高负载量 $\text{LaMnO}_x/\text{SBA-15}$ 的制备及其催化甲苯燃烧性能

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摘要: 采用逐层负载-孔道内氨/水蒸气原位羟化法制备了高负载量的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂, 并采用 X 射线衍射、 N_2 吸附-脱附和程序升温还原等技术对催化剂进行了表征, 考察了其催化甲苯燃烧的性能. 结果表明, 孔道内氨/水蒸气原位羟化提高了 LaMnO_x 活性物种在 SBA-15 孔道内的分散度和还原性, 显著改善了高负载量的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂的活性. 在空速 5000 h^{-1} 的条件下, 温度升至 205°C 时甲苯转化率即可达 50%, 较之普通浸渍法制得的催化剂上甲苯达到该转化率所需温度降低了约 105°C . 实验得到 $\text{LaMnO}_x/\text{SBA-15}$ 的适宜原位羟化处理温度为 60°C , 处理时间 40 min.

关键词: 高负载量; 镧; 锰; 复合氧化物; SBA-15; 原位羟化; 催化燃烧; 甲苯

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Preparation of Highly Loaded $\text{LaMnO}_x/\text{SBA-15}$ Catalyst and Its Toluene Combustion Performance

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Abstract: A highly loaded $\text{LaMnO}_x/\text{SBA-15}$ catalyst (60%) was prepared by step coating NH_3 /water vapor-induced internal hydrolysis (VIH) and characterized by X-ray diffraction, N_2 adsorption-desorption, and temperature-programmed reduction (H_2 -TPR). Its catalytic performance for toluene combustion was also evaluated. The results showed that the VIH process clearly improved the activity of the $\text{LaMnO}_x/\text{SBA-15}$ catalyst. Using a toluene concentration of 0.86% and a GHSV of 5000 h^{-1} , a 50% toluene conversion was obtained at 205°C for the $\text{LaMnO}_x/\text{SBA-15}$ sample prepared by the VIH process. This temperature was 105°C lower than that for the sample prepared by conventional impregnation. N_2 adsorption-desorption and H_2 -TPR revealed that the VIH process improved the distribution of the LaMnO_x active phase in the pores of SBA-15 and improved its reduction properties. The optimal VIH conditions were a temperature of 60°C and a reaction time of 40 min.

Key words: highly loaded; lanthanum; manganese; composite oxide; SBA-15; vapor-induced internal hydrolysis; catalytic combustion; toluene

为了保护大气环境, 挥发性有机物 (VOCs) 的消除已经成为当前环境催化的热点问题. 作为一种彻底高效的方法, 催化燃烧技术备受关注, 而以过渡金属复合氧化物为基础活性物种来制备高性能的 VOCs 燃烧催化剂, 是近年来催化燃烧的重点研究内容之一^[1~3]. 金属氧化物催化剂因比表面积较小而限制了其催化活性的提高, 常用的解决方案是将这些

金属氧化物负载到多孔材料表面, 得到负载型金属氧化物催化剂^[4,5], 因此这些催化剂性能还受制备方法、前驱体特别是载体性质的影响. 鉴于高比表面积材料可极大提高金属氧化物的分散度, 而孔道较大的材料则有利于具有特殊配位结构复合氧化物活性物种的生成^[6], 因此具备介孔孔道和大比表面积的 SBA-15 材料成为一种非常有应用前景的载体.

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Han 等^[7]采用普通液相浸渍法制备了纳米 $\text{MnO}_x/\text{SBA-15}$ 催化剂, 考察了其催化 CO 氧化的性能. Laugel 等^[8]则采取二相法分别制备了 $\text{Co}_3\text{O}_4/\text{SBA-15}$ 和 $\text{Mn}_3\text{O}_4/\text{SBA-15}$ 催化剂, 考察了其催化 CH_4 氧化的性能. Orlov 等^[9]和 Tsoncheva 等^[10]对 SBA-15 进行改性, 分别实现了 Mn 或 Co 氧化物的负载, 取得了较好的结果. Deng 等^[11]采取原位合成法制备了 $\text{LaCoO}_3/\text{SBA-15}$ 催化剂, 实现了 LaCoO_3 钙钛矿型氧化物的高度分散, 取得了较好的结果.

