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# 无模板剂两步法合成小颗粒 ZSM-5 沸石团聚体

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**摘要**: 在无模板剂存在下, 以硅酸钠为硅源采用简单的变温两步法, 通过控制高温预晶化时间, 在转动烘箱中成功合成了小颗粒 ZSM-5 沸石团聚体. 高温预晶化是为了加快反应液的成核, 而低温晶化是为了获得小的分子筛晶体. 运用 X 射线衍射, 扫描电镜, $NH_3$ 程序升温脱附和 $N_2$ 吸附-脱附等技术对合成的 ZSM-5 沸石进行了表征. 与一步法合成的微米级颗粒相比较, 两步法合成的小颗粒团聚体 ZSM-5 沸石具有较高比表面积和相同酸量. 得到的沸石的 Brönsted 酸位占主要部分, Lewis 酸位较少, 也说明 Al 基本进入沸石骨架中.

**关键词**: ZSM-5 沸石; 无模板剂; 团聚体; 两步合成法; 晶粒大小

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# Synthesis of Zeolite ZSM-5 Small Particle Aggregates by a Two-Step Method in the Absence of an Organic Template

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**Abstract:** The preparation of zeolite ZSM-5 without using a template was extensively investigated. Zeolite ZSM-5 small particle aggregates were synthesized in the absence of a template using sodium silicate as the silica source and by controlling the nucleation time at high temperature with a simple two-step method in a rotating autoclave on a spit within an oven. The first stage at higher temperature consisted of accelerating the nucleation and the second stage at lower temperature consisted of obtaining small crystals in the absence of a template. The resulting zeolites were characterized by X-ray powder diffraction, scanning electron microscopy, ammonia temperature-programmed desorption, and $N_2$ adsorption. Compared with the micron-sized zeolite crystals that are synthesized in the one-step method, zeolite ZSM-5 small particles prepared by the two-step method have a higher specific surface area and an equivalent acid site content. The sample synthesized by the two-step method mainly contains Brönsted acid sites and a few Lewis acid sites indicating that Al is incorporated into the framework of the zeolite.

**Key words:** ZSM-5 zeolite; template-free; aggregate; two-step synthesis; particle size

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ZSM-5 沸石因其独特均一的微孔和择形性结构, 而广泛用作非均相催化剂[1]. 例如, 在流化床催化裂化过程中, ZSM-5 作为催化剂的添加剂可以增加低碳烯烃的收率, 同时抑制甲烷的生成[2].

ZSM-5 沸石由美孚公司于 1972 年首次报道[3], 目前大都利用有机模板剂来合成[4~12]. 同时在正硅酸乙酯 (TEOS)、铝酸钠和氢氧化钠存在条件下, 很容易获得高结晶度的 ZSM-5 沸石. 为了获取尺寸

均一、分布窄的沸石, 通常使用大量的水以及模板剂来抑制晶体的生长速率. 尽管 $TPA^+$是一种优良的模板剂, 但成本高, 且脱除不完全容易造成孔道堵塞, 同时造成环境污染. 因此, 无模板剂法合成 ZSM-5 沸石成为分子筛合成的热点[13~21]. 利用乙醇或氨水取代 $TPA^+$已有报道[22], 但所得晶体较大, 结晶度不高. 无模板剂法合成 ZSM-5 沸石时需要严格地控制合成条件, 如原料的类型、母液组成、陈化时间和合成温度等. 这是因为与有模板剂体系相比, 这些参数的工作窗口都变窄了. Grose 和 Flanigen[13]首次在无有机模板剂条件下, 加与不加晶种, 于 200 °C 晶化 72 h 合成 ZSM-5 沸石. Shiralkar 等[23]研究了于 150~190 °C、晶化 46~220 h 合成 ZSM-5 沸石的相区问题, 可以获得硅铝比为 30~60 的 ZSM-5 沸石. Kim 等[24]报道了无模板剂条件下合成液组成的影响, 发现 $Na_2O:Al_2O_3 = 0.06$~0.20, $SiO_2:Al_2O_3 = 30$~80, 在 170 °C 都可制得 ZSM-5 沸石. Kalipcilar 等[19]考察了硅源性质对合成 ZSM-5 沸石的影响, 发现采用硅溶胶比硅酸制得的沸石结晶度更高. Kang 等[18]发现无模板剂硅酸钠为硅源时, 必须用硫酸或硫酸钠来调节合成母液中的氧化钠含量, 母液中硫酸钠含量对 ZSM-5 晶体性质有影响.

在有机模板剂存在下, 利用低温成核高温晶化的两步法可以制备 ZSM-5 小晶体颗粒. Sun 等[25]报道了采用两步法可以合成具有 300 nm 均一尺寸的 Fe-ZSM-5 沸石分子筛. Li 等[26]研究了两步法中的线性生长速率以及最终收率问题. 另外, 两步法也被广泛应用于合成 MFI 膜[27]. 比较而言, 无模板剂法合成 ZSM-5 沸石通常需要的时间更长. 这主要是因为无模板剂法在晶体诱导成核阶段不容易成核, 而有机模板法在结构导向剂的作用下更容易诱导成核. 从晶体动力学方面也可以看出, 无模板剂法合成 ZSM-5 沸石的成核活化能与生长活化能比有机模板法的要高出许多[24,28]. Kim 等[29]报道了无模板剂下采用高温成核低温晶化的两步法, 以硅溶胶为硅源得到尺寸分布窄的微米尺度的沸石, 晶体颗粒在 1~4 μm. 该两步法主要有两个优点: (1) 无模板剂时晶体的诱导时间很长, 但高温成核可以大大缩短诱导时间; (2) 低温晶化可以更容易控制晶体的生长速度, 以获得较小的晶体颗粒.

迄今为止, 无模板剂下不使用晶种合成 ZSM-5 晶体的研究还比较少, 尤其是采用廉价的硅酸钠为硅源的则更少[18]. 因此, 本文在转动烘箱中以硅酸钠为硅源, 采用两步法制备颗粒较小但团聚的 ZSM-5 沸石,并采用 X 射线衍射 (XRD), 扫描电镜 (SEM), $NH_3$ 程序升温脱附 ($NH_3$-TPD) 和 $N_2$ 吸附-脱附等技术对样品进行了表征, 考察了一步法中晶化温度和投料硅铝比对合成 ZSM-5 沸石颗粒大小的影响以及两步法中第一步预晶化时间等对所得 ZSM-5 晶体的影响.

