Microwave Assisted Synthesis of Nano Zeolite Seed for Synthesis Membrane and Investigation of its Permeation Properties for H_2 Separation

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ABSTRACT: *MFI-type zeolite membranes (ZSM-5) were prepared on α-alumina tubular supports and tested for separation of H_2/CO mixtures. The effect of pressure and temperature on H_2 and CO flows and selectivity was investigated. The best results in this work were obtained with a ZSM-5 membrane prepared over a porous α-alumina tube seeded with zeolite nanocrystals synthesized with microwave technique. In this case the H_2 permeance was obtained 2.8×10^{-6} mol/ (m^2.s.Pa) with a H_2/CO ideal selectivity of 4.9 at 373 K. The permeation results of four gas (H_2, CO, N_2, CH_4) on the synthesized membrane were also investigated.*

KEY WORDS: *Zeolite membrane, ZSM-5, Nano crystalline, Microwave heating, Gas Permeation, H_2/CO separation.*

INTRODUCTION

Gas separation membranes are widely used for hydrogen recovery, air separation and natural gas processing. The success of membrane systems in these applications stems from their inherent advantages of operational simplicity, space and weight efficiency, easy scalability, and low power consumption [1, 2]. Zeolite membranes are a kind of microporous inorganic membranes that have been reported in a wide variety of applications such as the separation of isomers, gas mixtures and pervaporation of alcohol-water mixtures [1, 3]. Zeolite membranes have great potential in separation and catalysis owing to their unique pore structures and adsorption properties, and their superior thermal, mechanical and chemical properties compared with polymeric membranes. The preparation and characterization of zeolite films on various supports has burgeoned over the past years [3-5]. In this work we investigate the properties of ZSM-5 zeolite membranes in nano scale with different characteristics for the selective separation of H_2 from mixtures with CO. ZSM-5 zeolite has smaller zeolitic

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pore size than FAU and would have stronger influence of adsorption hindrance. The aim of this work is study on the H_2 and CO permeation with increasing pressure and temperature. Molecular sieving is expected to play a significant role in the system investigated, due to the kinetic diameters of the molecules involved (2.89 nm for H_2 and 3.5 nm for CO), and the fact that they are considerably smaller than the MFI pore size (ca. 0.55 nm).

EXPERIMENTAL SECTION

Preparation of ZSM-5 zeolite membrane

The supports used here were porous α-Al_2O_3 tubes with an outer diameter of 16 mm, an inner diameter of 12.5 mm and a length of 62 mm. The average pore diameter and porosity of the alumina supports were about 150 nm and 43%, respectively. Before hydrothermal treatment, the support was washed in an ultrasonic bath for 15 min, rinsed with deionized water and derid in an oven for 48 h at 323K.

The Si and Al precursor solutions for the zeolite synthesis were prepared from aluminum hydroxide (Al $(OH)_3$, >98%, Merck) as alumina source and tetraethyl orthosilicate (TEOS, 98%, Merck) as silica source. Tetrapropylammonium hydroxide (TPAOH, 40 wt % solution, Merck) was used as structure directing agent and sodium hydroxide (NaOH, 99%, Merck) as alkali source. ZSM-5 membrane was synthesized using the secondary growth hydrothermal process in a teflon lined stainless steel autoclave under autogenous pressure at 453K. The seeding step was accomplished by microwave-assisted hydrothermal synthesis of Al-free MFI type (silicalite-1) zeolite nano-particles using a patented homemade microwave oven [4]. Synthesis batch composition, time and temperature have been chosen after a series of tests in order to minimize the consumption of TPAOH and optimize the crystal growth during the synthesis. The precursor a synthesize solution with molar composition of 9TPAOH: $25SiO_2$: $1450H_2O$: 100EtOH was prepared by stirring at room temperature for 4h. The mixture was aged for 24h at room temperature then was poured charged into a PTFE vessel and heated in the microwave oven. Two-stage syntheses were performed by heating the reactant mixture at 80°C (300 W) for 90 min, followed by increasing the temperature to 180°C (450 W) for 10 min. The synthesized nanocrystals were separated from the colloidal suspension by centrifugation at 13000 rpm, the liquid phase was decanted and the solid phase was re-dispersed in distilled water by using an ultrasonic disperser treatment. To remove the unreacted materials in the solution, the centrifugation - dispersion steps were repeated three times. For the slip-casting method seeding process of the inner surface of the α-alumina tube was performed three times (5 min each time) by using a 1 wt% seeding solution, which was prepared by dispersing of 5 g of the as synthesized 25 nm, sil-1 nanocrystals in 50 mL distilled water. Then, the seeded tubular support was dried overnight in laboratory environment then was dried for 12 h at 353 K in an oven.