上述研究中所用的氧化物负载量一般都不太高, 而有关高负载量氧化物催化剂的报道则相对较低. Yi 等^[12]采取微波辅助合成法制备了负载量为 60% 的纳米型 $\text{LaCoO}_3/\text{SBA-15}$ 催化剂, 并且没有引起明显的孔道堵塞. 除此之外, Krishnan 等^[13]采用氨/水蒸气孔道内原位诱导羟化方法 (VIH), 得到了负载量为 60% 的 $\text{ZrO}_2/\text{SBA-15}$, 并避免了催化剂的孔道堵塞. 该方法简便易行, 因此本文采用该方法来制备高负载量的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂, 并以甲苯催化燃烧为探针反应, 考察其催化燃烧性能.

1 实验部分

1.1 催化剂的制备

SBA-15 购自上海卓悦化工科技有限公司. $\text{LaMnO}_x/\text{SBA-15}$ 按照文献^[13]的方法制备. 首先将一定量的 $\text{Mn}(\text{NO}_3)_2$ (AR, 上海恒信化学试剂有限公司) 和 $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ 前驱体 (AR, 上海跃泾化工有限公司) 在室温下通过真空浸渍负载到 SBA-15 孔道内, 然后在真空干燥箱内于 60°C 处理 12 h. 为了改善其分散度, 采取逐层负载的方式来达到目标负载量. 将干燥后的样品装在称量瓶内放入含有聚四氟乙烯内衬的不锈钢反应釜, 釜内预置一定量的氨水. 将反应釜密闭, 加热到预定温度并维持一段时间, 取出样品干燥, 于 550°C 焙烧 4 h, 获得目标催化剂 $\text{LaMnO}_x/\text{SBA-15}(y)$, y 为负载次数, 整个过程中样品和氨水不直接接触. 同时为了对比, 同法制备了 $\text{MnO}_x/\text{SBA-15}(y)$, 并采用普通浸渍法制备了 $\text{LaMnO}_x/\text{SBA-15}(\text{im})$.

1.2 催化剂的表征

催化剂样品晶相采用日本岛津公司 ARL SCINTAG X'TRA 型 X 射线粉末衍射 (XRD) 仪分析. Ni 滤波, $\text{Cu K}\alpha$ 辐射源, 管电压 45 kV, 管电流 40 mA,

扫描范围 $2\theta=0.5^\circ\sim60^\circ$, 步长 $1.8^\circ/\text{min}$.

样品比表面积和孔分布等采用低温 (-196°C) N_2 吸附-脱附法在 Micromeritics ASAP 2020 型物理吸附仪上测定, 比表面积用 BET 方程计算, 孔体积和孔分布用 BJH 法计算. 测定前, 样品先在 350°C 预处理 4 h.

程序升温还原 (H_2 -TPR) 在 Micromeritics Autochem 2910 型化学吸附仪上进行. 样品先在 He 气中于 200°C 预处理 2 h, 然后切换到 5% H_2 -95% N_2 混合气并由 50°C 升温至 800°C , 气体流量 20 ml/min, 升温速率为 $10^\circ\text{C}/\text{min}$, TCD 检测耗氢量.

1.3 催化剂的评价

甲苯催化燃烧反应在常压连续流动气固微型反应装置上进行, 反应管为 $11\text{ mm} \times 350\text{ mm}$ 的石英玻璃管, 等温区长约 120 mm, 样品装填量为 0.2 g 催化剂 + 0.18 g 石英砂. 甲苯气体发生器置于冰水浴中保持 0°C , 调节两路气流量以控制反应气中甲苯浓度和空速分别为 0.86% 和 5000 h^{-1} . 反应尾气采用气相色谱 (Agilent 6890N) 在线分析, Porapak Q 填充柱, FID 检测器.