## 1 实验部分

### 1.1 ZSM-5 沸石的制备

以硅酸钠 (浙江省嘉善县助剂一厂, $SiO_2$ 质量分数 60%, $Na_2O$ 质量分数 20%) 为硅源, 硫酸铝 (上海美兴) 为铝源合成 ZSM-5 沸石. 称取一定量的硅酸钠, NaOH (上海国药集团) 依次加入到一定量的水中, 用磁力搅拌器搅拌均匀; 然后将一定量硫酸铝完全溶解在剩余的水中, 再加入一定量的硫酸 (衢州巨化). 将完全溶解的硫酸铝溶液缓慢滴入含有硅酸钠的溶液中, 室温搅拌 24 h. 合成液摩尔组成为 $18Na_2O:100SiO_2:xAl_2O_3:12SO_4^{2-}:4000H_2O$. $x$ 值分别为 1.67, 2 和 2.5, 对应的 $SiO_2:Al_2O_3$ 比 (简写为 SAR) 分别为 60, 50 和 40.

一步法: 将合成液转移至带有聚四氟内衬的高压釜中, 再将高压釜装到带有转轴的烘箱中, 转速 30 r/min. 在 150 或 190 °C, 晶化一定时间后取出, 急冷.

两步法: 将合成液转移至带有聚四氟内衬的高压釜中, 再将高压釜装到带有转轴的烘箱中, 转速 30 r/min. 在 190 °C, 预晶化一定时间后, 再降至 150 °C 晶化一定时间后, 取出, 急冷.

离心分离水热合成后的固体产物, 用去离子水反复洗涤至中性, 于 100 °C 烘干.

采用 $NH_4NO_3$ 溶液 (1 mol/L) 对干燥过的沸石样品在 80 °C 进行 3 次离子交换, 每次交换 2 h. 交换后用去离子水洗净, 于 100 °C 干燥过夜, 550 °C 焙烧 2 h.

### 1.2 ZSM-5 沸石的表征

XRD 分析在日本理学 Dmax-RA 型 XRD 仪上进行, 扫描范围 $2\theta = 5°$~$50°$ . 沸石的形貌及粒度分

布通过 Hitachi TM-1000 和 Hitachi S-4800 型 SEM 观测. 团聚体的粒径分布通过激光粒度仪 (Malvern 2000) 测得. $N_2$ 吸附-脱附等温线采用美国麦克公司的 ASAP 2020 型物理吸附仪测得. BET 法计算样品的比表面积, *t*-plot 法表征外比表面积等信息.

$NH_3$-TPD 实验时, 催化剂用量 0.1 g, 载气 He 流量 40 ml/min, 从室温升到 550 °C, 并保持 1 h. 然后降温到 100 °C, 再用流速为 9 ml/min 的 4% $NH_3$-96% He 混合气吸附 30 min, 再在 100 °C 吹扫 1 h. 然后以 10 °C/min 升温到 700 °C, TCD 检测 $NH_3$ 脱附信号.

催化剂的吡啶吸附红外光谱 (FT-IR) 表征在布鲁克公司的 TENSOR 27 型仪器上原位进行. 从室温以 10 °C/min 升到 450 °C, 保持 2 h 进行预处理. 降温至 150 °C 吸附吡啶 30 min, 升温到 200 °C 抽空 1 h, 差谱即为 200 °C 时吡啶吸附 FT-IR 谱.

## 2 结果与讨论

### 2.1 一步法中晶化温度和投料 SAR 对 ZSM-5 样品的影响

表 1 为一步法合成不同 ZSM-5 样品的合成条件及晶粒大小, 图 1 和图 2 分别为不同条件合成的 ZSM-5 沸石样品的 XRD 谱和 SEM 照片. 由图 1 可见, 所得样品都为结晶度较高的 MFI 结构的沸石. 由表 1 可见, 在同样的晶化温度下, 合成液的 $SiO_2/Al_2O_3$ 比 (SAR) 越低, 为达到相近的结晶度所需的晶化时间越长, 即合成液铝含量的增加会使晶化速率减慢. 晶化温度越高, 所需的晶化时间越短, 如合成液 SAR 为 60 时, 于 190 °C 晶化只需 16 h 就可得到比较高的结晶度, 而在 150 °C 晶化则需 34 h. 由图 2 可见, 晶化温度越高, 得到的晶体越大. 因为晶化温度高, 所形成的晶核生长越快. 如 SAR = 60 时, 190 °C 晶化后沸石颗粒为 2.0~6.0 μm; 150 °C 晶化为 1.0~4.0 μm. 合成液 Al 含量的增加使晶体颗粒趋于更小; 150 °C 晶化, SAR = 40 时沸石颗粒为 0.5~3.0 μm. 因此, 为获得小颗粒沸石, 必须降低晶化温度和合成液投料的 SAR. 合成液 SAR 为 40 时, 晶化时间为 36, 48 和 72 h 时, 结晶度分别为 75.0%, 80.2% 和 85.0%, 说明需要更长的晶化时间以提高样品的结晶度, 且很难达到 100%.

**表 1 一步法合成不同 ZSM-5 样品的合成条件及晶粒大小**

**Table 1** Reaction conditions and crystal size of different ZSM-5 samples prepared by the one-step method

| Sample[a] | SAR[b] | Synthesis temperature (°C) | Time (h) | Crystal size (μm) |
|---|---|---|---|---|
| A1 | 60 | 190 | 16 | 2.0–6.0 |
| A2 | 50 | 190 | 18 | 1.6–5.2 |
| A3 | 40 | 190 | 22 | 1.2–4.8 |
| B1 | 60 | 150 | 34 | 1.0–4.0 |
| B2 | 50 | 150 | 38 | 0.8–3.6 |
| B3 | 40 | 150 | 48 | 0.5–3.0 |

[a]The molar ratio of the synthesis hydrogel was $18Na_2O:100SiO_2:xAl_2O_3:12SO_4^{2-}:4000H_2O$. [b]$SiO_2/Al_2O_3$ ratio.