The secondary growth process consisted of hydrothermal growth of ZSM-5 zeolite crystals on the inner surface of seeded α-alumina tubular substrate using a clear synthesis solution with molar composition of 40TEOS: 1TPAOH: $2Al_2O_3$: 10NaOH: $20000H_2O$, which was prepared by hydrolysis of the TEOS and the TPAOH in H_2O for 5 h at room temperature, followed by addition of the $Al(OH)_3$ and NaOH solutions and stirring for 2 h. The outer surface of seeded α-Al_2O_3 tubular support was wrapped with teflon tape in order to prevent unwanted zeolite deposition on the external surface of the substrate, and placed in a teflon lined stainless steel autoclave containing 110 mL of synthesis solution and placed in a preheated oven at 453 K for 39 h. after synthesis, the autoclave was rapidly quenched to room temperature and the zeolite membrane was rinsed with deionized water and dried at 345 K for 24 h.

To remove the template molecules of the synthesized zeolite membrane it was first heated in O_2 atmosphere up to 350°C and held in this temperature for 6 h, then further heated to 450°C and held for 6h, then heated up to 500°C. heating and cooling rate of the heat treatment program was 18°C h^{-1} and 30°C h^{-1} respectively.

Characterization

Characterization of the zeolite nanocrystals

Chemical analyses were performed by FT- IR spectra with a Shimadzu 8400S spectrometer. X-Ray Diffraction patterns (XRD, Philips Analytical, Cu Kα radiation) were taken of the MFI powders. The crystallinity was determined from the peak area between 2θ=22-25° using a highly crystalline ZSM-5 sample as reference. The morphology and size of the MFI

nano-crystals were determined from the Transmission Electron Microscopy (TEM) images taken with a LEO912AB and Scanning Electron Microscopy (SEM) images taken with a VG2080537IR

Characterization of the zeolite membranes

A X-ray diffractometer was used to collect XRD data from the zeolite membranes. A SEM running at an acceleration voltage of 15 kV equipped with an Energy Dispersive X-ray (EDX) detector was used to record images and EDX data after coating with thin gold films. Cross-sectional fracture faces of the membranes on α-Al_2O_3 was studied using membranes cracked in two pieces and mounted vertically on studs.

Gas permeation experiments

The permeation setup consists of a temperature and pressure control system and the membrane test module. The membrane was sealed in the shell-and-tube membrane test module using Viton O-rings to ensure a leak-free seal. The module temperature was monitored using a K-type thermocouple and was maintained constant for each experiment by a heating tape and a temperature controller unit. The feed pressure was adjusted using pressure regulator and monitored using a pressure gauge, while the permeate pressure was kept at ambient. The permeate flux was measured using a bubble flow meter. The leak test experiment was conducted by subjecting the uncalcined membrane to high-pressure N_2 and measuring the permeate flux. Prior to template removal, the zeolite pores were inaccessible to diffusing molecules. Therefore, a defect-free membrane should be impervious to gas flow and the results of the leak test experiment can be used to quantify the nonzeolitic transport pathways present in the membrane. After leak test experiment, the membrane was calcined in a furnace under O_2 atmosphere. Single gases permeation measurements were dosed at different feed pressures (1.2-1.8 bar), but at a fixed permeate pressure (ambient pressure i.e. 1.01 bar). The experiment avoided the use of sweep gas. The permeance of four different gases (H_2, N_2, CH_4, CO) were measured and compared.