2 结果与讨论

2.1 催化剂的结构性质

图 1 是通过不同次数负载达到目标负载量, 然后采用氨/水蒸气孔道内原位诱导羟化法制得的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂的 N_2 吸附-脱附等温线和孔径分布. 由图可见, 所有样品均表现出 IV 型特征吸附等温线, 并且都具有 H1 型迟滞环. 这说明在负载了 60% 的 LaMnO_x 后, 样品仍保持了 SBA-15 的介孔结构. $\text{LaMnO}_x/\text{SBA-15}$ 的回滞环在较高的相对压力 (0.6~0.8) 下出现, 表明其孔道中发生了快速毛细凝聚, 而回滞环的扁平化和移动现象及其程度表明介孔孔径范围和孔径分布发生了变化, 意味着 SBA-15 材料孔结构有序性和规整性有所降低. 通过 1 次和 6 次逐层负载达到目标负载量的 $\text{LaMnO}_x/\text{SBA-15}(1)$ 和 $\text{LaMnO}_x/\text{SBA-15}(6)$ 催化剂的回滞环较为接近, 而通过 3 次负载所得 $\text{LaMnO}_x/\text{SBA-15}(3)$ 催化剂的回滞环则向着更低压力方向移动, 并出现在 0.5~0.7 之间, 意味着其孔径减小.

表 1 列出了各 $\text{LaMnO}_x/\text{SBA-15}$ 样品的比表面积、孔体积和平均孔径. 可以看出, 负载 LaMnO_x 活性

图 1 各 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂样品的 N_2 吸附-脱附等温线和孔径分布

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of different $\text{LaMnO}_x/\text{SBA-15}$ catalysts.

组分后, 催化剂的比表面积、孔体积和孔径较 SBA-15 材料都有所减小. 还可以看到, 在 $\text{LaMnO}_x/\text{SBA-15}$ 中, 通过 3 次负载和 VIH 处理所得的催化剂比表面积最大, 但是孔径却最小, 只有 6.37 nm, 这可能从某种程度上表明, LaMnO_x 活性组分以更为均匀的方式进入到 SBA-15 的孔道中.

图 2 是 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂的 XRD 谱. 可以看出, 所用 SBA-15 载体在 $2\theta = 0.5^\circ \sim 2^\circ$ 范围内出现 3 个衍射峰, 分别对应于 SBA-15 的 (100), (110) 以及 (200) 晶面. 当负载 LaMnO_x 后, 各特征峰强度均明显

图 2 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂样品的 XRD 谱

Fig. 2. XRD patterns of $\text{LaMnO}_x/\text{SBA-15}$ catalysts. (1) $\text{LaMnO}_x/\text{SBA-15(1)}$; (2) $\text{LaMnO}_x/\text{SBA-15(3)}$; (3) $\text{LaMnO}_x/\text{SBA-15(6)}$; (4) $\text{MnO}_x/\text{SBA-15(3)}$.

减弱, 表明 SBA-15 载体长程有序度有所下降, 或者说可能已经破坏了其部分晶相结构. 但是另一方面, 各 $\text{LaMnO}_x/\text{SBA-15}$ 以及 $\text{MnO}_x/\text{SBA-15}$ 催化剂上都没有出现 LaMnO_x 和 MnO_x 氧化物的特征峰, 可能意味着这些物种在 SBA-15 上高度分散, 或在 500°C 下没有形成明显的晶体结构.

图 3 是 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂样品的 H_2 -TPR 谱. 可以发现, $\text{MnO}_x/\text{SBA-15}$ 催化剂分别在 350 和 500°C 左右出现了一个还原峰, 一般可归属为 $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$ 和 $\text{Mn}^{2+} \rightarrow \text{Mn}^0$ 的分步还原^[14]. 而所有的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂只在 520°C 左右出现还原峰, 而且随着逐层负载和 VIH 处理次数的增加, 该还原峰面积显著提高. 还原峰位置向高温方向移动意味着尽管不能从 XRD 结果确定有 LaMnO_x 钙钛矿晶相生成, 但 La 的加入无疑与 MnO_x 产生了作用, 使其变得更稳定. 而还原峰面积的显著提高则表明, 逐层负载和 VIH 处理手段可使这些 LaMnO_x 活性物种在高负载量下的分布更为均匀, 暴露出更多的外表面, 使得更多的活性物种可在短时间内被还原.