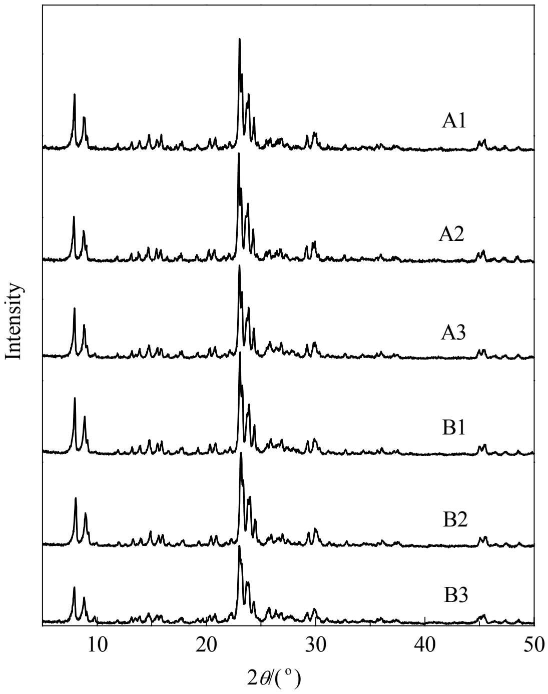

**图 1 不同条件制得 ZSM-5 样品的 XRD 谱**

**Fig. 1.** XRD patterns of the ZSM-5 samples prepared by different conditions.

### 2.2 两步法合成时间对 ZSM-5 样品的影响

为了缩短晶化时间和获得小颗粒的 ZSM-5 沸石, 采用 190 °C 短时间预晶化和 150 °C 晶化反应来合成. 高温预晶化可以促使晶核的生成, 短时间可以防止晶核进一步长大, 而低温晶化可以减缓后期晶核的生长速度, 有利于获得小颗粒沸石. 图 3 给出了不同高温预晶化样品的 XRD 谱. 可以看到, 高温预晶化 2 h, 反应产物还是无定形状态, XRD 谱中没有明显的特征衍射峰, 高温预晶化至 4 h, 反应产物的衍射峰有所增加, 即结晶度增加. 随着预晶化时间延长至 8 h, 样品出现明显的特征衍射峰. 表

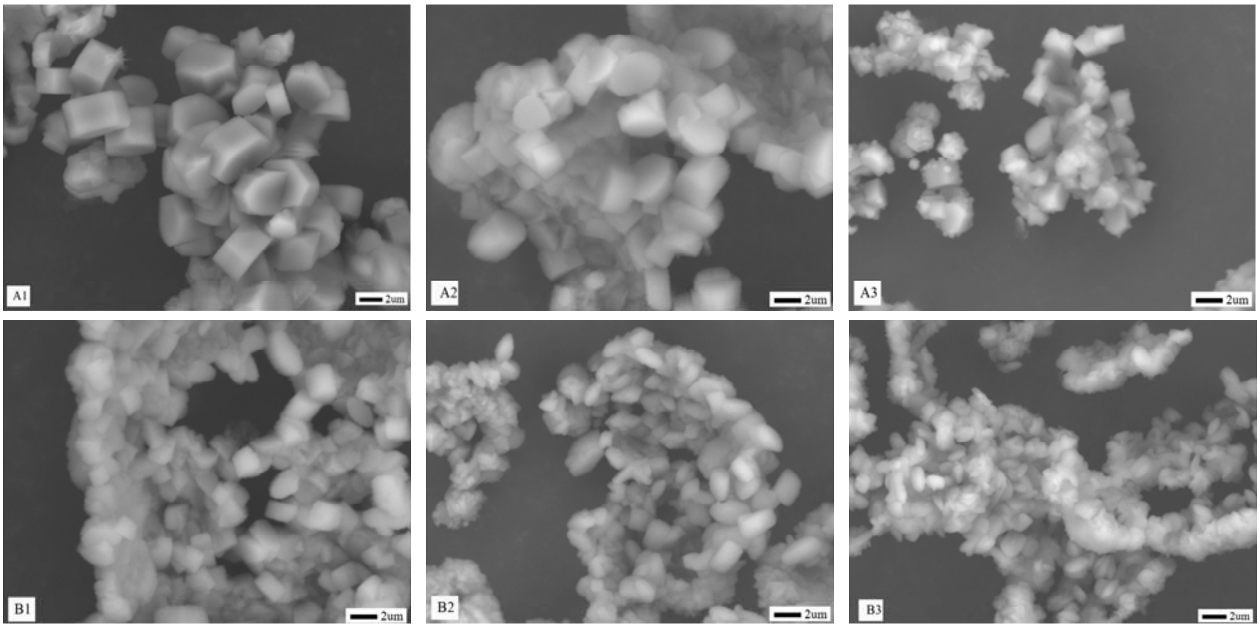

**图 2　不同条件下制得的 ZSM-5 样品的 SEM 照片**

**Fig. 2.**　SEM images of the ZSM-5 samples prepared under different conditions.

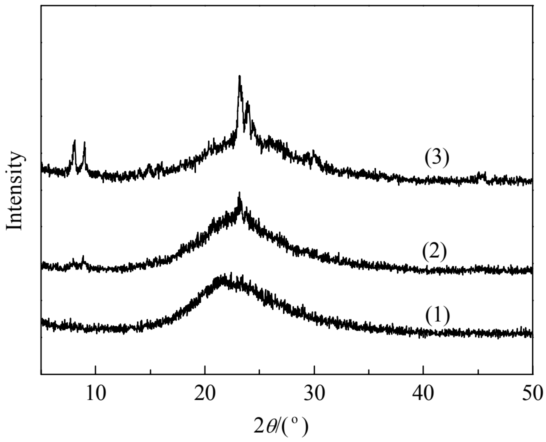

**图 3　高温预晶化不同时间 ZSM-5 样品的 XRD 谱**

**Fig. 3.**　XRD patterns of the ZSM-5 samples obtained upon using different nucleation times at high temperature. (1) 2 h; (2) 4 h; (3) 8 h.