RESULTS AND DISCUSSION

Fourier transform infrared analysis

The nanocrystalline ZSM-5 zeolites prepared by microwave technique were spectroscopically characterized using FT-IR and is shown in Fig. 1. From that, the infrared range features absorption peaks of ZSM-5 at 550, 800, 1100, 1225 and 1460 cm^{-1}. This is shown by the presence of the infrared band at 550 cm^{-1} which has been assigned to the fivemembered ring of the pentasil zeolite structure. Additional evidence for the nanosized ZSM-5 zeolite was the asymmetric stretch vibration of the T-O bond (at 1225 cm^{-1}, see Fig. 1), which has been assigned to external linkages (between TO_4 tetrahedral) and is a structure-sensitive IR band of ZSM-5 zeolite [2,10].

X-ray diffraction analysis

Because of XRD specification peaks that are in the range of $5<2\ \theta<50$, all experiments were done in this range.

The XRD pattern of the ZSM-5 nanocrystals is typical for MFI type zeolite powder, with the characteristic reflections at $2\theta = 7.9°–8.9°$ and $2\theta = 23°–24°$ (Fig. 2, top). Fig. 3 shows standard X-ray diffraction pattern for ZSM-5 zeolite [9]. The specification peaks in standard pattern are at $2\theta = 7.8°$ & $2\theta = 23°$and in synthesized nano zeolite are at $2\theta = 7.875°$ & $2\theta = 23.085°$. Comparing the results shows that synthesized powder is according to standard pattern and confirm the production of high purity ZSM-5 nanocrystals.

The XRD analysis of the zeolite/α-alumina samples after synthesis (Fig. 2, bottom) confirms the presence of ZSM-5 type zeolite on the surface of the α–alumina substrate. This experiment was done on a square slice of membrane syntesized on the inner surface of α–alumina tube. In order to further characterize the orientation of the crystals constituting the films, XRD data were collected on all films. The relative intensity of the reflections indicating that the zeolite crystallites are preferentially oriented. The XRD patterns show that films are oriented with the b-axis to the substrate surface, which is expected since the (010) face is the largest face of the films crystals.

Transmission electron microscopy analysis

The morphology of synthesized ZSM-5 zeolite powders was investigated by using TEM. Fig. 4 shows the typical shape of synthesized ZSM-5 zeolite nanocrystals. As shown in Fig. 3, nanosized ZSM-5 zeolite was in spherical and benzene crystal structure [2]. The particle size distribution of zeolite crystals were about 25 nm.

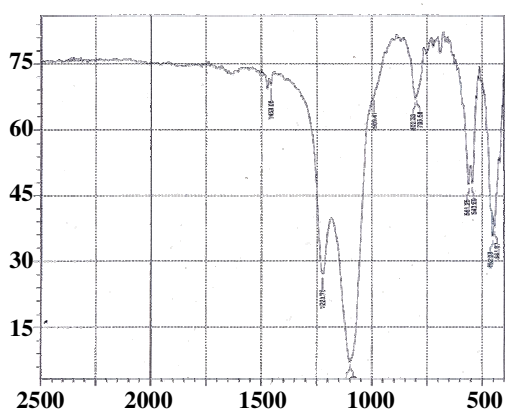

Fig. 1: IR spectra of nanosized ZSM-5 zeolite.

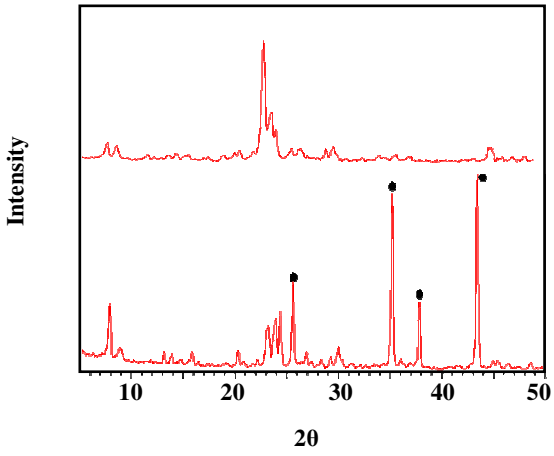

Fig. 2: X-ray diffraction patterns for ZSM-5 seeds prepared by MW-assisted synthesis (top) and ZSM-5 membrane on the α -alumina tube (bottom).

