纳米 ZSM-5 沸石对芳烃苯基化反应的催化性能

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摘要: 采用晶种有机硅烷化法合成了纳米团簇 ZSM-5 沸石, 考察了其在芳烃苯基化反应中的催化活性. X 射线衍射、N₂ 吸附和扫描电镜等结果表明, 该沸石为由约 20 nm 的小晶粒聚集成的团簇体, 并形成晶间中孔, 其具有的外表面积是普通 ZSM-5 沸石的 5 倍之多. NH₃-程序升温脱附和吡啶吸附的红外光谱结果显示, 沸石的纳米化可使其表面酸中心, 尤其是强酸中心的数目增多, 大大提高了大分子的酸性位可接近性. 在芳烃苯基化反应中, 纳米 ZSM-5 沸石克服了反应分子空间位阻对催化活性的影响, 表现出优异的催化活性, 363 K 时, 甲苯苯基化反应的速率常数是普通 ZSM-5 沸石的约 13 倍.

关键词: 纳米 ZSM-5 沸石; 有机硅烷化; 芳烃苯基化; 酸性; 可接近性

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Nanoscale ZSM-5 Zeolite for the Benzylation of Aromatic Hydrocarbons

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Abstract: ZSM-5 zeolite in the form of crystalline nanoclusters was synthesized from seeds functionalized by organosilane and its catalytic performance in the benzylation of aromatic hydrocarbon by benzyl chloride was investigated. The zeolite samples were characterized by X-ray diffraction, N₂ adsorption-desorption, and scanning electron microscopy. The results indicated that they were composed of aggregates of nanocrystals about 20 nm. They had high external surface area that was five times that of conventional ZSM-5. The amounts of acid sites were increased, which was indicated by acidity characterization by the Fourier transform infrared spectroscopy of adsorbed pyridine and temperature-programmed desorption of NH₃. Moreover, accessibility to the acid sites was improved by reducing the size of crystals to nanoscale. In the benzylation of aromatics by benzyl chloride, nanoscale ZSM-5 showed a much higher activity than conventional ZSM-5 because the diffusional limitation for the large reactant was decreased in the nanoscale ZSM-5 zeolite. The benzyl chloride conversion in the benzylation of toluene was 98% at 363 K for 10 h, which was 3.6 times higher than that over conventional ZSM-5. The apparent rate constant over the nanoscale ZSM-5 zeolite was ca. 13 times larger than that over conventional ZSM-5.

Key words: nanoscale ZSM-5 zeolite; organofunctionalization; aromatic benzylation; acidity; accessibility

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芳香族化合物的苯基化反应是石油化工产品、药物、香料、染料和农药合成等工业过程中非常重

要的一类反应^[1]。通常, 此类反应是在 FeCl_3 , AlCl_3 , BF_3 , HF 或 H_2SO_4 等酸催化剂作用下进行^[2,3], 存在催化剂再生和后处理困难、分离不便、腐蚀和有毒等不足。因此, 采用污染小、再生性强的固相催化剂是发展其绿色化学的必然趋势。其中固体酸沸石分子筛 (H-ZSM-5, H-Y 等) 因具有良好的酸性、择形性和热稳定性而成为研究的热点, 但其相对小的、单一的微孔结构和有限的外表面积严重限制了它在该类大分子反应中的应用^[4,5]。

为了解决微孔沸石对涉及大分子反应的扩散限制, 有序介孔材料 MCM-41, SBA-15 等的应用引起了人们广泛关注。通过将活性物种 Fe、Al、Ga、Cr 等引入介孔材料的骨架或负载于表面, 可使其在芳烃等大分子反应中表现出较高的催化活性^[6–10], 但是因介孔壁的无定形性和有限的金属负载量而导致水热稳定性和酸性较低, 致使其催化活性的提高仍受到一定限制。多级孔沸石催化剂不仅具有微孔沸石固有的高稳定性和强酸性, 而且可有效提高反应物和产物的扩散速率, 在许多大分子反应中表现出良好的催化活性^[11–16]。另外, 通过减小沸石晶粒尺寸以提高其外表面积和活性位有效利用率, 同样可大大促进沸石对大分子反应的催化性能^[17–20]。

本文以 N -[3-(三甲氧基甲硅基)丙基]- N' -(4-乙炔基苄基)乙二胺盐酸盐溶液 (Z-6032) 为硅烷化试剂, 采用晶种有机硅烷化法合成了纳米团簇的 ZSM-5 沸石, 并将其用于芳烃苄基化反应中, 研究了催化剂的孔结构与酸性对其催化性能的影响。