表 1 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂样品的比表面积和孔性质数据

Table 1 Physical properties of the $\text{LaMnO}_x/\text{SBA-15}$ catalysts

Sample*	BET surface area (m^2/g)			Pore volume (cm^3/g)	Average pore diameter (nm)
	Total	External	Micropore		
SBA-15	734.21	467.96	266.25	0.69	8.03
$\text{LaMnO}_x/\text{SBA-15(1)}$	248.41	211.73	36.68	0.46	7.41
$\text{LaMnO}_x/\text{SBA-15(3)}$	298.56	273.99	24.56	0.48	6.37
$\text{LaMnO}_x/\text{SBA-15(6)}$	255.92	219.45	36.47	0.49	7.78

*The numbers in the brackets are coating times.

图3 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂样品的 H_2 -TPR 谱

Fig. 3. H_2 -TPR profiles of $\text{LaMnO}_x/\text{SBA-15}$ catalysts. (1) $\text{LaMnO}_x/\text{SBA-15(1)}$; (2) $\text{LaMnO}_x/\text{SBA-15(3)}$; (3) $\text{LaMnO}_x/\text{SBA-15(6)}$; (4) $\text{MnO}_x/\text{SBA-15(3)}$.

2.2 $\text{LaMnO}_x/\text{SBA-15}$ 催化甲苯燃烧的性能

图4是采用普通浸渍法制备且未经VIH处理的不同 LaMnO_x 含量的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂催化甲苯燃烧的活性。可以发现, LaMnO_x 负载量的增加在一定程度上有利于提高 $\text{LaMnO}_x/\text{SBA-15}$ 的活性,甲苯的点火曲线向低温方向移动,但当 LaMnO_x 负载量达40%以上时,其变化就不再明显,表明此时各 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂的活性比较接近,增加的 LaMnO_x 未能再提高活性。这可能是过高的负载量造成了催化剂孔道的堵塞,使得增加的活性物种不能很好地起到催化作用,同时这也可能影响反应物和产物分子在催化剂孔道内的扩散速度,从整体上降低了负载量提高的作用。

图4 普通浸渍法制备的不同 LaMnO_x 含量 $\text{LaMnO}_x/\text{SBA-15}$ 催化甲苯燃烧的活性

Fig. 4. Catalytic performance of $\text{LaMnO}_x/\text{SBA-15}$ for toluene combustion with different amounts of LaMnO_x that were prepared by impregnation method. GHSV = 5000 h^{-1} , the same below.

图5是采用氨/水蒸气孔道内原位诱导羟化处理方法制备的负载量为60%的 $\text{LaMnO}_x/\text{SBA-15}$ 催化甲苯燃烧反应结果。可以发现,VIH处理显著提高了 $\text{LaMnO}_x/\text{SBA-15}$ 的活性,而其中又以 $\text{LaMnO}_x/\text{SBA-15(3)}$ 活性最高,甲苯的 T_{50} (即甲苯转化率达到50%时的温度)从普通浸渍法制备的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂上的 310°C 降至 205°C 。这不仅表明提高 LaMnO_x 负载量有利于提高 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂活性,更重要的是说明了VIH处理可以对催化剂的活性起到极为显著的促进作用。

图5 VIH处理制备的 $\text{LaMnO}_x/\text{SBA-15}$ 催化甲苯燃烧的活性

Fig. 5. Catalytic performance of $\text{LaMnO}_x/\text{SBA-15}$ for toluene combustion by $\text{NH}_3/\text{water vapor}$ -induced internal hydrolysis method.