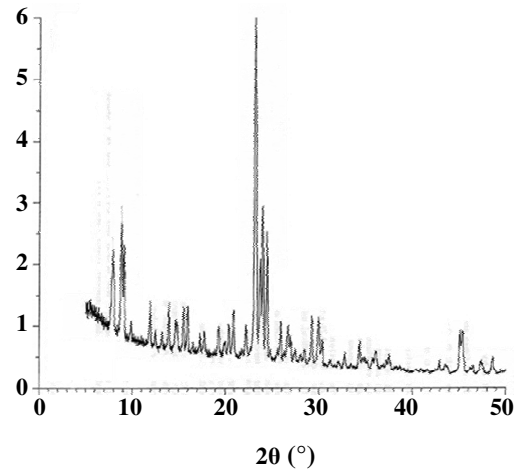

Fig. 3: Standard X-ray diffraction pattern for ZSM-5 zeolite [9].

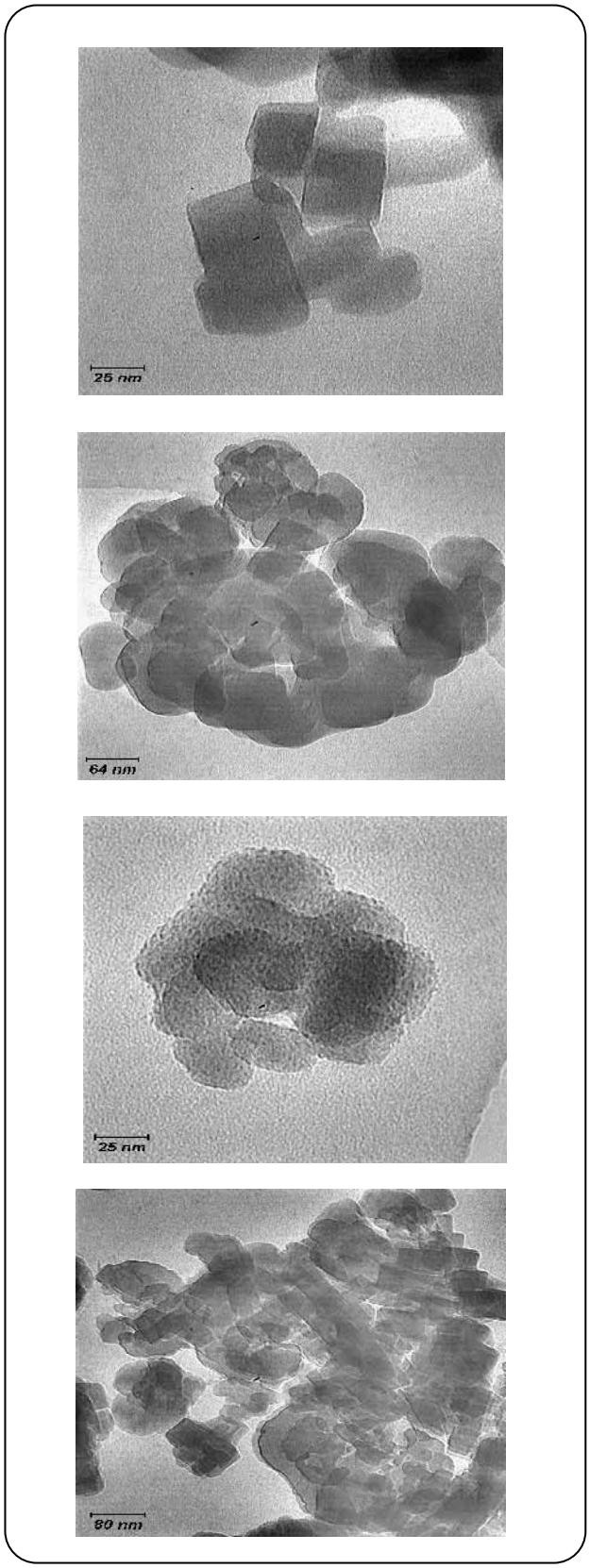

Fig. 4: TEM images of nanosized ZSM-5 zeolite.

Table 1: Single gas permeation through ZSM-5 membranes.

