第83回応用化学科セミナー

分子動力学法を用いた無機多孔体に関する研究

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内容

無機多孔質体･分子動力学法

ゼオライトの熱的挙動に関する研究
第20回ゼオライト研究発表会（東京, 2004）

均一メソポーラスシリカのモデリング
14th International Zeolite Conference
(Cape Town, 2004)

無機多孔質体

細孔径による多孔体の分類 (IUPAC)

マイクロ孔 (diameter < 2 nm)　メソ孔 (2 nm < diameter < 50 nm)　マクロ孔 (diameter > 50 nm)

ゼオライト　均一メソ多孔体
活性炭　Xerogel　Aerogel　Porous Glasses
Pillared Clays

均一な細孔径分布

ゼオライト
ミクロ孔を持つ結晶構造

均一メソ多孔体
界面活性剤等のミセルを
テンプレートとした細孔形成

Zeolites

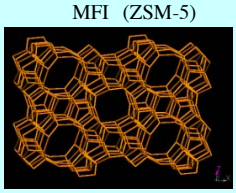
結晶性の多孔質アルミノケイ酸塩の総称
種々の骨格構造を有する

$(M_nAl_nSi_{1-n}O_2 \cdot H_2O)$

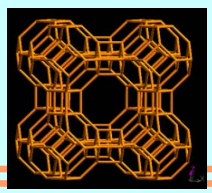
構造コード

AFW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EPI	ERI	ESV	ETR	EUO
FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	IFR	ISV	ITE
ITH	ITW	IWR	IWW	JBW	KFI	LAU	LEV	LIO	LOS	LOV	LTA
LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR
MSO	MTF	MTN	MTT	MTW	MWW	NAB	NAT	NES	NON	NPO	OBW
OFF	OSI	OSO	PAR	PAU	PHI	PON	RHO	RON	RRO	RSN	RTE
RTH	RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBS	SBT	SFE
SFF	SFG	SFH	SFN	SFO	SGT	SOD	SOS	SSY	STF	STI	STT
TER	THO	TON	TSC	UEI	UFI	UOZ	USI	UTL	VET	VFI	VNI
VSV	WEI	WEN	YUG	ZON							

MFI (ZSM-5)



LTA (zeolite A)



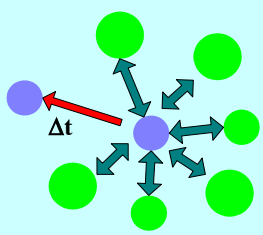
古典分子動力学（MD）法

古典力学に由来した運動方程式の計算

原子間の相互作用の計算

各原子の速度と位置

構造、物性



粒子（原子）数　数千～数万）

電子状態や化学結合は扱えない）

SiO_2の原子間相互作用モデル

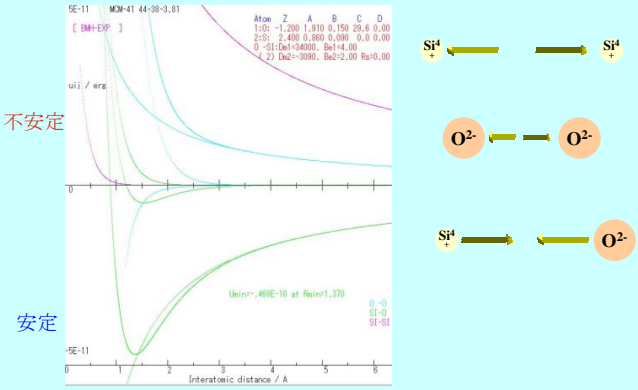
2中心力モデル

$$u_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r_{ij}} + f_0(b_i + b_j)\exp\left[\frac{(a_i + a_j - r_{ij})}{(b_i + b_j)}\right] - c_i c_j / r_{ij}^6$$
$$+ D_{1ij}\exp(-\beta_{1ij} r_{ij}) + D_{2ij}\exp(-\beta_{2ij} r_{ij})$$

	Z	a	b	c
O	-1.2	1.91	0.15	29.6
Si	2.4	0.86	0.09	0.0

	D_1	β_1	D_2	β_2
O-Si	31000	5.0	-3090	2.5

Potential Curves of SiO_2



ゼオライトの熱的挙動に関する研究

背景

ゼオライトの分子ふるい作用
　ゼオライトの細孔径に依存

ゼオライトの細孔径
　結晶構造から決定 振動により変動
　細孔径の温度変化　？

分子動力学法の利用

SiO_2ゼオライトの構造変化

負の熱膨張

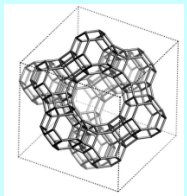
Faujasite　(Attfield and Sleight, 1998)
Chabazite and ITQ-4　(Woodcock and Lightfoot, 1999)
MWW, ITE, ISV, STF etc.

