Catalysis Communications 64 (2015) 110–113

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Preparation of silicalite-1@Pt/alumina core–shell catalyst for shape-selective hydrogenation of xylene isomers

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ARTICLE INFO

Article history:
Received 22 December 2014
Received in revised form 30 January 2015
Accepted 3 February 2015
Available online 7 February 2015

Keywords:
Core–shell
Silicalite-1 membrane
Platinum
Xylene
Hydrogenation

ABSTRACT

A silicalite-1@Pt/alumina core–shell catalyst that combined molecular sieving and hydrogenation was synthesized by coating silicalite-1 onto the surface of Pt/alumina pellet. While a Pt/alumina catalyst had no selectivity in the hydrogenation of xylene isomers, the silicalite-1@Pt/alumina core–shell catalyst showed much higher efficiency for the hydrogenation of *p*-xylene than for that of *m*- and *o*-xylene. The shape-selective hydrogenation catalyst has great potential for application in xylene separation.

1. Introduction

Zeolites are crystalline microporous aluminosilicates with periodic arrangements of cages and channels that have been found with extensive industrial applications as catalysts, adsorbents and ion exchangers [1]. Recent success in the preparation of zeolite membranes with good thermal, chemical, and structural stabilities has provided new opportunities for applications in gas, vapor and liquid separations [2–4]. One highly desirable process is the separation of *p*-xylene (kinetic diameter ~ 5.8 Å) from its bulkier *m*- and *o*-xylene isomers (kinetic diameter ~ 6.8 Å), which is of significant importance in petrochemical industry for the high value downstream products from *p*-xylene such as terephthalic acid, polyester resin and terylene [5]. The diameter of the pore opening of MFI zeolite (5.5 × 5.1 Å sized elliptical channels running along the a axis in a sinusoidal manner and 5.6 × 5.3 Å sized elliptical channels running straight along the b axis [6,7]) is approximately of the size of *p*-xylene, while the bulkier *m*- and *o*-xylene isomer molecules can face significant sterical hindrance within the confines of the zeolite pores. Therefore, due to molecular sieving through zeolitic pores, defect-free MFI zeolite membranes have high permselectivity for *p*-xylene over *o*-xylene and *m*-xylene [8–11].

Several groups have studied the separation of xylene isomers through MFI zeolite membranes [12–20]. Keizer et al. [12] reported that the separation factor of 0.62 kPa *p*-xylene and 0.52 kPa *o*-xylene vapor mixtures had a maximum value of about 60 between room temperature and 473 K. Xomeritakis et al. [13,14] studied an MFI-membrane synthesized on the surface of α-alumina disks to evaluate the separation of xylenes in the 295–548 K temperature range. The prepared membranes exhibited a *p*-xylene permeance of 2×10^{-8} $\mathrm{mol\,m^{-1}\,s^{-1}\,Pa^{-1}}$ at 373–398 K and *p*/*o* separation factors between 60 and 300. Lai et al. [15,16] reported the preparation of b-

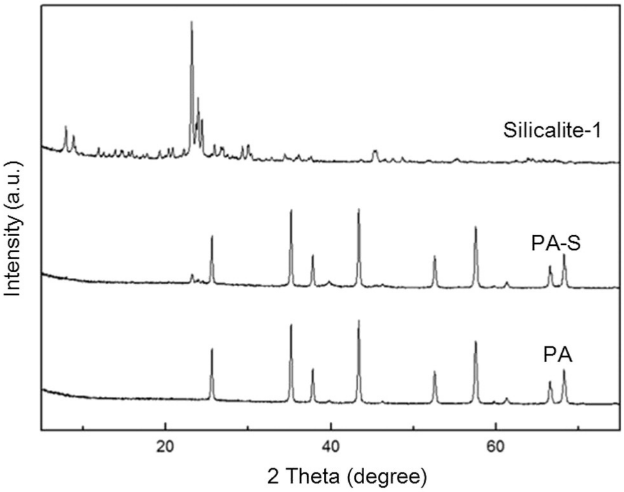

Fig. 1. XRD patterns of PA-S, PA and pure silicalite-1.