Permeance (10^{-7} mol/m^2.s.pa)			
H_2	CO	N_2	CH_4
32	1.6	17	54

Measurement at 298K

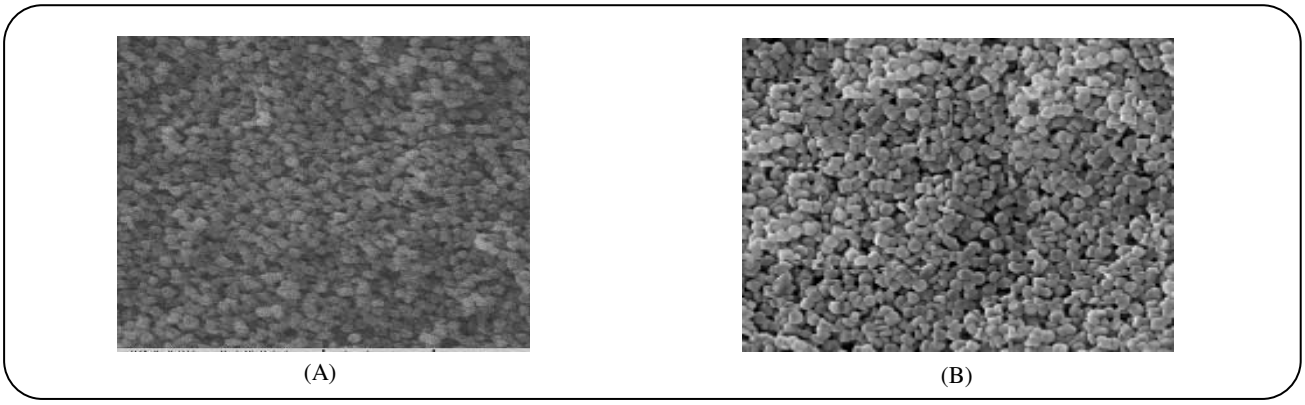

Fig. 5: SEM images of seeded α -Al_2O_3 support (A) and nanosized ZSM-5 zeolite membrane (B) the scale bar is equal to 1μm.

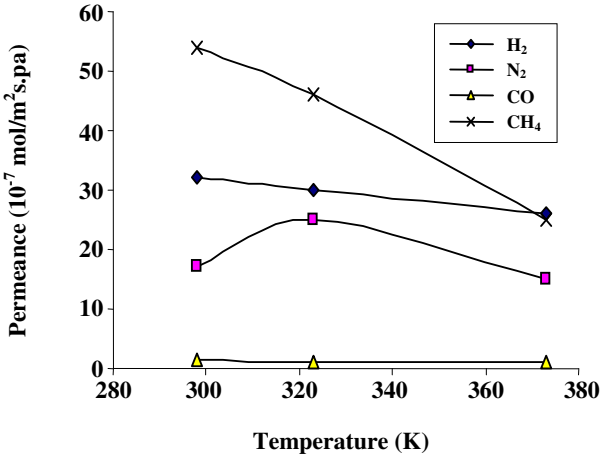

Fig. 6: Single gas permeances of H_2, CO, CH_4 and N_2 as a function of temperature Through a ZSM-5 membrane with a feed pressure of 1.4 bar.

SEM micrograph of different membranes

Fig. 5 shows SEM pictures of seeded α-Al_2O_3 support (A) and surface of ZSM-5 zeolite membrane (B). The seeded layer is continuously placed on α-Al_2O_3 surface because a set of experiments were done to reach the optimizing time and steps of seeding. The membrane surface is continuous. The top layer of membrane is about 2μm. which shows that use of nanoseeds is easier to form thin membrane.

Membrane permeation analysis

Fig. 6 shows the temperature dependency of permeances of some gases. Permeances for H_2 show a temperature dependency similar to *Knudsen* diffusion, the permeance decreases slightly with an increase in temperature. This is probably because the pore sizes which are effective for the permeation of H_2 are too large, in comparison with the molecular sizes, for molecular sieving or activated diffusion where permeances increase with temperature. On the other hand, CH_4 shows a decreasing tendency in permeance in a steeper slope than the case of H_2. The permeation mechanism can be simply described as surface diffusion, since these gases are thought to be adsorbed to the ZSM-5 zeolite. The steady-state permeation results on selected membranes are shown in Table 1.