1 实验部分

1.1 纳米 ZSM-5 沸石的合成

采用晶种有机官能团化法合成纳米 ZSM-5 沸石^[21]。按反应物投料摩尔配比 Al_2O_3 : 60SiO_2 : 11.5TPAOH : $1500\text{H}_2\text{O}$ 将异丙醇铝 (AIP, 分析纯, Aldrich)、正硅酸乙酯 (TEOS, 分析纯, Aldrich)、四丙基氢氧化铵 (TPAOH, 40% 水溶液, Alfa) 和蒸馏水加入三口烧瓶内, 于 363 K 回流搅拌 20 h, 预晶化形成 ZSM-5 晶种。随后加入一定量的 N -[3-(三甲氧基甲硅基)丙基]- N' -(4-乙炔基苄基)乙二胺盐酸盐溶液 (Z-6032, 40% 甲醇溶液, Dow Corning), 继续回流搅拌 10 h, 将晶种有机官能团化。然后将合成液转移至带有聚四氟乙烯衬里的不锈钢高压釜中, 密封、转

移至烘箱内, 于 453 K 晶化 3 d 后取出不锈钢釜, 迅速冷却至室温, 将上方清液倒掉, 取沉淀产物, 用去离子水反复洗涤至滤液为中性, 于 373 K 烘干, 873 K 通空气焙烧 5 h 以除去有机模板剂。

将焙烧过的沸石分子筛用 0.2 mol/L NH_4NO_3 溶液在 353 K 下离子交换 3 次, 每次 2 h, 交换完成后用蒸馏水洗涤 2 次, 于 373 K 烘干, 然后于 823 K 焙烧 5 h, 即制得 H 型 ZSM-5。合成过程中, 未加入硅烷化试剂 Z-6032 制备的沸石; 加入 Z-6032 的摩尔量为 TEOS 的 3% 和 7% 的样品分别记为 ZSM-5(1) 和 ZSM-5(2), 记为 ZSM-5N。

1.2 沸石的表征

X 射线衍射 (XRD) 分析在 Shimadzu XRD-6000 型衍射仪上进行。孔结构在 Quantachrome NOVA 1200 型吸附仪上测定, 实验在 77 K 进行。合成沸石的形貌通过 JEOL JSM-6700F 型扫描电镜 (SEM) 观测。 NH_3 程序升温脱附 (NH_3 -TPD) 实验在 Quantachrome Chembet-3000 型装置上进行。吡啶 (Py) 和 2,6-二甲基吡啶 (DMPy) 吸附的红外光谱 (FT-IR) 通过 Shimadzu IR Affinity-1 型傅里叶变换红外光谱仪测定, 酸量由对应特征吸收峰面积计算。

1.3 催化剂的评价

芳烃与苄基氯的液相苄基化反应在带有回流冷凝装置的 50 ml 三口烧瓶内进行, 温度由油浴控制。催化剂使用前在 773 K 通空气活化 5 h, 芳烃与苄基氯的摩尔配比为 55:1。首先将一定量芳烃与 0.15 g 催化剂加入烧瓶内, 在反应温度下充分搅拌 30 min, 然后加入 0.5 ml 苄基氯, 开始反应计时。间隔取样并通过气相色谱 (FID, HP-5 毛细管柱 (60 m $\times$ 0.32 mm $\times$ 1.00 μm)) 进行分析。

2 结果与讨论

2.1 沸石的晶相和形貌

图 1 为合成样品的 XRD 谱。由图可知, 所得样品均具有典型的 MFI 型沸石晶体结构。与 ZSM-5N 相比, ZSM-5(1) 和 ZSM-5(2) 沸石的特征衍射峰的强度减弱且明显宽化, 表明它们由微小的晶粒组成, 并由谢乐公式计算得知, 晶粒大小约为 20 nm (见表 1)。图 2 为 ZSM-5(1) 样品的 SEM 照片。可以看出, ZSM-5(1) 为 400~500 nm 的绒球状团簇, 而该团簇由约 20 nm 的小晶粒聚集而成; 而未加入硅烷化试

图 1 各 ZSM-5 沸石的 XRD 谱

Fig. 1. XRD patterns of ZSM-5 zeolite samples. (1) ZSM-5N (without organosilane, Z-6032, added); (2) ZSM-5(1) (with 3% organosilane, Z-6032, added); (3) ZSM-5(2) (with 7% organosilane, Z-6032, added).