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http://dx.doi.org/10.1016/j.catcom.2015.02.004
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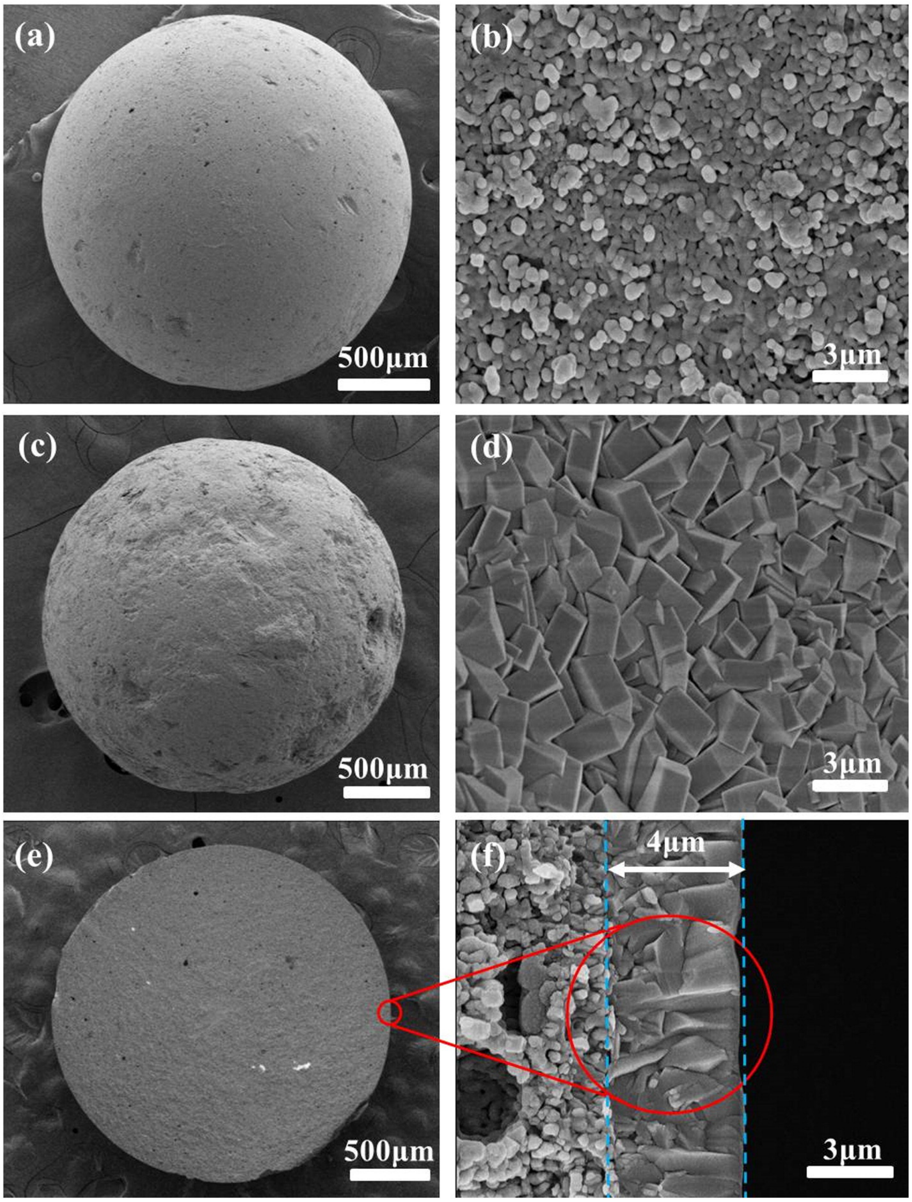


Fig. 2. (a, b) Top-view SEM images of the PA catalyst, (c, d) top-view SEM images and (e, f) cross-section SEM images of the PA-S core–shell catalyst under low (left) and high (right) magnifications.

