

### ZSM-5/MCM-41复合分子筛的合成与表征

张君涛<sup>1</sup>, 郝娜娜<sup>2</sup>, 王妮<sup>3</sup>

1. 西安石油大学 石油炼化工程技术研究中心, 陕西 西安 710065;
2. 上海新佑能源科技有限公司, 上海 201210;
3. 汉中市天然气投资发展有限公司, 陕西 汉中 723000

### Synthesis and characterization of ZSM-5/MCM-41 composite molecular sieves

ZHANG Jun-tao<sup>1</sup>, HAO Na-na<sup>2</sup>, WANG Ni<sup>3</sup>

1. Research Center of Petroleum Processing & Petrochemicals, Xi'an Shiyou University, Xi'an 710065, China;
2. Shanghai New-unity Energy Technology Co., LTD, Shanghai 201210, China;
3. Hanzhong Natural Gas Investment Development Co., LTD, Hanzhong 723000, China

- 摘要
- 参考文献
- 相关文章
- 点击分布统计
- 下载分布统计

全文: [PDF](#) (3454 KB) [HTML](#) (1 KB) 输出: [BibTeX](#) | [EndNote](#) (RIS) [背景资料](#)

**摘要** 以碱处理的ZSM-5浆液为硅铝源,通过水热自组装过程合成了介孔-微孔复合孔道结构的分子筛,并采用XRD、BET、HRTEM、Py-IR和水热处理等手段对合成分子筛进行了表征。结果表明,碱处理ZSM-5时的苛刻程度是影响复合分子筛合成的重要因素,适宜的碱处理条件为NaOH浓度1 mol/L、80℃时处理1 h。表征结果表明,复合分子筛具有规整互通的微孔-介孔梯级复合孔道结构,孔容、比表面积和平均孔径分别为0.63 mL/g,684 m<sup>2</sup>/g和3.76 nm,属典型的MCM-41结构;与MCM-41相比,复合分子筛的B酸(尤其是强B酸)酸量明显增强,水热稳定性显著提高。

**关键词:** 微孔-介孔复合分子筛 ZSM-5 MCM-41 水热合成

**Abstract:** ZSM-5/MCM-41 composite molecular sieves with multiple micro-mesoporous structure were hydrothermally synthesized via self-assembly by using the alkali-treated ZSM-5 seriflux as the source of silica and aluminum. The as-synthesized molecular sieves were characterized by XRD, N<sub>2</sub> adsorption, HRTEM, Py-IR, and hydrothermal treatment methods. The results showed that the crystallinity of the as-synthesized molecular sieves is dependent on the intensity of the alkali-treatment; the suitable alkali treatment conditions for ZSM-5 are 80℃ for 1 h with a NaOH concentration of 1 mol/L. The composite molecular sieves obtained exhibit a typical MCM-41 structure, with a hierarchical micro-mesoporous structure and large specific surface area. Compared with MCM-41, the ZSM-5/MCM-41 composite molecular sieves show higher quantity of Bronsted acid sites (especially strong ones) and higher hydrothermal stability.

**Key words:** micro-mesoporous composite molecular sieve ZSM-5 MCM-41 hydrothermal synthesis

收稿日期: 2013-02-25;

通讯作者: 张君涛(1971-),男,甘肃天水人,博士,副教授,主要从事炼油化工工艺及催化新材料研究,Email: zhangjt@xsysu.edu.cn。 E-mail: zhangjt@xsysu.edu.cn

引用本文:

张君涛,郝娜娜,王妮. ZSM-5/MCM-41复合分子筛的合成与表征[J]. 燃料化学学报, 2013, 41(10): 1268-1273.

ZHANG Jun-tao, HAO Na-na, WANG Ni. Synthesis and characterization of ZSM-5/MCM-41 composite molecular sieves[J]. J Fuel Chem Technol, 2013, 41(10): 1268-1273.

