM-5 prepared by liquid ion exchanged was studied [6].

The aim of this study was to investigate the effect of hydrothermal aging on the Fe species distributions and the SCR activity of different Fe-ZSM-5 catalysts with various Fe loadings. By studying the changes of Fe species and the activities of different Fe-ZSM-5 catalysts for NH<sub>3</sub>-SCR after hydrothermal aging, the mechanism of hydrothermal aging on Fe-ZSM-5 was elucidated.

#### 1 Experimental

#### 1.1 Catalyst preparation

The parent H-ZSM-5 and  $NH_4$ -ZSM-5 with  $SiO_2/Al_2O_3 = 25$  (Nankai University) were used.

Liquid IE method [6]. NH<sub>4</sub>-ZSM-5 (10 g) was added to 17.8 g/L FeCl<sub>2</sub>·4H<sub>2</sub>O solution with constant stirring with continuous flow of N<sub>2</sub> (100 ml/min) in a water bath at 80 °C. After 24 h, the mixture was filtered and washed with deionized water. The resulting powder was dried overnight at 110 °C and calcined at 550 °C for 6 h in air.

SSIE method. Three Fe-ZSM-5 catalysts with different iron contents were prepared by this method. H-ZSM-5 (5 g) and a suitable amount of anhydrous FeCl<sub>3</sub> were mixed in a ball mill for 1 h. Then the mixture was placed in a quartz tube reactor and heated to 600 °C with a temperature ramp of 5 °C/min in flowing N<sub>2</sub> (100 ml/min) and kept at this temperature for 2 h. At this point, the vaporized FeCl<sub>3</sub> exchanged with the H<sup>+</sup> of zeolite according to the reaction: FeCl<sub>3</sub>(g) +  $H^+_{zeol} \rightarrow [FeCl_2]^+_{zeol} + HCl(g)$  [14,18]. An alkali solution was used to neutralize HCl in the exhaust. After cooling with continuous flow of N<sub>2</sub>, the sample was washed with deionized water and dried at 110 °C overnight. Finally, the sample was calcined at 550 °C for 6 h in air.

IWI method [7]. A suitable  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  solution (8 ml) was added to 10 g of H-ZSM-5 with continued stirring to form a paste. The paste was aged in a closed container at room temperature for 24 h and then dried at 60 °C for 12 h and calcined at 550 °C for 6 h in air.

In this study, Fe-ZSM-5 catalysts were denoted as Fe(X)-*Y*, where *X* represented the mass percent of iron and *Y* represented the preparation method. For instance, a Fe-ZSM-5 prepared by the liquid IE method with 1.2% Fe was denoted as Fe(1.2)-IE. Hydrothermal aging was conducted at 700 °C in 10% H<sub>2</sub>O/air for 8 h.

#### 1.2 Activity measurements

The Fe-ZSM-5 catalysts were pelletized and sieved to 40–60 mesh. The reaction conditions were controlled as follows: 0.05% NO, 0.05% NH<sub>3</sub>, 5% O<sub>2</sub>, N<sub>2</sub> balance, total flow rate of 500 ml/min, 50 mg catalyst, and gas hourly space velocity (GHSV)  $\approx 3.3 \times 10^5$  h<sup>-1</sup>. The effluent gas was analyzed using an FT-IR spectrometer (Nicolet Nexus 670) equipped with a heated, low volume multiple-path gas cell (2 m). NO<sub>x</sub> conversion ( $X_{NOx}$ ) was calculated as follows:

 $X_{\text{NOx}} = (1 - ([\text{NO}] + [\text{NO}_2])_{\text{out}} / ([\text{NO}] + [\text{NO}_2])_{\text{in}}) \times 100\%$ 

The  $NH_3$  and NO oxidation activities of the catalysts were investigated in the same reaction conditions as in the  $NH_3$ -SCR activity test, with a feed gas composed of 0.05% NO or 0.05%  $NH_3$ , 5%  $O_2$ , and  $N_2$  balance.