表 1 ZSM-5 沸石的孔结构参数

Table 1 Pore structure properties of ZSM-5 samples

Sample	Si/Al Ratio ^a	Mean crystal size (nm)	A_{BET} (m ² /g)	A_{mic} (m ² /g)	A_{ext} (m ² /g)	V_{mic} (cm ³ /g)	D_{meso} (nm)
ZSM-5N	33	600 ^b	422	383	39	0.15	—
ZSM-5(1)	31	25 ^c (23 ^b)	515	364	151	0.13	2.5
ZSM-5(2)	31	20 ^c (19 ^b)	502	293	209	0.12	2.2

^aDetermination by ²⁹Si NMR. ^bEstimated from SEM and TEM. ^cCalculated from XRD by the Scherrer equation.

图 2 ZSM-5(1) 沸石的 SEM 照片

Fig. 2. SEM image of ZSM-5(1).

剂所制 ZSM-5N 样品为约 600 nm 的 coffin-like 形貌。由样品孔结构参数 (表 1) 可以看出, ZSM-5(1) 和 ZSM-5(2) 不仅保留了沸石固有的微孔, 而且由于小晶粒间的聚集而形成了 2~3 nm 的中孔, 晶粒的纳米化使其比表面积较 ZSM-5N 增加了 20%, 特别是外比表面积是 ZSM-5N 的 5 倍。

2.2 沸石的酸性

图 3 为合成所得各沸石样品的 NH₃-TPD 谱。

图 3 ZSM-5 沸石的 NH₃-TPD 谱

Fig. 3. NH₃-TPD profiles of ZSM-5 samples. (a) ZSM-5N; (b) ZSM-5(1); (c) ZSM-5(2).

可以看出, 虽然各样品酸中心分布相似, 存在三种酸中心, 即位于 573 K 内对应的弱酸中心, 573~673 K 内对应的中强酸中心以及 673~873 K 内对应的强酸中心。再结合样品上三种强度酸性点的分布 (表 2) 可见, 与 ZSM-5N 相比, 纳米 ZSM-5(1) 和 ZSM-5(2) 沸石的总酸量, 尤其是其中强酸中心的数量明显增加, 且二者的强酸中心所占比例增大。

表 2 为由纳米 ZSM-5 沸石吸附吡啶的 FT-IR 谱表征其表面酸性结果。由表可知, ZSM-5N, ZSM-5(1) 和 ZSM-5(2) 的 B 酸量分别为 70, 68 和 74 μmol/g, 相互比较接近; 而纳米 ZSM-5(1) 和 ZSM-5(2) 的 L 酸量较 ZSM-5N 沸石的增加了 2 倍以上, 这是由于纳米晶粒外表面存在大量的缺陷位且有部分非骨架 Al 物种出现而产生了较多的 L 酸中心。从不同温度吡啶脱附的 FT-IR 谱可以看出, ZSM-5(1) 和 ZSM-5(2) 表面的 B 和 L 强酸中心数

表 2 不同 ZSM-5 沸石的酸性
Table 2 Acidity of different ZSM-5 samples

Catalyst	Acid site distribution (%)			FT-IR-pyridine			
	< 573 K	573–673 K	673–873 K	Temperature (K)	B _{py} ^a /(μmol/g)	L _{py} ^a /(μmol/g)	ACI
ZSM-5N	52.0	24.2	23.8	423	70	25	0.05
				523	46	22	—
				623	38	15	—
ZSM-5(1)	45.4	23.2	31.4	423	68	83	0.38
				523	64	64	0.32
				623	55	31	0.28
ZSM-5(2)	42.9	25.0	32.0	423	74	79	0.60
				523	73	57	0.45
				623	60	26	0.43

^aCalculated from the integrated area of IR peaks at 1454 and 1545 cm⁻¹ after pyridine adsorption.

均比 ZSM-5N 沸石多, 与 NH₃-TPD 结果相符. 这表明沸石尺寸减到纳米级时, 沸石表面强酸中心数目大大增加. 另外, 通过 DMPy 吸附态的 FT-IR 谱可测得 B 酸活性位对于大分子的可接近性 (ACI)^[22], 结果见表 2. 结果显示, 423 K 时 ZSM-5(1) 和 ZSM-5(2) 的 ACI 分别为 0.38 和 0.60, 而 ZSM-5N 沸石的仅为 0.05, 可见, ZSM-5(1) 和 ZSM-5(2) 的可接近 B 酸量分别是 ZSM-5N 的 7.4 倍和 12.7 倍. 结果表明纳米 ZSM-5 沸石上大量的酸性位暴露在外表面或孔口, 对于具有较大动力学直径的 DMPy (0.67 nm) 仍具有很好的可接近性.