链接本文:

<http://rlhxzb.sxicc.ac.cn/CN/> 或 <http://rlhxzb.sxicc.ac.cn/CN/Y2013/V41/I10/1268>

#### 服务

- ▶ 把本文推荐给朋友
- ▶ 加入我的书架
- ▶ 加入引用管理器
- ▶ E-mail Alert
- ▶ RSS

#### 作者相关文章

- ▶ 张君涛
- ▶ 郝娜娜
- ▶ 王妮

- [2] SONG Chun-min, YAN Zi-feng. The new research progress of micro/mesoporous composite molecular sieves[J]. Journal of Molecular Catalysis (China), 2008, 22(3): 280-285.)
- [3] BECK J S, VARTULI J C, ROTH W J, LEONOWICZ M E, KRESGE C T, SCHMITT K D, CHU C T W, OLSON D H, SHEPPARD E W. A new family of mesoporous molecular sieve prepared with liquid crystal templates[J]. J Am Chem Soc, 1992, 114(27): 10834-10843.
- [4] BRANTON P J, HALL P G, SINQ K S W. Physisorption of nitrogen and oxygen by MCM-41, a model mesoporous adsorbent[J]. J Chem Soc, Chem Commun, 1993, (16): 1257-1258.
- [5] ROSALES HEMANDEZ M C, MENDIETA WEJEBE J E, VAZQUEZ ALCANTARA J I, MIRANDA RUVALCABA R, GARCIA SERRANO L A, TRUJILLO F J. Immobilization of cytochrome P-450 on MCM-41 with different silicon/aluminum ratios[J]. Micropor Mesopor Mater, 2005, 80(1/3): 25-31.
- [6] 张君涛, 张新年, 邱利民. 氨水介质中Al-MCM-41的合成与表征[J]. 西安石油大学学报(自然科学版), 2010, 25(2): 69-72.
- [7] ZHANG Jun-tao, ZHANG Xin-nian, QIU Li-min. Synthesis of mesoporous molecular sieve Al-MCM-41 in ammonia water and its characterization[J]. Journal of Xi'an Shiyou University (Natural Science Edition), 2010, 25(2): 69-72.)
- [8] KLOETSTRA K R, ZANDBERGEN H W, JANSEN J C, VAN BEKKUM H. Overgrowth of mesoporous MCM-41 on faujasite[J]. Micropor Mesopor Mater, 1996, 6(5/6): 287-293.
- [9] TRIANTAFYLLOIDIS K S, LAPPAS A A, VASALOSs I A, LIU Y, PINNAVAIA T J. Gas-oil cracking activity of hydrothermally stable aluminosilicate mesostructures (MSU-S) assembled from zeolite seeds: Effect of the type of framework structure and porosity[J]. Catal Today, 2006, 112(1/4): 33-36.
- [10] TRIANTAFYLLOIDIS K S, ILIOPoulos E F, ANTONAKOU E V, LAPPAS A A, WANG H, PINNAVAIA T J. Hydrothermally stable mesoporous aluminosilicates (MSU-S) assembled from zeolite seeds as catalysts for biomass pyrolysis[J]. Micropor Mesopor Mater, 2007, 99(1/2): 132-139.
- [11] VAN OERS C J, STEVENS W J J, BRUIJN E, MERTENS M, LEBEDEV O I, VAN TENDELOO G, MEYNEN V, COOL P. Formation of a combined micro and mesoporous material using zeolite Beta nanoparticles[J]. Micropor Mesopor Mater, 2009, 120(1/2): 29-34.
- [12] DI Y, YU Y, SUN Y Y, YANG X Y, LIN S, ZHANG M Y, LI S G, XIAO F S. Synthesis, characterization, and catalytic properties of stable mesoporous aluminosilicates assembled from preformed zeolite L precursors[J]. Micropor Mesopor Mater, 2003, 62(3): 221-228.
- [13] JI Y Y, WANG C Y, ZOU Y C, SONG J W, WANG J Y, LI F, XIAO F S. Design and synthesis of microporous and micro/mesoporous silica materials with excellent adsorption properties via self-assembly of silica species with tetraethyl ammonium in acidic aqueous media[J]. J Phys Chem C, 2008, 112(49): 19367-19371.