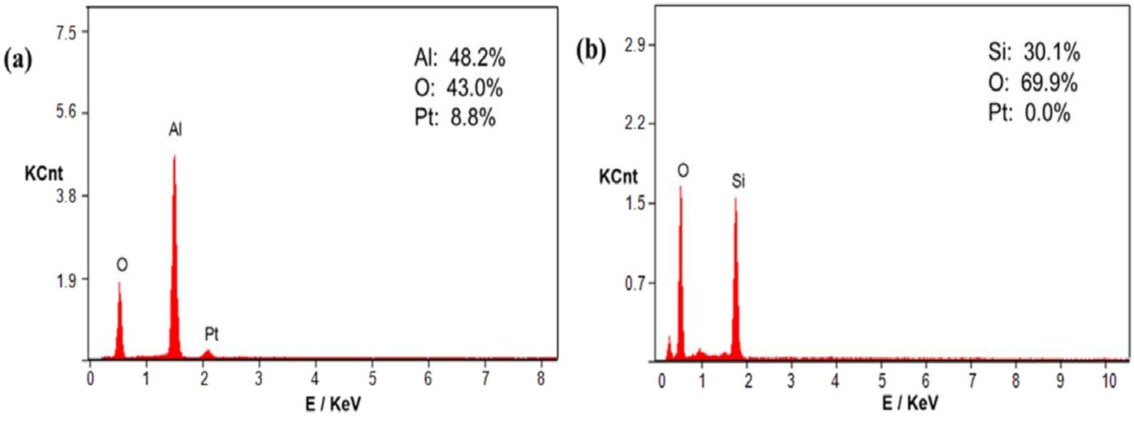


Fig. 3. Surface EDS analysis of (a) the bare PA catalyst and (b) the PA-S core–shell catalyst.

Table 1
Hydrogenation product yields over the PA and PA-S catalysts in the hydrogenation of single component xylene isomer.[a]

	Hydrogenation product yields (wt.%) [b]			Selectivity	
Catalysts	1,2-DC	1,3-DC	1,4-DC	p/o	p/m
PA	80.7	83.9	81.8	1.0	1.0
PA-S	0.8	2.4	75.6	94.5	31.5

[a] Reaction conditions: 473 K, 1.0 MPa, $W_{cat} = 2$ g, feed $= 4$ ml h^{-1}, WHSV $= 1.0$ h^{-1}, $F_{H_2} = 2400$ ml h^{-1}. Feed composition: single component xylene isomer.

[b] 1,4-Dimethylcyclohexane (1,4-DC), 1,3-dimethylcyclohexane (1,3-DC) and 1,2-dimethylcyclohexane (1,2-DC) are hydrogenation products of *p*-xylene, *m*-xylene and *o*-xylene, respectively.

oriented silicalite membranes synthesized on the surface of α-alumina disks. These membranes showed *p*/*o*-xylene separation factors (0.5 kPa/0.45 kPa) as high as 483 at 493 K with a *p*-xylene permeance of 2×10^{-7} $molm^{-1}$ s^{-1} Pa^{-1}.

Although these approaches were successful in demonstrating high selectivity for xylene separation, they are of limited practical potential because of prohibitive low fluxes [15]. Bakker et al. [17] indicated that the maximum permeation flux could be described by the equilibrium adsorption amount for xylenes through the MFI membrane. Thus, a combination of separation with catalysis is required to attain compatible separation fluxes and reaction rates. The selective conversion of reactant can break the equilibrium limitation on the membrane. Besides, diffusion is an activated process and the diffusivity increases with the reaction temperature, thus a catalytic reaction under high temperature will further enhance the diffusion efficiency through the membrane.

In this work, we report a catalyst with a core–shell structure that couples molecular sieving and hydrogenation. A Pt/Al_2O_3 hydrogenation catalyst was prepared as a core catalyst. One layer of silicalite-1 shell was successfully developed on the core catalyst. The silicalite-1@Pt/Al_2O_3 particles were then used for the hydrogenation of xylene isomers. The product selectivity for the silicalite-1@Pt/Al_2O_3 catalyst was compared with that for the naked Pt/Al_2O_3 core catalyst. This concept of core–shell catalyst has great potential to develop into a novel approach for xylene separation.