2.3 ZSM-5 沸石上芳烃苄基化催化反应

2.3.1 不同沸石催化剂的苄基化催化活性

图 4 为 ZSM-5(1)、ZSM-5(2) 和 ZSM-5N 催化剂上甲苯苄基化反应活性. 可以看出, 随着反应时间的增加, ZSM-5N 样品上苄基氯转化率增加非常

缓慢, 而纳米 ZSM-5 沸石上苄基氯转化率迅速增加. 于 363 K 反应 10 h 后, ZSM-5N 的苄基氯转化率仅为 27%, 而 ZSM-5(1) 和 ZSM-5(2) 沸石上的分别可达 90% 和 98%. 另外, 在反应产物中只检测到一苄基甲苯, 其中 *p*-苄基甲苯选择性达到了 92.6%, *o*-苄基甲苯选择性为 7.4%. 同时发现, 在实验条件下, 苄基氯转化率随反应时间的变化满足准一级动力学方程即: $\ln(1/(1-x)) = k_a(t-t_0)$. 式中 k_a 为一阶反应速率常数, x 为苄基氯的转化率, t 为反应时间, t_0 为达到平衡反应温度时所需的诱导期时间, 在苄基氯转化范围内, $\ln(1/(1-x))$ 对 t 作图为一一直线, 斜率即为 k_a 值. 由此可知, ZSM-5N 沸石上的反应速率常数 $k_a(N)$ 为 $5.2 \times 10^{-4} \text{ min}^{-1}$, 而 ZSM-5(1) 和 ZSM-5(2) 沸石上的速率常数 $k_a(1)$ 和 $k_a(2)$ 分别为 35.6×10^{-4} 和 $64.6 \times 10^{-4} \text{ min}^{-1}$, 分别是 $k_a(N)$ 的约 7 倍和 13 倍. 各催化剂活性顺序为 ZSM-5(2) > ZSM-5(1) > ZSM-5N.

沸石催化剂上甲苯苄基化反应过程为: 苄基氯被 B 酸质子化, 产生亲电试剂碳正离子中间体 (C₆H₅CH₂⁺), 该中间体进攻苯环, 形成苄基甲苯^[4,5]. B 酸在反应中起重要作用, 同时 L 酸的协同作用可有效提高其催化活性^[23,24]. ZSM-5N 沸石催化活性较低, 主要是由于它仅具有单一的微孔结构, 其孔口尺寸小于反应分子的动力学直径, 因而后者很难进入微孔孔道与活性位相互作用, 从而导致仅孔口和有限的外表面上的少量酸性位发挥催化作用. 而 ZSM-5(1) 和 ZSM-5(2) 沸石为纳米颗粒, 外比表面积和 B 酸可接近量显著增加, 且 L 酸量也是 ZSM-5N 沸石的 3 倍以上, 因此, B 酸和 L 酸的协同作用也提高了沸石的催化活性. 同时, 由于该类烷

图 4 ZSM-5 沸石在甲苯与苄基氯反应中的催化活性

Fig. 4. Catalytic activity of ZSM-5 samples in the benzylation of toluene by benzyl chloride (BC). Reaction conditions: catalyst 0.15 g, toluene/benzyl chloride molar ratio = 55, reaction temperature = 363 K (1) ZSM-5N; (2) ZSM-5(1); (3) ZSM-5(2).

基化反应主要发生在强酸中心位, 因此, 强酸中心数的增多也可进一步促进甲苯的苯基化反应. ZSM-5(2) 沸石较 ZSM-5(1) 具有更高的催化活性, 主要是由于前者可接近的酸中心数更高所致.

该反应的产物几乎全部为苯基甲苯, 而没有二苯基甲苯产生. 其原因可能为该反应条件下, 甲苯与苯基氯的摩尔比为 55:1, 大量的甲苯吸附在催化剂表面, 苯基氯高度分散, 不利于苯基甲苯与苯基氯的连续反应生成二苯基甲苯^[25].

2.3.2 温度对沸石样品催化性能的影响

不同温度下 ZSM-5(1) 沸石上苯基氯转化率见图 5. 由图可见, 当温度由 353 K 增至 373 K 时, 反应 10 h 后苯基氯转化率由 47% 逐渐提高到 97%. 353 K 时速率常数 k_a 为 $10.3 \times 10^{-4} \text{ min}^{-1}$, 363 K 时增至 $35.6 \times 10^{-4} \text{ min}^{-1}$, 增加了 2.5 倍; 至 373 K 时 k_a 为 363 K 时的 2.5 倍. 由图 6 所示的 Arrhenius 线性图可算得该反应在 ZSM-5(1) 沸石上的表观活化

图 5 温度对甲苯与苯基氯反应的影响

Fig. 5. Effect of temperature in the benzylation of toluene by benzyl chloride over ZSM-5(1). Reaction conditions: catalyst 0.15 g, toluene/benzyl chloride molar ratio = 55. (1) 353 K; (2) 363 K; (3) 373 K.