2 列出了两步法中高温预晶化 2, 4 和 8 h, 低温晶化不同时间所得样品的相对结晶度 (样品的相对结晶度都以样品 A1 作为基准). 可以看出, 高温预晶化时间越短, 达到高结晶度所需时间越长. 当高温预晶化 2 h 时, 低温晶化 18 h 所得沸石的结晶度为 90.4%; 至 22 h 时提高到 98.7%; 达 26 h 时沸石结晶度增加不大. 当高温预晶化 8 h 时, 低温晶化 10 h 所得沸石的结晶度就能达到 90.8%; 至 12 h 时增至 97.9%; 然而低温晶化 16 h 时, 沸石结晶度增加不大, 为 98.9%.

**表 2　两步法不同 ZSM-5 样品合成条件及相对结晶度**

**Table 2**　Reaction conditions and relative crystallinity for various ZSM-5 samples prepared by the two-step method

| Sample$^a$ | Synthesis time (h) | | Relative crystallinity |
|---|---|---|---|
| | at 190 °C | at 150 °C | (%) |
| C1 | 2 | 18 | 90.4 |
| C2 | 2 | 22 | 98.7 |
| C3 | 2 | 26 | 99.0 |
| D1 | 4 | 14 | 93.2 |
| D2 | 4 | 18 | 98.5 |
| D3 | 4 | 22 | 99.1 |
| E1 | 8 | 10 | 90.8 |
| E2 | 8 | 12 | 97.9 |
| E3 | 8 | 16 | 98.9 |

$^a$SAR = 40.

图 4 为不同晶化时间制得 ZSM-5 样品的 XRD 谱. 可以看出, 采用两步法获得的三个沸石样品都具有 MFI 结构, 具有相近的结晶度. 图 5 为这些样品的 SEM 照片. 可以看出, 高温预晶化 2 h, 低温晶化 22 h 所得样品 C2 的颗粒大小与一步法 150 °C 晶化 48 h 获得的样品 B3 接近. 可见两步法可大幅缩短总合成时间. 当高温预晶化 4 h, 低温晶化 18 h 样品 D2 颗粒明显减小, 但出现团聚现象, SEM 照片看不出颗粒之间的间隙. 当高温预晶化 8 h, 低温晶化 12 h, 样品 E2 同样也是小颗粒团聚体. 如果采用动态光散射测粒径时, 小颗粒团聚体很容易沉降到底部, 所测的只是悬浮在分散液中的一部分颗粒, 很

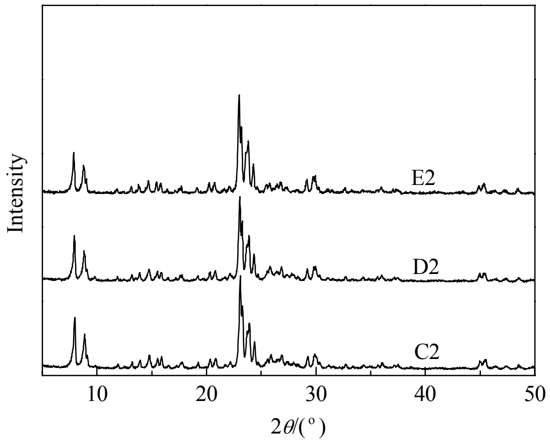

**图 4　两步法合成 ZSM-5 样品的 XRD 谱**

**Fig. 4.**　XRD patterns of the ZSM-5 samples by the two-step method.

难获得整体颗粒大小数据. 因此本文采用激光粒度仪测定粒径分布, 因为在整个测量过程中颗粒处在超声振动状态, 不容易沉降, 得到的数据比较准确, 结果见图 6. 可以看出, 所得颗粒粒径分布很广, 从小于 1 μm 到几十个 μm. 小于 1 μm 的颗粒属于基本粒子, 从 SEM 照片上也可以看出这种基本小颗粒小于 1 μm, 而达到十几甚至几十个微米的颗粒属于团聚颗粒, 只是团聚大小不同造成的. 与 Kim 等[24]人利用两步法合成 ZSM-5 沸石相比, 本文所得样品具有更小的一次颗粒. 这是因为反应溶液中 $Na_2O$ 含量增加所致. 碱度的增加有利于生成更多的晶核, 而在后期的低温晶化过程中, 核的数量多有利于形成小晶体, 这与晶种法合成小颗粒分子筛类似.

图 7 为不同样品的 $N_2$ 吸附-脱附曲线, 表明所得到的样品具有典型的微孔. 表 3 中列出了它们的织构性质. 不难看出, 样品 D2 具有的比表面积最高, 达到 367 $m^2/g$, 颗粒的外表面积为 63 $m^2/g$; 而样品 C2 和 E2 的比表面积和外比表面积都略小于 D2. 当高温成核时间太短, 所形成的核数量太少, 无定形营养居多, 要想得到高结晶度沸石, 后期低温晶化必须要较长的时间, 从而导致晶核容易吸收营养而长大成较大的颗粒; 如表 2 所示, 高温成核 2 h, 低温需晶化 26 h, 由于前期成核消耗的营养少, 所以后期长时间的低温晶化导致晶体颗粒偏大; 当高温成核时间太长, 所形成的核多且已经长成大核, 具有较高结晶度, 但容易长成晶体较大的颗粒, 如高温成核 8 h, 虽然低温晶化只需 16 h, 但由于前期晶核结