#### 1.3 Catalyst characterization

The elemental composition of the samples was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, OPTIMA 2000). For digestion, 50 mg of each sample was dissolved in a mixture of acids (HNO<sub>3</sub>:HCl:HF = 5:1:1, v/v). The mixture was placed in a water bath at 80 °C for 1 h. For analysis, 1 ml H<sub>3</sub>BO<sub>3</sub> saturated solution was added to the residue of the dissolved mixture and filled up to 25 ml with water.

 $N_2$  adsorption-desorption isotherms were obtained at -196 °C using Autosorb (IQ) (Quantachrome). Prior to  $N_2$  adsorption, the samples were degassed at 300 °C for 5 h. Specific surface areas were determined by the single point BET model calculation. Total pore volumes of the catalysts at highest relative pressure are given here.

Powder XRD measurements were carried out on a Panalytical X-ray diffractometer (the Netherlands, X'Pert PRO MPD) with Cu  $K_a$  as the radiation resource. The data were collected for  $2\theta$  from 5° to 60° with a stepsize of  $0.02^{\circ}$ .

UV-Vis DRS spectra were recorded by Hitachi UV3010 (Japan). BaSO<sub>4</sub> was used as the reference material. The Fe-ZSM-5 catalysts were diluted with  $BaSO_4$  at a ratio of 1:4 [18,21]. The spectra were converted with the Kubelka-Munk (K-M) function F(R) for comparison.

In situ DRIFTS experiments of NH<sub>3</sub> adsorption over Fe-ZSM-5 catalysts were performed on an FT-IR spectrometer (Nicolet Nexus 670) in order to investigate the Brønsted acidity of the catalysts [25]. Each sample was pretreated at 550 °C in a flow of 20% O<sub>2</sub>-80% N<sub>2</sub> (v/v) for 20 min, then purged with pure N<sub>2</sub> for 20 min and cooled down to 150 °C in N<sub>2</sub>. Then, the samples were exposed to a flow of 1% NH<sub>3</sub>-99% N<sub>2</sub> and the spectra were recorded until NH<sub>3</sub> adsorption saturation.

#### 2 Results and discussion

#### 2.1 Catalytic activity

Figure 1 shows the NO<sub>x</sub> conversion in the NH<sub>3</sub>-SCR reaction over various Fe-ZSM-5 catalysts. Figure 1(a) and (b)–(d) showed the results of the fresh and aged catalysts, respectively. As shown in Fig. 1(a), the SCR activities of Fe-ZSM-5 catalysts prepared by different methods with similar Fe loadings of 1.2% were quite different. NO<sub>x</sub> conversion at temperatures ranging from 190 to 350 °C decreased in the sequence Fe(1.2)-IE > Fe(1.1)-SSIE > Fe(1.2)-IWI. However, at temperature above 350 °C, NO<sub>x</sub> conversion of the three catalysts showed the opposite sequence and Fe(1.2)-IWI showed the best performance. Similarly, compared with Fe(3.1)-IWI, Fe(3.5)-SSIE showed higher SCR activity at lower temperatures but lower activity as temperatures above 350 °C.

Wasaki et al. [14] mentioned that the SCR activity of Fe-ZSM-5 was more dependent on the preparation method than on the Fe loading. For a given preparation method, the SCR activity of Fe-ZSM-5 can be enhanced by increasing the Fe loading. Qi et al. [9] reported that the activity of Fe-ZSM-5 increased with Fe loading but reached amost maximum when the Fe loading was 2.5%. Brandenberger et al. [19] also reported that the NO<sub>x</sub> conversion increased with Fe loading when Fe/Al was less than 0.45 and then decreased for higher exchange degree. Our results showed that higher activity could be achieved by higher Fe loadings. The SCR activities of Fe(3.5)-SSIE and Fe(3.1)-IWI were much higher than those of Fe(1.2)-SSIE and Fe(1.2)-IWI. Fe(6.6)-SSIE showed somewhat lower NO<sub>x</sub> conversion than Fe(3.5)-SSIE in the whole temperature range. We deduced that overly high Fe loading might plug pores in the zeolite and some of the active Fe sites could not participate in the reaction, on the basis of the lower pore volume of Fe(6.6)-SSIE compared to

that of Fe(3.5)-SSIE (Table 1) [17]. These results indicated that there is an optimum Fe loading for preparing Fe-ZSM-5 from a parent zeolite with a given Si/Al ratio.