2. Experimental

Alumina (Al_2O_3) pellets (2.0–2.3 mm, Sasol Co.) were used as support for the preparation of a 1.0 wt.% Pt/Al_2O_3 core catalyst by impregnation with an aqueous solution of chloroplatinic acid hexahydrate ($H_2PtCl_4 \cdot 6H_2O$). The Pt/Al_2O_3 core catalyst, named PA, was pre-modified with a 3.0 wt.% TPAOH solution, followed by the adsorption of silicalite-1 nanoparticles. One layer of silicalite-1 shell was synthesized on the thus-treated PA core catalyst using secondary hydrothermal synthesis, with a reaction solution composition of $0.4TPAOH/1.0TEOS/160H_2O$, at 443 K for 3 days. The obtained silicalite-1 membrane coated Pt/Al_2O_3 catalyst was named PA-S.

More detailed descriptions of the synthesis, characterization and catalytic test were presented in the Supplementary material.

Table 2
Hydrogenation product yields over the PA-S catalyst in the hydrogenation of equimolar binary *p*/*o* xylene.[a]

Hydrogenation product yields (wt.%)		Selectivity
1,4-DC	1,2-DC	*p*/*o*
34.7	2.04	17.0

[a] Reaction conditions: 473 K, 1.0 MPa, $W_{cat} = 2$ g, feed $= 4$ ml h^{-1}, WHSV $= 1.0$ h^{-1}, $F_{H_2} = 2400$ ml h^{-1}. Feed composition: 50 wt.% *p*-xylene and 50 wt.% *o*-xylene.

Table 3
Hydrogenation product yields over the PA-S catalyst in the hydrogenation of equimolar binary *p*/*m* xylene.[a]

Hydrogenation product yields (wt.%)		Selectivity
1,4-DC	1,3-DC	*p*/*m*
39.3	2.9	13.6

[a] Reaction conditions: 473 K, 1.0 MPa, $W_{cat} = 2$ g, feed $= 4$ ml h^{-1}, WHSV $= 1.0$ h^{-1}, $F_{H_2} = 2400$ ml h^{-1}. Feed composition: 50 wt.% *p*-xylene and 50 wt.% *m*-xylene.

3. Results and discussion

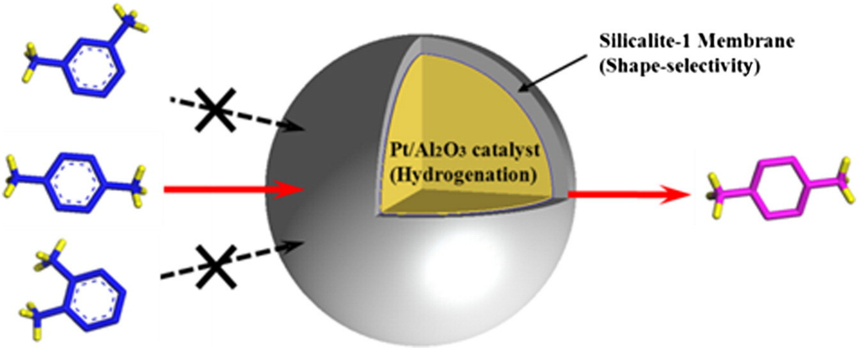
3.1. Catalyst characterization

X-ray diffraction (XRD) patterns of the naked PA catalyst, PA-S core–shell catalyst and pure MFI zeolite are presented in Fig. 1. For the PA catalyst, only the peaks of crystalline α-Al_2O_3 were observed. For the silicalite-1 coated PA-S catalyst, X-ray diffraction peaks belonging to silicalite-1 appeared at $2\theta = 7.9°$, 8.9° and 23.5° by comparing with pure silicalite-1 zeolite, indicating that silicalite-1 membrane had successfully crystallized on the PA core catalyst.