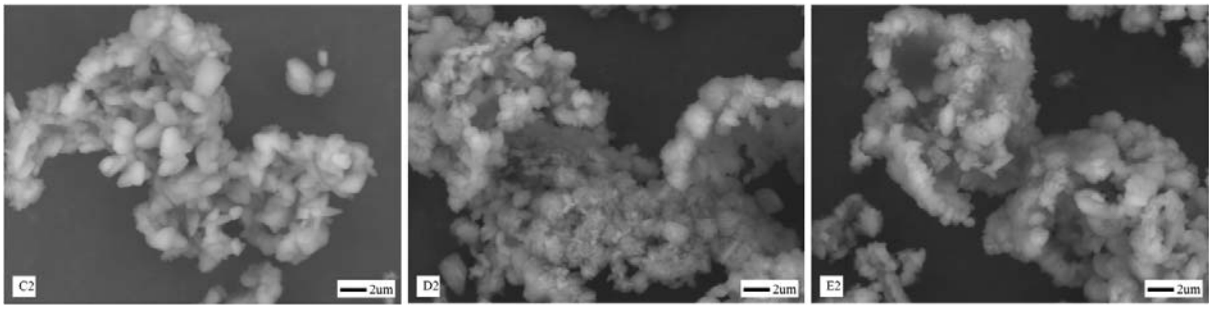

**图 5　两步法合成 ZSM-5 样品的 SEM 照片**

**Fig. 5.**　SEM images of ZSM-5 samples.

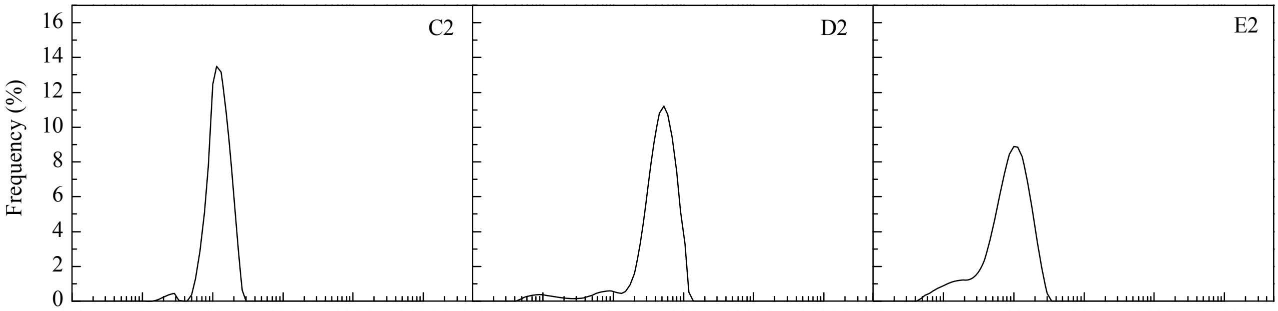

**图 6　两步法合成 ZSM-5 样品的粒径分布**

**Fig. 6.**　Particle size distributions of the ZSM-5 samples.

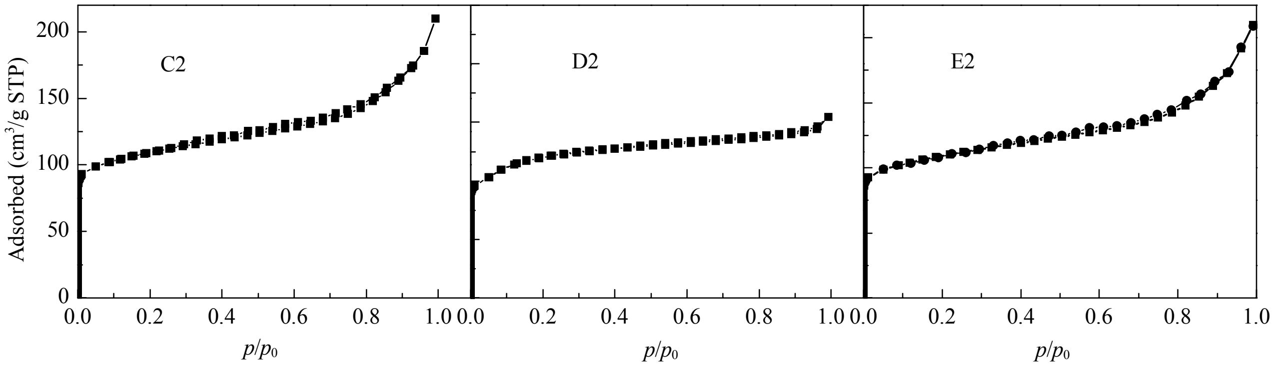

**图 7　不同 ZSM-5 样品的 $N_2$ 吸附-脱附曲线**

**Fig. 7.**　$N_2$ adsorption-desorption isotherms of different ZSM-5 samples.

**表 3　不同 ZSM-5 样品的织构性质**

**Table 3**　The textural properties of various ZSM-5 samples

| Sample | BET surface area ($m^2$/g) | Micropore volume ($m^3$/g) | Micropore area ($m^2$/g) | External surface area ($m^2$/g) |
|---|---|---|---|---|
| B3 | 307 | 0.12 | 258 | 49 |
| C2 | 314 | 0.12 | 266 | 48 |
| D2 | 367 | 0.13 | 304 | 63 |
| E2 | 335 | 0.13 | 277 | 58 |

晶度高, 且已经长大, 因此后期低温晶化更容易生长成较大颗粒晶体. 当生成的核数量适当, 这种晶核消耗溶液的营养生成颗粒不是很大的晶体, 但这种晶体在无模板剂的条件下容易形成团聚. 因此, C2 和 E2 的外比表面积比 D2 的小.

### 2.3　两步法与一步法合成的 ZSM-5 沸石的酸性

图 8 为一步法和两步法合成沸石的 $NH_3$-TPD 谱. 图中出现的脱附峰低温 (220 °C 左右) 和高温 (430 °C 左右) 脱附峰分别对应于沸石的强酸和弱酸. 由图可见, 尽管沸石的颗粒大小和比表面积等不同, 但其 $NH_3$-TPD 谱变化不大, 说明沸石的酸量差别不大. 图 9 为上述沸石的吡啶吸附 FT-IR 谱, 图中 1550 和 1450 $cm^{-1}$ 处出现的峰分别对应于沸石的 Brönsted 酸位和 Lewis 酸位. 由图可见, 所得沸石样品的 Lewis 酸位很少, 主要以 Brönsted 酸位为主要, 也说明 Al 基本进入沸石骨架. 综上可见两步法合成的沸石样品酸性与一步法的相同. 这种小颗粒团聚体 ZSM-5 沸石具有很好的工业化应用前景.