Figure 1(b)–(d) shows the  $NO_x$  conversions of the catalysts after aging at 700 °C in 10% H<sub>2</sub>O/air for 8 h. A decrease in SCR activity was observed for all Fe-ZSM-5 catalysts after hydrothermal aging. The difference between Fe-ZSM-5 catalysts in NO<sub>x</sub> conversion became less distinct after aging. Aged Fe(1.2)-IE and Fe(1.1)-SSIE showed slightly higher activity compared with aged Fe(1.2)-IWI. Based on similar performance of aged SSIE and IE prepared Fe-ZSM-5 in SCR reactions, it seemed that the enhancement of the hydrothermal stability could not be simply realized by higher Fe loadings. At temperatures below 400 °C, the activity of all catalysts was decreased by hydrothermal aging, while at high temperatures (T > 400 °C), the activity of the catalysts prepared by the IE and SSIE methods was increased. Brandenberger et al. [6] also reported an increase in NO<sub>x</sub> reduction performance at high temperatures  $(T > 500 \text{ }^{\circ}\text{C})$  by hydrothermal aged Fe-ZSM-5. It was suggested that hydrothermal aging decreased the Fe active sites for the low temperature activity and increased the Fe active sites for the high temperature activity.

The NO oxidation and NH<sub>3</sub> oxidation activities of fresh and aged Fe-ZSM-5 catalysts prepared by the SSIE method are compared in Fig. 2. The profile showed that the activities of NH<sub>3</sub> oxidation and NO oxidation were decreased by hydrothermal aging. The oxidation of NO to NO<sub>2</sub> over Fe<sup>3+</sup> sites was proposed as the slow step of the NH<sub>3</sub>-SCR at low temperatures by some researchers [14,15,24]. Therefore, a decrease in the activity of NO oxidation might be one of the contributing factors which resulted in the loss of low temperature activity for aged Fe-ZSM-5. At high temperatures, the oxidation of the reducing agent, NH<sub>3</sub>, could result in a decrease in NO conversion. The decrease in the oxidation of NH<sub>3</sub> for aged Fe-ZSM-5 catalysts could explain the increase of NO<sub>x</sub> conversion at high temperatures.

#### 2.2 Catalyst characterization and discussion

#### 2.2.1 Surface area and pore volume

As shown in Table 1, the surface area and pore volume of the parent H-ZSM-5 decreased after loading with iron. For a given preparation method, the surface area and pore volume decreased with increasing Fe loading. The lowest surface area and pore volume were observed for Fe(6.6)-SSIE. After aging, the pore volume of Fe-ZSM-5 seemed unchanged and the surface area decreased slightly, compared with the fresh catalyst.

Figure 3 shows the XRD patterns of fresh Fe-ZSM-5 catalyst and a mechanical mixture of 5% a-Fe2O3 with H-ZSM-5. The typical XRD peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> could be observed at  $2\theta$  of  $33.1^{\circ}$ ,  $35.6^{\circ}$ ,  $40.9^{\circ}$ , and  $49.5^{\circ}$  [9,14,15]. The observed peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the patterns of Fe(6.6)-SSIE and Fe(3.1)-IWI indicated that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with particle size larger than 3-5 nm was presented in these two samples [9,14,15]. However, no peak for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase was detected for Fe(3.5)-SSIE, which had Fe loading slightly higher than Fe(3.1)-IWI. The data indicated that the IWI method to prepare Fe-ZSM-5 is more favorable in producing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> than catalyst prepared by the SSIE method. Qi et al. [9] and Iwasaki et al. [14] also observed that, the XRD peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were presented in the Fe-ZSM-5 with high Fe loadings. Additionally, the Fe-ZSM-5 prepared by impregnation exhibited a higher intensity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> peaks than those prepared by CVD [14]. The XRD patterns of aged catalysts showed little difference from those of fresh catalysts (data not shown). There were no detectable peaks of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for the aged Fe-ZSM-5 as well as the fresh catalysts. The calculated results for the particle size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> according to the XRD peak at  $2\theta$  of  $33.1^{\circ}$  showed that, after hydrothermal aging, the particles sizes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on Fe(3.1)-IWI and Fe(6.6)-SSIE increased by about 6% and 10%, respectively.