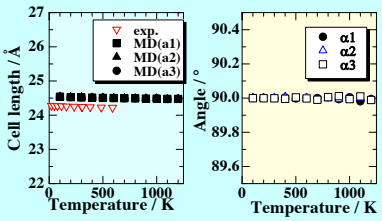
- Siliceous Ferrierite (Bull et al., 2003)
  Pnnm ⟷ Immm　**負の熱膨張）**
- MFI　monoclinic ⟷ orthorhombic

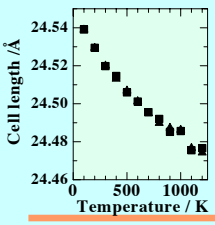
目的

– SiO_2組成ゼオライトの構造熱的挙動
　格子定数変化
　　Faujasite, Chabazite, ITQ-4, ZSM-11
　細孔径変化
　　ZSM-11

Faujasiteの構造変化

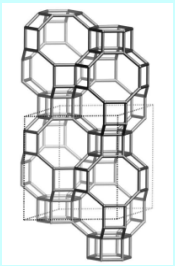


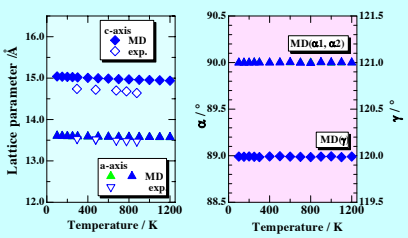




Cubic　：　維持
熱膨張係数　負

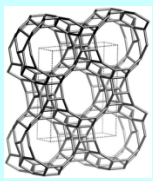
Chabazitの構造変化

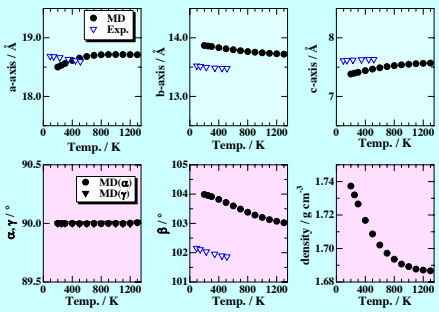




Hexagonal　維持
熱膨張係数　負

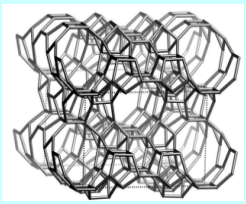
ITQ-4の構造変化



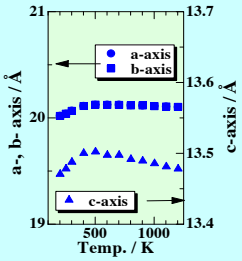


ZSM-11の構造変化

計算サイズ　unit cell 12個　(2×2×3
)

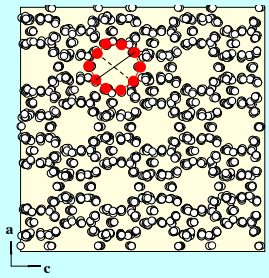


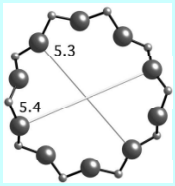
MD計算結果



400K　程度で対称性に変化　相転移？）(Fyfe et al.,1989)