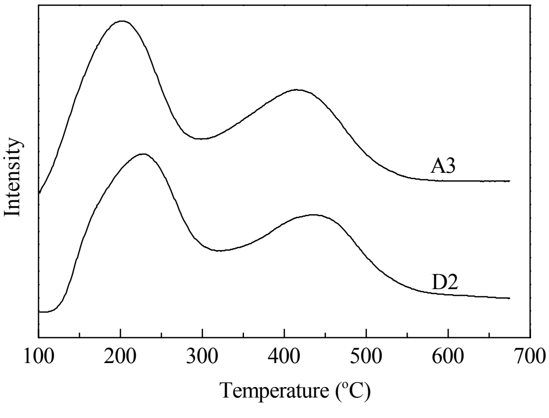

**图 8　不同 ZSM-5 样品的 $NH_3$-TPD 谱**

**Fig. 8.**　$NH_3$-TPD profiles of different ZSM-5 samples.

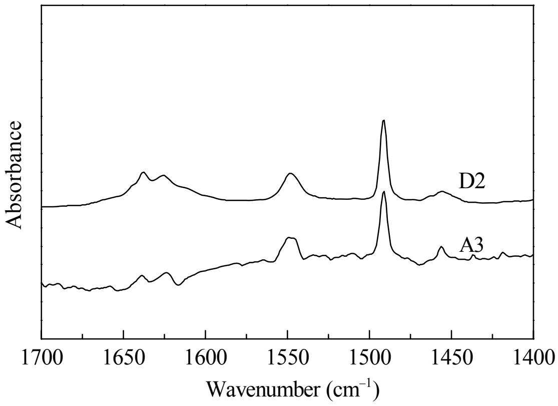

**图 9　不同 ZSM-5 样品的吸附吡啶红外光谱**

**Fig. 9.**　FT-IR adsorption spectra of different ZSM-5 samples at 200 °C.

## 3　结论

系统地研究了无模板剂一步法中晶化温度和硅铝比对合成 ZSM-5 沸石颗粒的影响. 采用简单的两步法, 在无模板剂的条件下, 通过控制高温成核时间, 成功合成了具有小颗粒团聚体. 随着基本颗粒的减小, 团聚体 ZSM-5 沸石的比表面积和外表面积都有所增加. 相同硅铝比时, 两步法合成的小颗粒 ZSM-5 沸石的酸量与一步法的差别不大, 说明 Al

基本上进入了沸石的骨架, 且合成时间大大缩短.

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## 英 译 文

## *English Text*

Zeolites have been widely used in the chemical industry as solid acid heterogeneous catalysts especially in oil refining and petrochemistry because of their unique catalytic activity and shape selectivity [1]. For example, zeolite ZSM-5 acts as an additive catalyst and improves the yield of light alkenes along with the suppression of undesirable products such as methane in the fluidized catalytic cracking (FCC) process [2].

Since the synthesis of zeolite ZSM-5 was first reported by Mobil in 1972 [3], the synthesis of zeolite ZSM-5 by the hydrothermal method with an organic template [4–12] has been widely reported. Highly crystalline ZSM-5 has been synthesized easily by a hydrothermal method using a mixture containing silica sol, sodium aluminate, and sodium hydroxide together with organic template cations such as $TPA^+$ and $TEA^+$. To obtain a narrow and uniform crystal distribution, abundant amounts of $TPA^+$ and water are used and this suppresses the crystallization rate. Despite the excellent template effect of $TPA^+$ cations they cause many adverse problems such as high production cost, organic species contained in the channel system because of incomplete decomposition, and environment problems from the thermal decomposition of organic species.

Therefore, the synthesis of zeolite ZSM-5 without a template is a hot topic in the study of the zeolite synthesis [13–21]. ZSM-5 has been synthesized successfully using ethanol and ammonia instead of $TPA^+$ [22], however, its crystallite size was found to be relatively large and its crystallinity was relatively low. For the synthesis of zeolite ZSM-5 in the absence of a template, synthetic conditions such as types of raw material, mother liquid composition, aging time, and crystallization temperature should be strictly controlled because the working windows of these parameters are narrower compared with templated systems. Grose and Flanigen [13] first reported the synthesis of organic-free ZSM-5 after 68–72 h of reaction at 200 °C with/without seed. Shiralkar and Clearfield [23] investigated the compositional constraints during the synthesis of ZSM-5 at 150–190 °C for 46–220 h in which pure ZSM-5 was obtained using a $SiO_2/Al_2O_3$ ratio between 30 and 60. Kim et al. [24] reported the effect of molar composition in the template-free synthesis of ZSM-5 and found that pure ZSM-5 could be obtained using a $Na_2O/Al_2O_3$ ratio of 0.06–0.20 and a $SiO_2/Al_2O_3$ ratio of 30–80 at 170 °C. Kalipcilar et al. [19] investigated the influence of the silica source for a template-free synthesis of ZSM-5 and found that more crystalline ZSM-5 could be obtained using silica sol than silicic acid. Kang et al. [18] reported that the concentration of $Na_2O$ should be adjusted with sulfuric acid or sodium sulfate on the template-free synthesis of ZSM-5 with sodium silicate as a silica source and that the concentration of sodium sulfate in the synthesis mixture influenced the properties of the final product.

Small crystals can be acquired by a temperature-varying two-step method (lower temperature for nucleation and higher temperature for crystal growth) in templated systems. For example, Sun et al. [25] synthesized small crystal Fe-ZSM-5 with a uniform crystallite size of about 300 nm using this method. Li et al. [26] investigated the linear growth rate and final yield of silicalite using the two-step temperature-varying process. The two-step temperature-varying technique was also applied to the synthesis of a MFI type zeolite membrane [27]. Compared with templated systems it is obvious that it takes longer to synthesize ZSM-5 zeolites in the absence of a template because it is more difficult to form nuclei during nucleation with the template-free method than the template method. Concerning the kinetics of crystallization the nucleation and growth activation energies of the template-free method are much higher than those of the template method [24,28]. On the other hand, the nucleation stage at higher temperature leads to accelerated nucleation and this is followed by the crystallization stage at lower temperature for the control of crystallite size and the size distribution in the absence of a template with a silica sol as the silica source and this has been reported by Kim et al. [29]. The crystallite size was in the micron range (1–4 μm). There are two benefits to this method: (1) since nucleation occurs over a long time in the crystallization process the nucleation time is dramatically reduced at higher temperature; (2) the crystallite size is easily controlled at lower temperature on a crystallization stage.