The top-view SEM images in Fig. 2(a) and (c) show the whole surface morphologies of the PA catalyst and the PA-S core–shell catalysts. Both the PA and PA-S catalysts have spherical structures with the diameters around 2 mm. From the magnified surface images of the PA and PA-S catalyst in Fig. 2(b) and (d), it can be clearly observed that the surface of the PA-S catalyst had been covered by one layer of silicalite-1. Fig. 2(e) and (f) shows the cross-section SEM images of the PA-S catalyst under different magnifications. A well-intergrown and uniform zeolite shell coated on the surface of the PA core catalyst could be distinguished. The thickness of this silicalite-1 layer is about 4 μm. The elemental distributions of the PA pellet surface before and after the MFI zeolite coating are presented in Fig. 3(a) and (b). On the bare PA catalyst surface, a Pt peak can be detected, but there is no Pt signal visible on the surface of the PA-S core–shell catalyst after the zeolite coating step. This indicates that the PA core catalyst is completely enwrapped by this integrated silicalite-1 membrane.

3.2. Catalyst evaluation results

The PA-S catalyst was used for the selective hydrogenation of xylene isomers to investigate the effect of the silicalite-1 coated core–shell structure. For comparison, the naked PA catalyst was also studied under the same reaction conditions. The hydrogenation experiments were carried out with single component xylene isomer and a mixture of equimolar binary *p*/*o*-xylene and binary *p*/*m*-xylene, respectively, as the feeds. Hydrogenation product yields of single component xylene isomer over the two catalysts are presented in Table 1. When silicalite-1 crystals without Pt were used for the reaction, no catalytic activity was observed, so the silicalite-1 coating on the catalyst acted not as a catalyst but as a membrane. For each xylene isomer, there was only one corresponding hydrogenation product. That is, *p*-xylene was hydrogenated to produce 1,4-dimethylcyclohexane (1,4-DC), *m*-xylene was hydrogenated to produce 1,3-dimethylcyclohexane (1,3-DC) and *o*-xylene was hydrogenated to produce 1,2-dimethylcyclohexane (1,2-DC). For the naked PA core catalyst, the yield of 1,4-DC, 1,3-DC and 1,2-DC all exceeded 80 wt.%, demonstrating that the bare PA core catalyst has no selectivity in the hydrogenation of the three xylene isomers. In contrast, for the PA-S core–shell catalyst, the hydrogenation conversion of *p*-xylene was only slightly lower (75.6 wt.%) than that over the PA catalyst (81.8 wt.%), while the yield of 1,3-DC and 1,2-DC was much lower than over the bare PA catalyst. This indicates that the hydrogenation of *m*-xylene and *o*-xylene was strongly suppressed on the PA-S catalyst. The ideal *p*/*o* hydrogenation selectivity on the PA-S catalyst (the ratio of the conversion of *p*-xylene to that of *o*-xylene) was as high as 94.5, which was much higher than that of the PA catalyst (about 1.0). The high ideal *p*/*m*



Scheme 1. Selective hydrogenation model of xylene isomers over the PA-S core–shell catalyst.

selectivity of 31.5 was also obtained on the PA-S catalyst. The selective hydrogenation performance of the PA-S catalyst using binary *p*/*o* xylene and binary *p*/*m* xylene feeds is shown in Tables 2 and 3, respectively. The real *p*/*o* and *p*/*m* hydrogenation selectivities of 17.0 and 13.6, respectively, were obtained, indicating that the PA-S catalyst also realized high *para*-selectivities for binary *p*/*o* and *p*/*m* xylene mixtures.

The excellent *para*-selectivity is a consequence of diffusion resistance, that is, the silicalite-1 membrane imposes sterical restriction on the transport of *m*-xylene and *o*-xylene molecules relative to *p*-xylene molecules. As illustrated in Scheme 1, when xylene isomers contact the silicalite-1 shell, *p*-xylene is able to diffuse through the pores, reach the Pt active site in the core, then undergo a hydrogenation, and finally the produced 1,4-DC diffuses out. The bulkier isomers, *m*-xylene and *o*-xylene, may be too large to diffuse into the pores easily or at greatly reduced rates, suppressing their further hydrogenation to generate 1,3-DC and 1,2-DC. As a result, the hydrogenation conversions of *m*-xylene and *o*-xylene were decreased sharply over the PA-S catalyst compared to those over the PA catalyst. The excellent catalysis and separation performance of the zeolite-coated PA-S catalyst confirmed that this silicalite-1 membrane realized high-flux and high-selectivity of *p*-xylene. Besides, the high permeability and reaction efficiency contributed to the combination of catalytic reaction and separation. The diffusion limitation on the silicalite-1 membrane was broken by the selective conversion of *p*-xylene to its hydrogenation product.