图 6 ZSM-5(1) 沸石上甲苯与苯基氯反应的 Arrhenius 线性图

Fig. 6. Arrhenius plot for the benzylation of toluene over ZSM-5(1).

能 E_a 为 121.4 kJ/mol.

2.3.3 不同芳烃化合物的苯基化反应

将纳米 ZSM-5(1) 沸石用于苯和 1,3,5-三甲苯与苯基氯的反应, 反应温度为 363 K, 其它同前. 结果显示, 在该反应条件下, 苯和 1,3,5-三甲苯的速率常数分别为 2.8×10^{-4} 和 $48.3 \times 10^{-4} \text{ min}^{-1}$, 催化活性顺序为 1,3,5-三甲苯 > 甲苯 > 苯, 与经典傅-克烷基化反应机理相符, 给电子取代基团的引入使苯基氯的反应速率提高. 这说明纳米 ZSM-5(1) 沸石在该类反应中克服了空间位阻的影响, 对于 1,3,5-三甲苯的苯基化反应仍具有较高的催化活性, 其转化率可达 94%.

2.4 催化剂的重复使用性

在催化剂用量 0.15 g、甲苯与苯基氯初始摩尔比 55:1、363 K 反应 10 h 的条件下, 考察了纳米 ZSM-5(1) 沸石的重复使用性. 催化剂使用后, 通过过滤、洗涤、干燥、焙烧进行再生. 结果表明, 第一次使用时, 苯基氯转化率为 90.0%, 经再生两次重复使用时, 苯基氯转化率分别略降为 88.2% 和 86.5%, 重复使用性较好.

3 结论

采用沸石微晶有机硅烷化法合成了纳米团簇 ZSM-5 分子筛. 结果表明, 在纳米沸石晶粒表面形成了较多的结构缺陷, 有效地增加了其表面酸中心的强度和外表面积, 从而提高了酸活性位的可接近性. 与普通 ZSM-5 沸石相比, 纳米团簇 ZSM-5 沸石减少了空间位阻效应, 对于较大分子 1,3,5-三甲苯的苯基化反应具有良好的催化活性和再生性. 可见, 纳米晶粒沸石在有机大分子催化反应中具有良好的应用前景.

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英 译 文

English Text

The benzylation of aromatics is an important class of acid reactions for the synthesis of many industrially important compounds used in the pharmaceutical, fragrances, dye, and agrochemical industries [1]. Traditionally, these reactions are catalyzed by liquid acid catalysts, such as FeCl_3 , AlCl_3 , BF_3 , HF, and H_2SO_4 [2,3]. However, these catalysts present many problems, such as corrosion, high toxicity, and difficulties in separation, post-handling, and catalyst recovery. Therefore, it is desirable to replace these liquid catalysts by solid catalysts that are reusable and easily separated from the

reactants. Acidic zeolites, such as H-ZSM-5, HY, and H β , have generated a lot of interest due to their strong acidity, shape selectivity, and thermal stability, but previous studies indicated that these zeolites have poor activity for the benzylation reaction because of poor accessibility and diffusion limitation resulting from their microporous networks [4,5].

The discovery of ordered mesoporous silica materials with pore sizes in the range of 2.0–30.0 nm, such as MCM-41 and SBA-15, was of considerable interest for the heterogeneous catalysis of many organic reactions [6–10]. Various approaches have been reported to enhance the catalytic activity of the mesoporous materials. For instance, other phases (Fe, Al, Ga or Cr as metal oxides or chlorides) have been introduced into the framework of the mesoporous silica materials or are supported in their channels. However, these ordered mesoporous materials exhibit poor hydrothermal stability and weak acidity compared with zeolites because of the amorphous walls of the mesoporous materials. Therefore, the mesoporous materials are not practical as heterogeneous catalysts at present. Another type of porous materials, hierarchical zeolites, have exhibited excellent catalytic performance in many reactions with large molecules because they have good stability and strong acidity like conventional zeolites, and also good mass transfer [11–16]. Besides these, nanoscale zeolites have much larger external surface areas, shorter diffusion path lengths, and more accessible active sites than conventional zeolites, and therefore they have shown good catalytic performance for reactions with large molecules [17–20].