- [14] 郑均林, 张晔, 吴东, 孙予罕. MFI沸石前驱体和硅酸钠共组装制备水热稳定的管状介孔分子筛[J]. 化学学报, 2004, 62(14): 1357-1361.
- [15] ZHENG Jun-Lin, ZHANG Ye, WU Dong, SUN Yu-Han. Synthesis of hydrothermally stable mesoporous aluminosilicates with tubular morphology from MFI zeolitic precursors and sodium silicates[J]. Acta Chimica Sinica, 2004, 62(14): 1357-1361.)
- [16] ZHENG J L, ZHAI S R, WU D, SUN Y H.  $S^+X^-I^+$  route to mesostructured materials from fau and beta zeolite precursors: A comparative study of their assembly behaviors in extremely acidic media[J]. J Solid State Chem, 2005, 178(5): 1630-1636.
- [17] CHEN H Y, XI H X, CAI X Y, QIAN Y. Experimental and molecular simulation studies of a ZSM-5/MCM-41 micro-mesoporous molecular sieve[J]. Micropor Mesopor Mater, 2009, 118(1/3): 396-402.
- [18] 冀德坤, 李术元, 丁福臣, 赵如松. ZSM-5/MCM-41复合分子筛汽油降烯烃反应条件考察[J]. 石油炼制与化工, 2011, 42(1): 53-58.
- [19] JI De-kun, LI Shu-yuan, DING Fu-chen, ZHAO Ru-song. An investigation in the reaction conditions of gasoline olefin reduction over ZSM-5/MCM-41 composite molecular sieve[J]. China Petroleum Processing and Petrochemicals, 2011, 42(1): 53-58.)
- [20] 陈艳红, 李春义, 杨朝合. 以十六烷基三甲基溴化铵为模板剂合成MCM-41/ZSM-5复合分子筛的研究[J]. 燃料化学学报, 2011, 39(12): 944-949.
- [21] CHEN Yan-hong, LI Chun-yi, YANG Zhao-he. Synthesis of MCM-41/ZSM-5 composite molecular sieves with CTAB as template[J]. Journal of Fuel Chemistry and Technology, 2011, 39(12): 944-949.)
- [22] JERRMY B R, SIDDIQUI M A B, AITANI A M, SAEED M R, AL-KHATTAF S. Utilization of ZSM-5/MCM-41 composite as FCC catalyst additive for enhancing propylene yield from VGO cracking[J]. J Porous Mater, 2012, 19(4): 499-509.
- [23] TANG Q, XU H, ZHENG Y Y, WANG J F, LI H S, ZHANG J. Catalytic dehydration of methanol to dimethyl ether over micro-mesoporousZSM-5/MCM-41 composite molecular sieves[J]. Appl Catal A: Gen, 2012, 413-414: 36-42.
- [24] LI H S, HE S C, MA K, WU Q, JIAO Q Z, SUN K N. Micro-mesoporous composite molecular sieves H-ZSM-5/MCM-41 for methanol dehydration to dimethyl ether: Effect of  $SiO_2/Al_2O_3$  ratio in H-ZSM-5[J]. Appl Catal A: Gen, 2013, 450: 152-159.
- [25] 宋春敏, 姜杰, 乔柯, 孟祥滨, 阎子峰. 微孔-介孔复合结构分子筛的合成及表征研究[J]. 分子催化, 2006, 20(6): 294-299.
- [26] SONG Chun-min, JIANG Jie, QIAO Ke, MENG Xiang-bing, YAN Zi-feng. The synthesis and characterization of micro/mesoporous composite molecular sieves[J]. Journal of Molecular Catalysis (China), 2006, 20(6): 294-299.)
- [27] NEI C, HUANG L M, ZHAO Y Z. Performance of mesoporous aluminosilicate of the MCM-41[J]. Appl catal, 2003, 240(1/2): 29-40.
- [28] 徐如人, 庞文琴, 于吉红. 分子筛与多孔材料化学[M]. 北京: 科学出版社, 2004.
- [29] XU Ru-ren, PANG Wen-qin, YU Ji-hong. Zeolites and porous materials[M]. Beijing: Science Press, 2004.)
- [30] WOOLERY G L, KUEHL G H, TIMKEN H C. On the nature of framework Brønsted and Lewis acid sites in ZSM-5[J]. Zeolites, 1997, 19(4): 288-296.