还可以看出,VIH处理次数对催化剂活性也有重要影响,处理次数太少固然不利于 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂活性的提高,但处理次数太多不仅使操作过程变得复杂,也不利于催化剂的活性提高。结合催化剂的吸附等温曲线和孔分布结果可以看出,随着处理次数的增加,活性物种在 SBA-15 的孔道内分布更为均匀。但由于 SBA-15 水热稳定性不够高,而每一次VIH处理过程都不可避免地会和水接触,这样过于频繁的水处理可能引起 SBA-15 孔道结构的坍塌,使其比表面积降低,从而在总体上削弱了VIH处理的效果。总体而言,分3次处理达到目标负载量是比较合适的。

SBA-15 的孔道结构对水比较敏感,而在VIH处理过程中不可避免与水蒸气接触,从而影响 SBA-15 和 $\text{LaMnO}_x/\text{SBA-15}$ 的性质,图5中VIH处理次数对 $\text{LaMnO}_x/\text{SBA-15}$ 活性的影响也证明了这一点。因此,

需要通过实验进一步获得较为合适的操作条件(如温度和压力),以降低 VIH 处理对 $\text{LaMnO}_x/\text{SBA-15}$ 性能的影响。

图 6(a) 是不同温度 VIH 处理后的 $\text{LaMnO}_x/\text{SBA-15}$ 上甲苯燃烧活性结果。可以发现,随着处理温度的升高, $\text{LaMnO}_x/\text{SBA-15}$ 催化剂活性先增加后降低,并在 60°C 时达到最高。这是符合预期的。虽然在高温下氨/水蒸气的压力更高,分子运动也更为活跃,更加有利于 LaMnO_x 活性物种的分布,但与此同时,高温下水蒸气含量也必然随之升高,对 SBA-15 孔道的影响也就越明显,最终影响 VIH 处理的效果。这两方面的综合作用使得处理温度存在最佳值。除温度之外,处理时间也可能存在一个最佳值。图 6(b) 的结果表明,在 60°C 处理 40 min 最佳。

图 6 VIH 处理温度和处理时间对 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂活性的影响

Fig. 6. Influence of VIH temperature (a) and time (b) on the catalytic performance of $\text{LaMnO}_x/\text{SBA-15}$ catalysts.

3 结论

采用逐层负载-孔道内氨/水蒸气原位羟化法制备了高负载量的 $\text{LaMnO}_x/\text{SBA-15}$ 催化剂。较之普通浸渍法,这种方法可使得 LaMnO_x 活性物种更多地进入且更为均匀地分布于 SBA-15 孔道内部,从而大大

提高了 LaMnO_x 氧化物的比表面积和分散度,同时还改善了 LaMnO_x 氧化物的还原性能,最终提高了 LaMnO_x 氧化物催化剂催化甲苯燃烧的活性。该方法有望成为制备催化活性组分含量较高的负载型分子筛催化剂的一种好方法,在制备大比表面积非贵金属氧化物催化剂方面有着良好的应用价值。

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英 译 文

English Text

The reduction of volatile organic compounds (VOCs) has been a popular topic in environmental catalysis as the prevention of harmful VOCs entering the atmosphere is of interest. As a thorough and highly efficient technology, catalytic combustion has attracted much attention and it has been important in the preparation of highly active catalysts containing transient metal complex oxides as the basic active species [1–3]. The main shortcoming of metal oxides is their poor specific surface area, which reduces the activity increase in these catalysts. Therefore, many studies have fo-

cused on a solution to this problem and it has been a conventional route to load oxides into a porous material to obtain supported metal oxide catalysts [4,5]. Apart from the active oxide properties, the performance of supported catalysts is mainly influenced by the preparation method and the precursors but mostly by the support materials. With their high specific surface areas the supports can raise the dispersion of metal oxides and active oxides with special coordinate structures form more easily in the large pores of the supports [6]. Therefore, SBA-15 is considered to be a very promising support for its mesoporous structure and large specific surface area.