Few studies have been reported on the synthesis of zeolite ZSM-5 in the absence of an organic template without seed especially with cheap sodium silicate as the silica source [18]. In this study, we report the synthesis of zeolite ZSM-5 small particle aggregates using a two-step method in the absence of an organic template and with sodium silicate as the silica source in a rotating autoclave on a spit within an oven. The resulting zeolites were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), ammonia temperature-programmed desorption ($NH_3$-TPD), and $N_2$ adsorption. The effects of crystallization temperature for the one-step method and the $SiO_2/Al_2O_3$ ratio (SAR) of the stock on the particle size were studied. The effect of nucleation time for the two-step method on the final particle size was also studied.

## 1 Experimental

### 1.1 Synthesis of zeolite ZSM-5

Sodium silicate (Zhejiang Jiashan Auxiliary Agent Factory, $SiO_2$ 60 wt.%, $Na_2O$ 20 wt.%) was used as the silica source and aluminum sulfate ($Al_2(SO_4)_3\cdot18H_2O$, Shanghai Meixing) was used as the alumina source for the synthesis of ZSM-5 without an organic template. A pre-determined amount of sodium silicate and NaOH (Sinopharm Chemical Reagent Co. Ltd) were dissolved in deionized water with stirring in a beaker (I). Sulfuric acid (Quzhou Juhua) and aluminum sulphate were dissolved in the remaining water in another beaker (II). The solution in beaker II was added slowly into beaker I. The molar composition was $18Na_2O:100SiO_2:xAl_2O_3:12SO_4^{2-}:4000H_2O$, $x$ = 1.67, 2, and 2.5, corresponding to SAR of 60, 50, and 40.

One-step method: The solution was placed in an autoclave and the autoclave was rotated at 30 r/min in an oven at 190 or 150 °C for different periods of time. After the synthesis the suspension in the autoclave was quenched.

Two-step method: The solution was placed in an autoclave and the autoclave was rotated at 30 r/min in an oven at 190 °C for different periods of time. The temperature was then decreased to 150 °C and kept at this temperature for different periods of time. After the synthesis the suspension in the autoclave was quenched.

After crystallization the synthesized product was centrifugated, rinsed with distilled water and dried at 100 °C for 12 h. The sample was transformed into the $NH_4^+$ form by ion-exchange with an $NH_4NO_3$ solution and the washing-filtration-drying steps were repeated 3 times. The H form was obtained by calcination at 550 °C for 2 h.

### 1.2 Characterization of zeolite ZSM-5

XRD analyses (Dmax-RA) were performed using Cu $K_\alpha$ radiation to identify the product phase and to calculate the crystallinity. The morphology was identified by SEM (Hitachi TM-1000 and FE-SEM Hitachi S-4800). The size distribution of the particles were measured using laser light-scattering (LLS, Malvern 2000). Nitrogen adsorption isotherms were obtained using Micromeritics ASAP 2020 equipment. The extant surface area was obtained by the $t$-plot method and the total surface area was obtained by the BET equation.

$NH_3$-TPD was carried out with a quartz reactor, a TCD detector and 100 mg of sample at atmospheric pressure. The system was pretreated at 550 °C for 1 h in a flow of He (40 ml/min). After cooling to 100 °C, $NH_3$ (4%) was introduced with He (96%) flow until saturation. The sample was purged in He flow for 1 h to remove physically adsorbed $NH_3$. Desorption was then performed under the same He flow at a ramp of 10 °C/min to 700 °C.

The zeolite sample was dehydrated using an infrared (IR) cell at 450 °C for 2 h under vacuum. Pyridine was introduced to the IR cell at 150 °C. Pyridine adsorption IR spectra of the zeolite catalysts were obtained at ambient temperature using a Bruker Tensor 27 after desorption at 200 °C.

## 2 Results and discussion

### 2.1 Effects of crystallization temperature and the SAR during the one-step method

The synthesis conditions used to obtain the ZSM-5 products with similar crystallinity in the one-step method is shown in Table 1. SEM images and the XRD patterns of the ZSM-5 samples at different crystallization temperatures with different SAR are shown in Fig. 1 and Fig. 2, respectively. As shown in Fig. 1, all the samples were highly crystalline with a typical zeolite ZSM-5 structure. As shown in Table 1, it is obvious that more time was required to obtain equivalent crystallinity using the same crystallization temperature at a higher SAR ratio. This means that an increase in the Al content reduced the crystallization rate. As shown in Table 1, a shorter crystallization time was required to obtain high crystallinity with the higher reaction temperature. The sample with a SAR value of 60 required 16 h to become highly crystalline at a reaction temperature of 190 °C while it required 34 h to become highly crystalline at a reaction temperature of 150 °C. From the SEM images, the higher crystallization temperature led to larger crystals. The nuclei grew rapidly at the higher crystallization temperature. For the sample with a SAR of 60 the crystallite size was about 2.0–6.0 μm at a reaction temperature of 190 °C while the crystallite size was about 1.0–4.0 μm at a reaction temperature of 150 °C. Reducing the SAR led to a smaller crystallite size. For the sample with a SAR of 40 the crystallite size was about 0.5–3.0 μm at a reaction temperature of 190 °C. Therefore, the crystallization temperature and SAR should be as low as possible to obtain small crystals. The crystallinity of the sample (SAR=40) obtained at the crystallization time of 36, 48, and 72 h was 75.0%, 80.2%, and 85.0%, respectively. And it was difficult to achieve 100% crystallinity under these conditions.