- [1] 赵晓波, 王文举, 郭新闻, 王祥生.  $\text{Al}_2\text{O}_3$ 孔结构对纳米HZSM-5基催化剂改质FCC汽油性能的影响[J]. 燃料化学学报, 2013, 41(11): 1343-1348.
- [2] 周振奎, 李琢, 王博, 彭伟才, 李建青, 吴晋沪. ZSM-5的水热改性及其在合成气经二甲醚制汽油中的应用[J]. 燃料化学学报, 2013, 41(11): 1349-1355.
- [3] 赵岑, 刘冬梅, 魏民, 孙志岩, 王海彦. 多级孔ZSM-5分子筛的制备及催化噻吩烷基化性能研究[J]. 燃料化学学报, 2013, 41(10): 1256-1261.
- [4] 石冈, 林秀英, 范煜, 鲍晓军. ZSM-5分子筛的脱硅改性及加氢改质性能[J]. 燃料化学学报, 2013, 41(05): 589-600.
- [5] 杨瑞娟, 杨冬花, 武正簧, 冯晓娜, 窦涛, 吴忠华, 李志宏, 闫泽, 王凡, 汤琼. 含铁微孔EU-1/ZSM-5复合分子筛的合成和表征[J]. 燃料化学学报, 2013, 41(05): 601-606.
- [6] 陈娇娇, 陈冠益, 马文超, 马隆龙, 王铁军, 张琦, 吕微. 生物油模型化合物催化裂化制备芳香烃的实验研究[J]. 燃料化学学报, 2013, 41(02): 183-188.
- [7] 肖何, 高俊华, 胡津仙, 章斌, 刘平, 张侃. 酸碱改性HZSM-5分子筛上甲醇制取均四甲苯的研究[J]. 燃料化学学报, 2013, 41(01): 102-109.
- [8] 钦柏豪, 杨运泉, 刘文英, 王威燕, 杨余, 何兵. 表面活性剂对水热法合成 $\text{MoS}_2$ 加氢脱硫催化剂的影响[J]. 燃料化学学报, 2012, 40(11): 1384-1389.
- [9] 苗青, 董梅, 牛宪军, 王浩, 樊卫斌, 王建国, 秦张峰. 含镓ZSM-5分子筛的制备及其在甲醇芳构化反应中的催化性能[J]. 燃料化学学报, 2012, 40(10): 1230-1239.
- [10] 李娟, 海航, 闫常峰, 胡蓉蓉, 么志伟, 罗伟民, 郭常青, 李文博. 焙烧温度对二甲醚水蒸气重整制氢  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3+\text{H}-\text{ZSM-5}$ 双功能催化剂性能的影响[J]. 燃料化学学报, 2012, 40(10): 1240-1245.
- [11] 吉媛媛, 满毅, 王焕茹, 杨菁. 黏合剂对其ZSM-5分子筛成型物裂解石脑油的影响[J]. 燃料化学学报, 2012, 40(06): 727-731.
- [12] 许烽, 董梅, 荀蔚勇, 黄立志, 李俊汾, 樊卫斌, 秦张峰, 王建国. ZSM-5分子筛的粒径可控合成及其在甲醇转化中的催化作用[J]. 燃料化学学报, 2012, 40(05): 576-582.
- [13] 李莎, 李玉平, 狄春雨, 张鹏飞, 潘瑞丽, 窦涛. TPAOH/NaOH混合碱体系对ZSM-5沸石的改性及其催化性能研究[J]. 燃料化学学报, 2012, 40(05): 583-588.
- [14] 王俊刚, 李德宝, 黄巍, 贾丽涛, 孙志强, 刘斌, 孙予罕. 还原-氧化预处理对双孔道钴基催化剂催化性能的影响[J]. 燃料化学学报, 2012, (04): 441-446.
- [15] 盛清涛, 凌开成, 李振荣, 赵亮富. 热处理对HZSM-5结构、酸性及催化乙醇脱水反应性能的影响[J]. 燃料化学学报, 2012, (04): 494-500.

版权所有 © 《燃料化学学报》编辑部

本系统由北京玛格泰克科技发展有限公司设计开发 技术支持: support@magtech.com.cn