#### 2.2.3 UV-Vis DRS

UV-Vis DRS has been widely used to study Fe species on Fe-zeolites [14,17,21,]. Although it cannot distinguish between isolated and binuclear Fe species, UV-Vis spectra can ascribe different Fe species on the Fe-ZSM-5 to isolated Fe<sup>3+</sup> species (bands below 300 nm), oligmeric clusters (between 300-400 nm), and Fe<sub>2</sub>O<sub>3</sub> particles (above 400 nm) [14,17,21,]. Brandenberger et al. [19] suggested that the contribution of different Fe species on Fe-ZSM-5 to SCR activity strongly depended on the temperature. At temperatures below 300 °C, the SCR activity was observed to be primarily caused by monomeric iron sites. However, at 300–400 °C, 400–500 °C, and above 500 °C, the contribution of dimeric iron species, oligomeric species, and Fe<sub>2</sub>O<sub>3</sub> particles, respectively, became important. The K-M converted UV-Vis spectra of the fresh and aged Fe-ZSM-5 catalysts were compared in Fig. 4. The intensity of bands below 300 nm decreased and that above 400 nm increased for all catalysts after aging.

The UV-Vis spectrum for each Fe-ZSM-5 was deconvoluted into subbands. The percentage of each band with respect to the total area of the spectrum was shown in Table 2, in which  $I_1$ ,  $I_2$ , and  $I_3$  represented the percentage of the area of the subbands at  $\lambda \le 295$  nm, 300 nm  $< \lambda \le 400$  nm, and  $\lambda > 400$  nm, respectively [17,21]. These results showed that after

aging the values of  $I_1$  decreased whereas  $I_2$  and  $I_3$  increased. This suggested that hydrothermal aging resulted in a decrease in the relative concentration of isolated Fe<sup>3+</sup> species and an increase in the relative concentration of oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters and Fe<sub>2</sub>O<sub>3</sub> particles on Fe-ZSM-5. Our UV-Vis DRS results supported the mechanism of hydrothermal deactivation of Fe-ZSM-5 proposed by Brandenberger et al. [6] that hydrothermal aging led to the migration of isolated Fe<sup>3+</sup> species from iron exchange sites and the formation of small iron clusters.

From Fig. 4 and Table 2, it can be seen that at similar Fe loadings, the Fe-ZSM-5 prepared by the SSIE method exhibited a higher relative concentration of isolated Fe<sup>3+</sup> species and higher value of  $I_1$ , whereas the Fe-ZSM-5 prepared by the IWI method contained more oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters and  $Fe_2O_3$  particles, with higher values of  $I_2$  and  $I_3$ . These results suggested that at the similar Fe loadings the distribution of iron species in Fe-ZSM-5 prepared by various methods were quite different, which resulted in the different SCR activities. With the same preparation method, the value of  $I_1$  decreased with increasing Fe loading. Fe(3.5)-SSIE and Fe(3.1)-IWI showed higher  $NO_x$  conversion than Fe(3.5)-SSIE and Fe(3.1)-IWI. Brandenberger et al. [19] reported that for Fe-ZSM-5 prepared by the IE method with exchange degree (Fe/Al) below 0.45, the activity of the catalyst at low temperature (below 300 °C) was determined by the concentration of monomeric iron sites. These results indicated that in order to obtain high SCR activity, optimizing the Fe loadings and maximizing the amount of isolated Fe<sup>3+</sup> species should be considered when preparing Fe-ZSM-5 catalysts.