4. Conclusion

A core–shell catalyst was shown to couple molecular sieving and hydrogenation. One layer of silicalite-1 membrane with a thickness of 4 μm was successfully coated onto the surface of Pt/Al_2O_3 catalyst by a hydrothermal synthesis method. In the hydrogenation of xylene isomers, the silicalite-1@Pt/Al_2O_3 catalyst showed much higher efficiency for the hydrogenation of *p*-xylene than for that of *m*- and *o*-xylene. The ideal *p*/*o* and *p*/*m* hydrogenation selectivities of 94.5 and 34.5, respectively, as well as the real *p*/*o* and *p*/*m* hydrogenation selectivities of 17.0 and 13.6, respectively, were obtained at 473 K due to the selective permeation of *p*-xylene into the Pt/Al_2O_3 particle through the silicalite-1 layer.

Acknowledgments

This work was financially supported by the National Natural Science Fund of China (Grant No. U1162203) and the Fundamental Research Funds for the Central Universities (14CX06049A and 14CX02058A).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.02.004.

References

[1] M.E. Davis, Nature 417 (2002) 813–821.
[2] T.C. Bowen, R.D. Noble, J.L. Falconer, J. Membr. Sci. 245 (2004) 1–33.
[3] C.M. Braunbarth, L.C. Boudreau, M. Tsapasis, J. Membr. Sci. 174 (2000) 31–42.
[4] J. Coronas, R.D. Noble, J.L. Falconer, AICHE J. 43 (1997) 1797–1812.
[5] K. Li, M. Hsu, I. Wang, Catal. Commun. 9 (2008) 2257–2260.
[6] H.H. Funke, A.M. Argo, J.L. Falconer, R.D. Noble, Ind. Eng. Chem. Res. 36 (1997) 137–143.
[7] C. Bärlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, 5th ed. Structure Commission of the International Zeolite Association by Elsevier, Amsterdam, 2001.
[8] C. Zhang, Z. Hong, J. Chen, X. Gu, W. Jin, N. Xu, J. Membr. Sci. 389 (2012) 451–458.
[9] L.B. Young, S.A. Butter, W.W. Kaeding, J. Catal. 76 (1982) 418–432.
[10] H. Karsh, A. Culfaz, H. Yucel, Zeolites 12 (1992) 728–732.
[11] D.M. Ruthven, M. Eic, E. Richard, Zeolites 11 (1991) 647–653.
[12] K. Keizer, A.J. Burggraaf, Z.A.E.P. Vroon, H. Verweij, J. Membr. Sci. 147 (1998) 159–172.
[13] G. Xomeritakis, Z. Lai, M. Tsapasis, Ind. Eng. Chem. Res. 40 (2001) 544–552.
[14] G. Xomeritakis, S. Nair, M. Tsapasis, Microporous Mesoporous Mater. 38 (2000) 61–73.
[15] Z. Lai, G. Bonilla, I. Diaz, J.G. Nery, K. Sujaoti, M.A. Amat, E. Kokkoli, O. Terasaki, R.W. Thompson, M. Tsapasis, D.G. Vlachos, Science 300 (2003) 456–460.
[16] Z. Lai, M. Tsapasis, Ind. Eng. Chem. Res. 43 (2004) 3000–3007.
[17] W.J.W. Bakker, L.J.P. van den Broeke, F. Kapteijn, J.A. Moulijn, AICHE J. 43 (1997) 2203–2214.
[18] G. Xomeritakis, M. Tsapasis, Chem. Mater. 11 (1999) 875–878.
[19] X. Gu, J. Dong, T.M. Nenoff, D.E. Ozokwelu, J. Membr. Sci. 280 (2006) 624–633.
[20] A.M. Tarditi, G.I. Horowitz, E.A. Lombardo, J. Membr. Sci. 281 (2003) 692–699.