Han et al. [7] prepared a nanostructured $\text{MnO}_x/\text{SBA-15}$ catalyst for CO oxidation by impregnation. Laugel et al. [8] prepared $\text{Co}_3\text{O}_4/\text{SBA-15}$ and $\text{Mn}_3\text{O}_4/\text{SBA-15}$ using the binary-solvent method and studied its performance during CH_4 oxidation. Orlov et al. [9] and Tsoncheva et al. [10] loaded Mn and Co oxides onto SBA-15 using a modified method. Deng et al. [11] obtained a highly dispersed $\text{LaCoO}_3/\text{SBA-15}$ catalyst by in situ synthesis.

However, the loading content of the oxides was not very high in these studies and there are only a few reports concerning the increase of loading content. Yi et al. [12] prepared a 60% nanocrystalline $\text{LaCoO}_3/\text{SBA-15}$ catalyst by a microwave-assisted process and this process did not cause any obvious pore blocking. Krishnan et al. [13] reported an NH_3 /water vapor-induced internal hydrolysis (VIH) method for the post-synthesis coating of 60% zirconia in the mesopore walls of SBA-15 and this prevented pore blocking in the catalysts. It seems that the method is a convenient and efficient way to prepare highly loaded oxide catalysts. We adopted the VIH method to produce a highly loaded $\text{LaMnO}_x/\text{SBA-15}$ catalyst and investigated its catalytic performance using toluene combustion as the probe reaction.

1 Experimental

1.1 Preparation of the catalysts

SBA-15 was purchased from Shanghai Zhuoyue Chemical Company. $\text{LaMnO}_x/\text{SBA-15}$ was prepared according to Ref. [13]. First, suitable amounts of $\text{Mn}(\text{NO}_3)_2$ (AR, Shanghai Hengxin Chemical Agents) and $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (AR, Shanghai Yuejing Chemical Agents) were added to the pores of SBA-15 by vacuum impregnation at room temperature. The mixture was then dried at 60 °C for 12 h in a vacuum drying oven. To further improve the dispersion of the active phase we obtained the target aimed for by step coating. The dry sample was then transferred to a weighing bottle and placed in a Teflon coated kettle with a suitable amount of aqueous ammonia. The kettle was then heated to a preset temperature and kept at that temperature for a specific

amount of time. The sample was then dried at 60 °C and calcined at 550 °C for 4 h to obtain the target catalyst. The sample was not in direct contact with the aqua ammonia. The catalysts were labeled as $\text{LaMnO}_x/\text{SBA-15}(\gamma)$ according to the coating times. We also prepared $\text{MnO}_x/\text{SBA-15}(\gamma)$ with the VIH method and $\text{LaMnO}_x/\text{SBA-15}(\text{im})$ with a conventional impregnation method to compare with $\text{LaMnO}_x/\text{SBA-15}(\gamma)$.

1.2 Characterization of the catalyst

X-ray diffraction (XRD) patterns of the $\text{LaMnO}_x/\text{SBA-15}(\gamma)$ catalysts were obtained using a Shimadzu ARL SCINTAG X'TRA diffractometer with $\text{Cu } K_\alpha$ radiation and with Ni filtration. Its other operating parameters were 45 kV and 40 mA with a scan speed of 1.8°/min in the range of $2\theta = 0.5^\circ\text{--}60^\circ$.

The specific surface area and pore size distribution were measured using low temperature (−196 °C) N_2 adsorption-desorption on a Micromeritics ASAP 2010 apparatus. The specific surface area was obtained using Brunauer-Emmett-Teller equations (BET). An estimate of the average diameter of the primary mesopores was derived from the Barrett-Joyner-Halenda formula (BJH). Before the experiment the samples were dehydrated at 350 °C for 4 h.

H_2 temperature-programmed reduction (H_2 -TPR) was recorded on a Micromeritics Autochem 2910 chemisorption apparatus. Before the experiment the sample was treated at 200 °C for 2 h in a He flow and then the flow was switched to 5% H_2 -95% N_2 and heated from 50 °C to 800 °C. The flow velocity was 20 ml/min and the heating rate was 10 °C/min.