### 2.2 Effects of crystallization time for each step in the two-step method

To reduce the crystallization time and to obtain ZSM-5 zeolites with small particles a two-step method was adopted: a higher temperature (190 °C) for nucleation followed by a lower temperature (150 °C) for crystallization. The first step at higher temperature was carried out to accelerate nucleation and the second step at lower temperature was carried out to control the crystallite size at a low crystallization rate. XRD patterns for the zeolites with different nucleation times at the higher temperature (190 °C) are shown in Fig. 3. No detectable zeolite ZSM-5 peak was observed after a reaction time of 2 h. Some small peaks were present for the sample synthesized after a nucleation time of 4 h. Some significant zeolite ZSM-5 peaks were observed at a nucleation time of 8 h. The crystallinity of various samples that were prepared over different crystallization times at 150 °C and different nucleation times (2, 4, and 8 h) at 190 °C is shown in Table 2 (the crystallinity of sample A1 was used as a standard). When a shorter time is used at higher temperature a longer crystallization time is required at lower temperature to obtain a highly crystalline compound. The sample that was nucleated at 190 °C over 2 h was 90.4% crystalline when crystallized at 150 °C over 18 h. Its crystallinity increased to 98.7% after a crystallization time of 22 h and it did not increase significantly upon prolonging the crystallization time to 26 h. For the sample nucleated at 190 °C over 8 h the crystallinity reached 90.8% when crystallized at 150 °C over 10 h. It reached 97.9% upon prolonging the crystallization time to 12 h and 98.9% upon prolonging the crystallization time to 16 h.

Samples C2–E2 with high crystallinity and short crystallization time that were nucleated at 190 °C over 2, 4, and 8 h and then crystallized at 150 °C over 22, 18, and 12 h were characterized using various techniques. From their XRD patterns (Fig. 4) the C2–E2 samples were highly crystalline and had a MFI structure. From SEM images (Fig. 5) the particle size of sample C2 (190 °C 2 h, 150 °C 22 h) is similar to that of sample B3 (150 °C 48 h). The crystallization time was shortened from 48 h for the one-step method to 24 h for the two-step method. The particle size of sample D2 (190 °C 4 h, 150 °C 18 h) decreased substantially. The boundary between the particles could not be clearly observed by SEM. The particles of sample E2 (190 °C 8 h, 150 °C 12 h) just like sample D2 were small aggregates. It should be mentioned that the abundant aggregation observed in these samples made it difficult to evaluate the dominant population of the particles by DLS. Since the particle aggregates easily caused sediment to form at the bottom of the DLS cell during measurement, DLS just gave information about the particles floating in the suspension. Since the aggregates did not easily deposit at the bottom of the cell with ultrasonic treatment the data measured by LLS is relatively accurate. Therefore, LLS with ultrasonic treatment was employed to measure the particle size distribution of our samples. It is clear from Fig. 6 that our samples have a broad size distribution. The size of the aggregates ranged from 1 μm to 10 μm. Particles smaller than 1 μm are thought to be primary particles. Particles larger than 10 μm are particle aggregates. The aggregates are of different size because they consist of a different number of primary particles. Compared with the ZSM-5 zeolite reported by Kim [24] the primary particle size was found to be smaller in this study because the $Na_2O$ concentration of the reaction liquid was higher. The increased alkalinity benefits the formation of nuclei. The increased nuclei benefit the growth of small particles at the lower temperature crystallization stage. This is similar to the synthesis of small particles using the seeded method.

The $N_2$ adsorption-desorption isotherms of the various ZSM-5 samples shown in Fig. 7 indicate that these samples are pure micropore materials. The textural properties of the various ZSM-5 samples are shown in Table 3. A BET calculation shows that sample D2 (190 °C 4 h, 150 °C 18 h) had the highest specific surface area (367 $m^2/g$) and external surface area (63 $m^2/g$). The specific surface area and external surface area of samples C2 and E2 are smaller than that of sample D2. When the time duration at the higher temperature was too short not enough nuclei formed and most of the synthesis solution was amorphous. In this case, to obtain a highly crystalline product a longer crystallization time is required for the lower temperature crystallization stage. The formed nuclei were easily sustained and grew into large crystals. As shown in Table 2 the sample was composed of larger crystals because the formation of nuclei consumed less solution species and the nuclei thus grew into larger particles when nucleated at 190 °C over 2 h and upon crystallization at 150 °C over 26 h. When exposed to a higher temperature for too long the formed nuclei grew into large nuclei. The large nuclei had significant crystallinity and tended to grow into large crystals. For example, the sample nucleated at 190 °C over 8 h and crystallized at 150 °C over 16 h consisted of larger crystals because the large nuclei that formed at 190 °C over the longer time easily grew into large particles. When an appropriate amount of nuclei were generated the formed nuclei grew into small particles and consumed the solution species. The small particles then stuck together to form aggregates in the absence of an organic template. Therefore, the external surface areas of samples C2 and E2 are smaller than that of sample D2.

### 2.3 Acidity characterization of the samples prepared by the two-step method and the one-step method

Figure 8 shows the $NH_3$-TPD profile of the samples synthesized by the two-step method and the one-step method. Two $NH_3$ desorption peaks are present. The $NH_3$ desorption peak at ~220 °C is associated with weak acid sites and the other peak at higher than 430 °C is associated with strong acid sites. The two ZSM-5 zeolites D2 and A3 with different crystallite sizes and different specific surface areas gave almost the same $NH_3$-TPD profiles. These two zeolites, therefore, had almost the same number of acid sites. The pyridine adsorption results on the samples synthesized by the two-step method and the one-step method are shown in Fig. 9. Basic pyridine adsorbed on the Brönsted acid sites (as a pyridinium ion) resulted in bands at 1550 and 1450 $cm^{-1}$ came from pyridine coordinated with the Lewis acid sites. It is clear that the sample that was synthesized by the two-step method mainly had Brönsted acid sites and only a few Lewis acid sites indicating that Al atom was incorporated into the framework of the zeolite. The small ZSM-5 zeolite particles have great potential for industrial applications.

## 3 Conclusions

The effects of the crystallization temperature on the one-step synthesis and the $SiO_2/Al_2O_3$ ratio (SAR) of the mother liquid on particle size were studied. Zeolite ZSM-5 small particle aggregates were synthesized in the absence of a template by controlling the nucleation time at a higher temperature using a simple two-step method. The specific surface area and the external surface area increased as the particle size decreased. Compared with the micron-sized zeolite crystals synthesized by the one-step method the zeolite ZSM-5 small particle aggregates prepared by the two-step method had an equivalent amount of acid sites indicating that the Al atoms were incorporated into the framework of the zeolite. The synthesis time is thus reduced significantly.

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