In the present work, we prepared nanoscale ZSM-5 zeolite from seeds functionalized with an organosilane using *N*-[3-(Trimethoxysilyl)propyl]-*N'*-(4-vinylbenzyl) as the silylating agent. The catalytic activity of the nanoscale ZSM-5 zeolite in the benzylation reaction of aromatic hydrocarbon was evaluated, and the effects of pore structure properties and acidity are discussed.

1 Experimental

1.1 Zeolite preparation

The samples were synthesized from seeds functionalized with an organosilane according to reference [21]. The molar composition of the synthesis gel was $\text{Al}_2\text{O}_3\cdot 60\text{SiO}_2\cdot 11.5\text{TPAOH}\cdot 1500\text{H}_2\text{O}$. Aluminium isopropoxide (AIP, analytical pure, Aldrich) and tetraethyl orthosilicate (TEOS, analytical pure, Aldrich) were used as aluminum and silicon sources, respectively. Tetrapropylammonium hydroxide (TPAOH, 40% H_2O , Alfa) was used as a structure directing template. In a typical synthesis, AIP, TEOS, TPAOH, and distilled water were mixed together and stirred at 363 K for 20 h in a three-necked flask attached to a condenser to get the

zeolite seeds. The zeolite seeds were functionalized with organosilane by reaction with *N*-[3-(Trimethoxysilyl)propyl]-*N'*-(4-vinylbenzyl) solution (Z-6032, 40% methanol, Dow Corning) at 363 K for 10 h. The added molar amounts of organosilane were 0.03 and 0.07 per mol TEOS. The resulting mixture was crystallized in a Teflon-lined stainless-steel autoclave at 453 K for 3 d. The product was thoroughly washed with distilled water and dried at 373 K overnight, and then calcined in air at 873 K for 5 h to remove organic molecules. The synthesized samples were ion exchanged three times with a 0.2 mol/L NH_4NO_3 solution under stirring at 353 K for 2 h and calcined in air at 823 K for 5 h to obtain the H form of the zeolites. The samples were denoted as ZSM-5(1) and ZSM-5(2) according to the added amounts of organosilane. The conventional ZSM-5 zeolite used as the reference sample was synthesized using the same molar composition and synthesis condition but without the organosilane (denoted ZSM-5N).

1.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with $\text{Cu } K_\alpha$ radiation. Pore structure properties were determined by nitrogen adsorption-desorption isotherms at 77 K on a Quantachrome NOVA 1200. The size and morphology of the synthesized samples were obtained by scanning electron microscopy (SEM, JEOL JSM-6700F instrument). NH_3 temperature-programmed reduction (NH_3 -TPD) of ZSM-5 samples was carried out on a Quantachrome Chembet-3000 chemisorption analyzer. IR spectra of adsorbed pyridine and adsorbed 2, 6-lutidine were collected with a Shimadzu IR Affinity-1 FT-IR spectrometer. The density of acid sites was obtained from the integrated area of characteristic absorption peaks.

1.3 Catalyst testing

The liquid phase benzylation of aromatic hydrocarbons with benzyl chloride (BC) was carried out in a 50 ml three-necked flask equipped with a reflux condenser. The catalysts were activated in air at 773 K for 5 h before the reaction. The molar ratio of aromatic hydrocarbon and BC was 55. In a typical run, aromatic hydrocarbon and 0.15 g catalyst were mixed in the flask and stirred for 30 min at reaction temperature. Then 0.5 ml of BC was added, and this moment was used as the initial reaction time. Liquid samples were withdrawn periodically and analyzed with a gas chromatograph equipped with a FID detector and a 60 m HP-5 capillary column.

2 Results and discussion

2.1 Crystalline morphology of the samples

The XRD patterns of the ZSM-5 zeolite samples are shown in Fig.1. ZSM-5N, ZSM-5(1), and ZSM-5(2) all exhibited the MFI crystalline structure. Lowering and widening of the diffraction peaks for the ZSM-5(1) and ZSM-5(2) samples, compared with reference ZSM-5N, were distinctly observed, which indicated the presence of nanometer-sized crystals. The crystal sizes of the samples calculated by the Scherrer equation were about 20 nm (Table 1). Figure 2 is a typical SEM image of the ZSM-5(1) sample, and showed that ZSM-5(1) consisted of particles of 400–500 nm aggregated from small grains of 20 nm. The morphology of ZSM-5(1) was very different from the conventional ZSM-5N crystals that were coffin-like. The pore structural properties of the ZSM-5 samples obtained from N_2 adsorption-desorption isotherms are shown in Table 1. The data indicated that samples ZSM-5(1) and ZSM-5(2) crystallized from the silanized seeds not only had the inherent microporous structure but new mesoporous structures of 2–3 nm were formed by the aggregating of nano-crystals. Moreover, nanoscale ZSM-5(1) and ZSM-5(2) possessed higher BET specific surface areas of 515 and 502 m^2/g , and external surface areas of 151 and 209 m^2/g , respectively. In comparison, the BET specific surface area and external surface area of ZSM-5N were 422 and 39 m^2/g , respectively.