1.3 Catalytic tests

The catalytic tests were carried out in an atmospheric continuous-flowed gas-solid microreactor. The reaction tube was a 350 mm × 11 mm quartz glass tube with an isothermal zone 120 mm long. The loading of catalysts was 0.2 g catalyst diluted with 1.8 g of quartz sand. The toluene bubbler was kept at 0 °C in an ice-water bath. The GHSV was 5000 h^{-1} and the concentration of toluene was 0.86%. The outlet gas was analyzed online with an Agilent 6890N GC, Porapak Q column, and an FID detector.

2 Results and discussion

2.1 Catalyst characterization

Figure 1 shows the N_2 adsorption-desorption isotherms and the pore size distribution of the $\text{LaMnO}_x/\text{SBA-15}(\gamma)$ catalysts prepared by step-coating and VIH process, respectively. From Fig. 1(a) all the samples exhibit a type IV iso-

therm and a H1 type hysteresis loop. This indicates that the mesoporous structure of SBA-15 is retained after 60% LaMnO_x loading. The hysteresis loop of the $\text{LaMnO}_x/\text{SBA-15(y)}$ samples was presented at a high p/p_0 (0.6–0.8) and this indicated that fast capillary condensation occurred in the mesopores. Loop flattening and movement indicates a change in average pore diameter and in pore size distribution. All the results indicated an order reduction in the SBA-15 pore structure. The hysteresis loops of $\text{LaMnO}_x/\text{SBA-15(1)}$ and $\text{LaMnO}_x/\text{SBA-15(6)}$ are close to each other. The loop moved to the lower pressure attitude for the $\text{LaMnO}_x/\text{SBA-15(3)}$ and appeared at about p/p_0 0.5–0.7.

Table 1 gives the specific surface area and pore volume data for the $\text{LaMnO}_x/\text{SBA-15(y)}$ catalysts. The specific surface areas, pore volumes, and pore diameters of the samples were smaller than that of SBA-15 after the loading of LaMnO_x . Among all the $\text{LaMnO}_x/\text{SBA-15(y)}$ catalysts the specific surface area of $\text{LaMnO}_x/\text{SBA-15(3)}$ was the highest while its pore diameter was the smallest, i.e., 6.37 nm. It seems that the LaMnO_x active species entered the pores to a higher degree and scattered better on the pore walls of the SBA-15 support.

Figure 2 shows the XRD patterns of the $\text{LaMnO}_x/\text{SBA-15(y)}$ catalysts. Three peaks were present in the range of $2\theta = 0.5^\circ\text{--}2^\circ$ in the diffractogram of the SBA-15 support. These peaks correspond to the (100), (110), and (200) crystal faces. After LaMnO_x loading all the peak heights decreased and this shows that the loading influenced and destroyed a part of the SBA-15 support structure. However, none of the patterns showed characteristic LaMnO_x peaks. Additionally, the $\text{MnO}_x/\text{SBA-15}$ pattern did not show MnO_x peaks. These results might indicate a high degree of dispersion for these species or that these species do not form stable crystal structures after calcination at 500 °C.

Figure 3 shows H_2 -TPR profiles of the $\text{LaMnO}_x/\text{SBA-15(y)}$ catalysts. For $\text{MnO}_x/\text{SBA-15}$, two reduction peaks were present at 350 and 500 °C and these are believed to originate from the reduction of Mn^{4+} to Mn^{2+} and Mn^{2+} to Mn^0 [14]. For $\text{LaMnO}_x/\text{SBA-15(y)}$, this peak was present at around 520 °C and it increased in strength with an increase in step-coating and VIH time. This movement of the peak to a higher temperature means that La interacts with the MnO_x species and stabilizes the structure although it is still uncertain if a perovskite or another crystal structure is formed. The increase in peak intensity indicates that the step-coating and VIH methods can scatter the LaMnO_x species more uniformly in the pores of SBA-15 under highly loaded. Therefore, more species are exposed to the outer environment and can thus be reduced in a shorter amount of time.