Ideal selectivity is the ratio of single-gas permeances and for a ZSM-5 membrane synthesized with a Si/Al ratio of 20 in the gel, the maximum H_2/CO ideal selectivity was 4.9 at 373 K, with a H_2 permeance of 2.8×10^{-6} mol/m^2·s·Pa. Compared with literature results [6 - 8] under the same conditions, the ZSM-5 membrane synthesized in this study shows higher permeance for H_2. This is because of the suitable calcination process that removes all template molecules from membrane pore structures. These defect free membranes are good for gas

Table 2: Comparison of the permeation data with our results (ambient temperature except where noted).

Source	Film thickness	Single gas permeance (10^{-7} mol/m^2.s.pa)	
		H_2	CH_4
[8]	1.5	0.107	-
Present study	2	32	54
[6]	2	2.8[a]	0.97[a]
[7]	5-10	2.3	-

[a] *323K*

separation. The other reason for high permeance is thickness of membrane that is because of use of nano seed in secondary growth synthesis.(Table 2)

CONCLUSIONS

This study describes a new technique for synthesis of nano zeolite seeds based on a novel extension of the traditional hydrothermal method. The overall conclusions on membrane synthesis via the technique and the membrane characterization can be summarized as follows:

- The procedure for synthesis microwave seeds uses TPAOH less than previous reported work therefore it is an economically viable method with high crystallinity and yield.
- The microwave technique in producing of nanosized seeds for ZSM-5 membrane reduces significantly the synthesis time.
- Similar size and morfology of these nanoparticles result in a thinner membrane with high permeation.
- The permeability of H_2 is in comparison to the literatures.

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REFERENCES

[1] Sebastian V., Kumakiri I., Bredesen R., Menendez M., Zeolite Membrane for CO_2 Removal: Operating at High Pressure, *Journal of Membrane Science*, **292**, p. 92 (2007).

[2] Cheng Y., Wang L., Sheng Li J., Chuan Yang Y., Sun X., Preparation and Characterization of Nanosized ZSM-5 Zeolites in the Absence of Organic Template, *Materials Letters*, **59**, p. 3427 (2005).

[3] Mabande G.T.P., Pradhan G., Schwieger W., Hanebuth M., Dittmeyer R., Selvam T., Zampieri A., Baser H., Herrmann R., A study of Silicalite-1 and Al-ZSM-5 Membrane Synthesis on Stainless Steel Supports, *Microporous and Mesoporous Materials*, **75**, p. 209 (2004).

[4] Kazemian H., Farhadi F., Design and Manufacturing of a Laboratory Microwave Oven by using a Kitchen Microwave Oven, Iranian Patent no. 41171 (2007).

[5]. Au L.T.Y, Yeung K.L., An Investigation of the Relationship Between Microstructure and Permeation Properties of ZSM-5 Membranes, *Journal of Membrane Science*, **194**, p. 33 (2001).

[6] Heng S., Lau P., Yeung K., Djafer M., Schrotter J., Low Temperature Ozone Treatment for Organic Template Removal from Zeolite Membrane. *Journal of Membrane Science*, **243**, p. 69 (2004).

[7] Dong J, Lin Y.S., Hu M.Z.-C., Peascoe R.A., Payzant E.A., Template-Removal-Associated Microstructural Development of Porous-Ceramic-Supported MFI Zeolite Membranes, *Micropor. Mesopor. Mater*, **34**, p. 241 (2000).

[8] Hedlund J., Noak M., Kolsch P., Creaser D., Caro J., Sterte J., ZSM-5 Membranes Synthesized without Organic Templates Using a Seeding Technique. *Journal of Membrane Science*, **159**, p. 263 (1999).

[9] Baerlocher Ch., Meier W.M., Olson D.H., "Atlas of Zeolite Framework Types". 5th Ed., Elsevier (2001).

[10] Lesthaeghe D., Vansteenkiste P., Verstraelen T., Ghysels A., Okamoto K., Kirschhock C.E.A., Martens J.A., Speybroeck V.V., Waroquier M., MFI Fingerprint: How Pentasil-Induced IR Bands Shift During Zeolite Nanogrowth , *J. Phys. Chem.,***112**, p. 9186 (2008).