#### 2.2.4 DRIFTS

Negative bands ascribed to surface hydroxyl stretching can be observed on the spectra of Fe-ZSM-5 after NH<sub>3</sub> adsorption due to the interaction of surface hydroxyls with NH<sub>3</sub>. Figure 5(a) showed the DRIFTS spectra of fresh Fe-ZSM-5 catalysts after saturated NH<sub>3</sub> adsorption in the region from 3750 to 3450  $\text{cm}^{-1}$ . The band at 3610  $\text{cm}^{-1}$  was assigned to the OH stretch of Brønsted acidic sites, and the band at 3660 cm<sup>-1</sup> was assigned to OH groups associated with extra-framework Al [6]. The relative concentration of Brønsted acidic sites can be determined from the intensity of the band at 3610  $\text{cm}^{-1}$  [6]. The band at 3610  $\text{cm}^{-1}$  on H-ZSM-5 showed a decrease in the intensity after Fe loading. With increasing Fe loading, the intensity of the band at 3610 cm<sup>-1</sup> on Fe-ZSM-5 prepared by the same method decreased. The lowest intensity of the band at 3610 cm<sup>-1</sup> was observed for Fe(6.6)-SSIE. For all aged Fe-ZSM-5 catalysts, the band at 3610 cm<sup>-1</sup> became too weak to be observed after NH<sub>3</sub> adsorption. Figure 5(b) showed the FT-IR spectra of all aged Fe-ZSM-5 catalysts compared with Fe(6.6)-SSIE). These results indicated that the concentration of Brønsted acidic sites on catalysts was significantly decreased by hydrothermal aging in accordance with Brandenberger et al. [6,25]. The role of Brønsted acidity in the NH3-SCR of NO is still under debate. Brandenberger et al. [25] pointed out that the acidity of the Fe-ZSM-5 was not a prerequisite for high activity at low temperatures. Schwidder et al. [26] revealed that large reaction rates could be achieved with non-acidic Fe-ZSM-5 catalysts in NH<sub>3</sub>-SCR of NO. However, they also suggested that the decomposition of NH<sub>4</sub>NO<sub>2</sub> might be the rate-limiting step at low temperatures, and the presence of Brønsted sites opened an addition reaction channel for acid-catalyzed decomposition of NH<sub>4</sub>NO<sub>2</sub>, resulting in high activity [26]. In the current study, high NH<sub>3</sub>-SCR activity at high temperatures was still achieved by aged Fe-ZSM-5 catalysts with significantly decreased Brønsted acidic sites. This suggested that the activity of Fe-ZSM-5 on NH<sub>3</sub>-SCR might be independent of Brønsted acidic sites at high temperatures.

#### 3 Conclusions

The activity of Fe-ZSM-5 catalysts at low temperature was significantly decreased by hydrothermal aging at 700 °C in 10% H<sub>2</sub>O for 8 h. Whereas when the temperature was above 400 °C, the activity of the aged catalysts increased. Fe-ZSM-5 prepared by IWI method which contained fewer isolated Fe<sup>3+</sup> species and more large-size Fe<sub>2</sub>O<sub>3</sub> particles performed well at high temperatures, but was inferior at low temperatures. Fe-ZSM-5 with high Fe loading and more isolated Fe<sup>3+</sup> sites could be obtained using SSIE methods, butextreamly higher Fe loading might result in negative effects on SCR activity. Hydrothermal aging significantly decreased the activity at low temperature and slightly increased the activity at high temperature. The differences between the NH<sub>3</sub>-SCR activities of Fe-ZSM-5 catalysts prepared by various mehods were unobvious after aging. Our results indicated that the enhancement of the hydrothermal stability can not be simply considered by improving the preparation methods. According to our characterization results, after hydrothermal aging, the surface area of the catalysts decreased slightly, while the pore volume seemed unchanged. The relative concentration of isolated Fe<sup>3+</sup> species decreased and the concentration of oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters as well as Fe<sub>2</sub>O<sub>3</sub> particles increased. Brønsted acidity of the catalysts also significantly decreased.

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