2.2 Catalytic performance of $\text{LaMnO}_x/\text{SBA-15}$ for toluene combustion

Figure 4 shows the catalytic performance of the $\text{LaMnO}_x/\text{SBA-15(im)}$ that was prepared by conventional impregnation. The LaMnO_x content increase was helpful in increasing the activity of $\text{LaMnO}_x/\text{SBA-15}$ catalyst to some extent. With an increase in the loading content, the resultant curves initially moved to the low temperature region. However, when the loading content increased to above 40%, the curves changed very little indicating that the activities of the $\text{LaMnO}_x/\text{SBA-15}$ catalysts were close to each other and that the high LaMnO_x content did not result in higher activity. The reason for this might be that the large amount of LaMnO_x blocked up the pores of SBA-15 and this trapped the inner active species. Pore blocking also influenced the mass transfer efficiency of the reactant and this was counteracted by the increase in LaMnO_x content.

We then studied the catalytic performance of the 60% $\text{LaMnO}_x/\text{SBA-15(y)}$ that was modified by the VIH process and Fig. 5 shows the results. The VIH process clearly improved the activity of $\text{LaMnO}_x/\text{SBA-15}$. For the $\text{LaMnO}_x/\text{SBA-15(3)}$ sample that possessed the highest activity the T_{50} of toluene (the temperature where the toluene conversion reached 50%) was only 205 °C, which was 105 °C lower than that for the sample prepared by conventional impregnation. These results show that a suitable preparation method is needed to maximize the activity of the LaMnO_x species on SBA-15 and the VIH method can be used for this.

It also seems that the VIH process run times had an important influence on the activity of $\text{LaMnO}_x/\text{SBA-15}$. Too few run times were not enough to adequately scatter the LaMnO_x species while too many runs complicated the preparation process and might not always be favorable for activity increase. According to the isothermals and the pore size distribution characterization, the VIH runs number increase can let the more LaMnO_x species enter into the SBA-15 pores and the LaMnO_x species are scattered much better on the pore walls. However, the hydrothermal stability of SBA-15 is not very good and it is unavoidable to contact with H_2O vapor. Therefore, too many VIH run times would cause the collapse of the SBA-15 pore structure, the decrease of the catalyst surface area and the weakening of the effect of the VIH method. According to the experimental results, we conclude that three run times is optimal.

The pore structure of SBA-15 is sensitive to H_2O , which influences the properties of $\text{LaMnO}_x/\text{SBA-15(y)}$ clearly, as shown in Fig. 5. Therefore, suitable VIH operation conditions need to be determined to alleviate the negative influences. Apart from the number of run times, the temperature and processing time are considered to be important factors too.

Figure 6 shows the influence of VIH temperature and reaction time on the activity of $\text{LaMnO}_x/\text{SBA-15}$. The VIH temperature clearly has an influence (Fig. 6(a)). With an

increase in VIH temperature the LaMnO_x/SBA-15 activity increases initially and then decreases. The highest activity was at 60 °C. The optimal temperature was in line with our expectation. At high temperatures the pressure of NH₃/H₂O vapor is high and molecular movement is more active, which is good for the dispersion of the LaMnO_x species. However, the amount of H₂O vapor increases at higher temperatures and this influences the pore structure of SBA-15 more severely. The coexistence of both effects results in an optimal temperature. Similar to the effect of temperature an optimal time exists for the dispersion of the LaMnO_x species but this has little influence on the pore structure of SBA-15. Figure 6(b) shows that the optimal time was about 40 min at 60 °C.

3 Conclusions

Step-coating and NH₃/water vapor-induced internal hy-

drolysis was used to prepare a highly loaded LaMnO_x/SBA-15 catalyst. Compared with conventional impregnation this method results in more LaMnO_x species being incorporated into the SBA-15 pores and a more uniform distribution of the species is evident. Therefore, the specific surface area and dispersion of the LaMnO_x species increases greatly. This method improves the reduction property of the LaMnO_x species leading to a large increase in activity of the LaMnO_x oxide catalyst. The NH₃/water vapor-induced internal hydrolysis method is a very efficient way to prepare a zeolite supported catalyst containing a large amount of active phase. This method is potentially very useful for the preparation of non-noble metal oxide catalysts with high specific surface areas.

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