2.2 Acidity study

The acidity of the ZSM-5 samples was determined by NH_3 -TPD (Fig. 3). The results are summarized in Table 2. Weak (400–573 K), moderate (573–673 K), and strong (673–873 K) acid sites were found on all three samples. Compared with ZSM-5N, the total acid sites and amount of strong acid sites of ZSM-5(1) or ZSM-5(2) were increased, and the ratio of strong acid sites to total acid sites was increased.

Py-IR and lutidine-IR were used to study the type and distribution of acid sites on the nano-ZSM-5 samples. The calculated results are listed in Table 2. The amounts of Brönsted acid sites on the surface of ZSM-5N, ZSM-5(1), and ZSM-5(2) were nearly the same, and were 70, 68, and 74 $\mu\text{mol/g}$, respectively. But the amounts of Lewis acid sites on nanoscale ZSM-5(1) and ZSM-5(2) were three times more than that on the conventional ZSM-5N. This was probably because of abundant defect sites on the external surface and extra-framework Al species in the nanoscale zeolites. The infrared spectra of pyridine absorbed at different temperatures showed that the amounts of strong Brönsted and Lewis acid sites on nanoscale ZSM-5(1) and ZSM-5(2) were more than that on ZSM-5N, which was consistent with the NH_3 -TPD results. The accessibility index (ACI) [22] was

derived from the infrared spectra of absorbed 2,6-lutidine with 0.67 nm kinetic diameter. As shown in Table 2, the ACI for 2,6-lutidine over ZSM-5N, ZSM-5(1), and ZSM-5(2) samples were 0.05, 0.38, and 0.60, respectively, which were proportional to the external surface areas of the zeolites. Therefore the enhanced accessibility to 2,6-lutidine on the nanoscale ZSM-5 zeolites was due to a large number of acid sites exposed on the external surface or pore mouths.

2.3 Catalytic activity of the ZSM-5 samples

2.3.1 Catalytic activity of different ZSM-5 zeolite

The conversion of BC in the benzylation of toluene over the ZSM-5 catalysts is shown in Fig. 4. The catalytic activities of the nanoscale ZSM-5 catalysts increased rapidly with reaction time, but there was only a small increase with zeolite ZSM-5N under the same conditions. The reaction product was only benzyltoluene, and the isomeric selectivity for *p*-benzyltoluene and *o*-benzyltoluene were 92.6% and 7.4%, respectively. After a reaction time of 10 h at 363 K, the BC conversions over ZSM-5(1) and ZSM-5(2) reached 90% and 98%, respectively, whereas that over ZSM-5N was only 27%. The kinetic data for the benzylation of toluene in excess toluene over the ZSM-5 zeolite catalysts could be fitted well to a pseudo-first order rate law: $\ln(1/(1-x)) = k_a(t-t_0)$, where k_a is an apparent rate constant, x is fractional conversion of benzyl chloride, t is reaction time, and t_0 is the induction period corresponding to the time required to reach the reaction temperature. A plot of $\ln(1/(1-x))$ versus $(t-t_0)$ gave a linear relation over a range of benzyl chloride conversion. The apparent rate constant k_a of ZSM-5N was $5.2 \times 10^{-4} \text{ min}^{-1}$ at 363 K, while those of ZSM-5(1) and ZSM-5(2) were 35.6×10^{-4} and $64.6 \times 10^{-4} \text{ min}^{-1}$, respectively, which were ca. 7 times and 13 times higher than that of ZSM-5N, respectively. The order of activity of the samples was ZSM-5(2) > ZSM-5(1) > ZSM-5N, which was consistent with the external surface areas of the catalysts.

The benzylation of toluene over a zeolite is a typical acid catalyzed reaction. An accepted reaction mechanism is that Brönsted acid sites on the surface of the zeolite polarize the benzyl chloride to form an electrophilic carbocation ($\text{C}_6\text{H}_5\text{CH}_2^+$). The electrophilic species attacks the benzene ring resulting in the formation of benzyltoluene [4,5]. Brönsted acid sites play a key role in the benzylation reaction. Lewis acid sites can also accelerate the catalytic reaction [23, 24]. The poorer catalytic activity of ZSM-5N may be that there was only the small microporous structure of the zeolite which limit the accessibility of reactant molecules to the acid active sites and the diffusion of product molecules from the inner micropores to the external surface. The higher activities of nanoscale ZSM-5(1) and ZSM-5(2) can possibly be as-

cribed to the large external surface areas resulting in more accessibility to the Brönsted acid sites and Lewis acid sites in the nanoscale zeolites. Moreover, the existence of more strong acid sites on the surface of nanoscale ZSM-5 is beneficial to the benzylation reaction, so the catalytic activity over the nanoscale ZSM-5 was much higher than that over the conventional ZSM-5.

In addition, no dibenzyltoluene was detected in the reaction, that is, the product was only benzyltoluene. This result is associated with the high dilution of BC resulting in the existence of an excess of toluene on the catalyst surface, which decreased the further reaction of benzyltoluene and BC [25].

2.3.2 Influence of reaction temperature

The effect of temperature on the reaction rate was investigated by conducting the reaction at 353, 363, and 373 K, respectively. As shown in Fig. 5, the catalytic activity of the catalyst gradually increased with the reaction temperature. The conversion of BC increased from 47% to 97% after 10 h of the reaction time, when the temperature was increased from 353 to 373 K. The apparent rate constants k_a are $10.3 \times 10^{-4} \text{ min}^{-1}$ at 353 K and $35.6 \times 10^{-4} \text{ min}^{-1}$ at 363 K, respectively. The difference is nearly 3.5 times. Upon increasing the reaction temperature up to 373 K, k_a is $91.9 \times 10^{-4} \text{ min}^{-1}$, which is 2.5 times higher than that at 363 K. An Arrhenius plot of the first order rate constants at different temperatures (Fig. 6) gave the apparent activation energy E_a for ZSM-5(1) as 121.4 kJ/mol.

2.3.3 Benzylation of various substituted aromatic compounds

The benzylation of benzene, toluene, and 1,3,5-trimethylbenzene with benzyl chloride over the nanoscale ZSM-5(1) catalyst was conducted at 363 K for 10 h with a 55:1 ratio of aromatic hydrocarbon to BC and 0.15 g catalyst. The apparent rate constants k_a for the benzylation of benzene and 1,3,5-trimethylbenzene were 2.8×10^{-4} and $48.3 \times 10^{-4} \text{ min}^{-1}$ at 363 K, respectively. Together with the results above, this gave the trend for the benzylation of benzene, toluene, and 1,3,5-trimethylbenzene as 1,3,5-trimethylbenzene > toluene > benzene, which conformed to the classical alkylation mechanism of the Friedel-Crafts reaction, where the benzylation rate of the aromatic hydrocarbon is enhanced when electron donating groups are introduced in the aromatic rings. The results indicated that diffusional limitation for the large reactant was eliminated in the nanoscale zeolite, and as a result, the conversion of BC reached 94% even with 1,3,5-trimethylbenzene.

2.4 Recycling of the catalyst

In order to investigate the reusability of the nanoscale ZSM-5(1) zeolite, it was recycled and reused at the same reaction conditions. The regeneration of the catalyst was achieved by filtration, washing with acetone, drying at 363 K, and calcination at 773 K for 8 h in air. The results showed that there was only a very small change in the BC conversion after three recycles. For the fresh catalyst, the conversion of BC was 90.0%, which became 88.2% and 86.5% for the second and third recycles, respectively. It was concluded that the nanoscale ZSM-5(1) zeolite has high activity and stability and can be recycled in the benzylation reaction.

3 Conclusions

A ZSM-5 zeolite formed of nanoclusters was synthesized from seeds functionalized with organosilane. The ultrasmall

nanocrystals have greatly enhanced external surface areas. Compared with the conventional ZSM-5 zeolite, there are more Lewis acid sites and stronger acid sites on the nanoscale ZSM-5, and their amounts increased with increasing external surface area. The large external surface area and more pore mouths in nanoscale ZSM-5 improved the accessibility to acid sites of large molecules. In the benzylation of aromatics by benzyl chloride, the nanoscale ZSM-5 zeolite gave a much higher activity than ZSM-5 due to the decrease of diffusion limitation for large molecules, as well as improved acidity resulting from the small crystal size. The zeolite catalyst can be used repeatedly and retained its catalytic activity in the benzylation reaction. These results indicated that nanoscale ZSM-5 has potential applications in reactions with large molecules.

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