ZSM-11の細孔構造

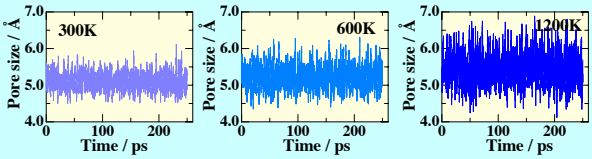


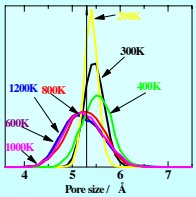


酸素イオンサイズ　2.7Å

ZSM-11の酸素原子の位置

細孔の熱挙動



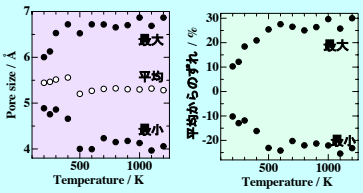


細孔径

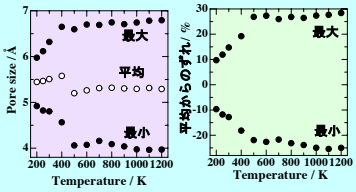
400K　まで　増加

600K　以上　分布が類似

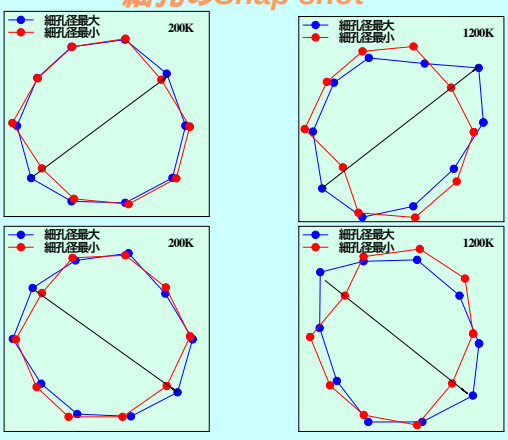
ZSM-11の細孔径変化



12 Unit cellの平均値



細孔のSnap shot



SiO_2ゼオライトの熱的挙動

Faujasite, Chabazite, ITQ-4

負の熱膨張を再現

ZSM-11

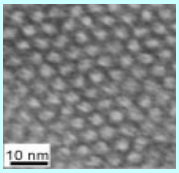
500Kから負の熱膨張

最大細孔径　400Kまで　大きく増加

600K以上　ほぼ一定

均一メソポーラスシリカのモデリング

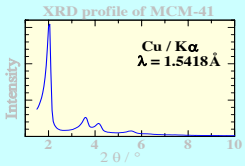
高表面積
均一細孔径
細孔構造の規則的な配列



多様な合成法

Cationic ion ($C_nH_{2n+1}N(CH_3)_3$ ion)
MCM-41
FSM-16 - hexagonal phase

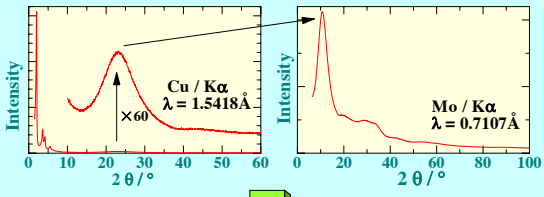
Block copolymer (PEO-PPO-PEO)
SBA-15



Pore Wall of Mesoporous silica

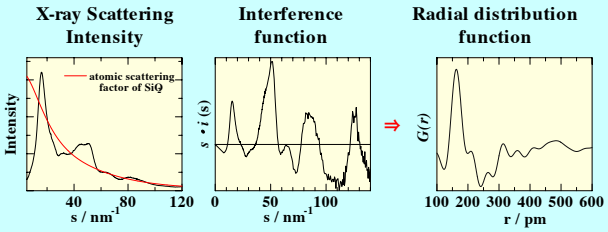
Amorphous $SiO_{2-x}(OH)_{2x}$

Structure Analysis ⇒ NMR, IR, EXAFS



Radial distribution function analysis using X-ray diffraction methods

Procedure of radial distribution function analysis



Fourier Transform

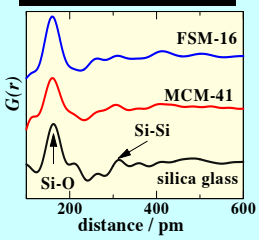
Composition of mesoporous silica

$SiO_{2-x}(OH)_{2x}$ ⇒ SiO_2

Intensity of X-ray scattering from H atom ⇒ little

Comparison of structure to Silica glass

Correlation Function



Results of XRD Analysis

Sample	r_{Si-O}*/ pm	r_{Si-Si}*/ pm	references
Silica glass	163	314	[4]
	162	312	[1]
MCM-41	161	307	[4]
	160	305	[2]
	160	300	[3]
FSM-16	160	310	[4]

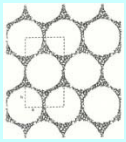
[1] Mozzi and Warren (1969)
[2] Pophal et al. (1997)
[3] Pophal and Fuess (1999)
[4] Ookawa et al. (2001)

Si-O distance MCM-41, FSM-16 = Silica glass
Si-Si distance MCM-41, FSM-16 < silica glass

Discussion in detail with structure model

Previous works - Modeling of MCM-41 using MD

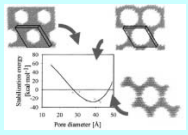
Feuston and Higgins, 1994



Parallel two micelles packed in a hexagonal arrangement

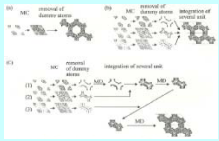
Relaxation at 900K

Kleestorfer et al., 2001



Modeling from quartz structure setting H^+ on the surface

Oumi et al., 2002



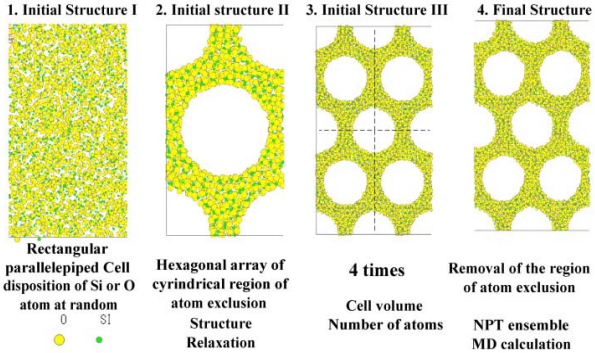
Modelingwith combination of MD and MC methods

The differences of the structure between the pore wall of MCM-41 and silica glass have not been discussed.

Aim of this work

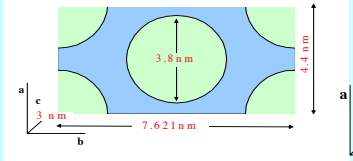
MCM-41 type silica was made under the different condition and the comparison of our experimental results.

Modeling method of MCM-41 type mesoporous silica by using molecular dynamics

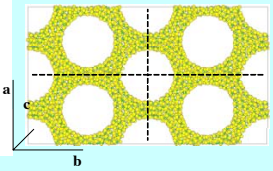


Initial Structure II and III

Initial Structure II



Initial Structure III



b/ a=$\sqrt{3}$

Hexagonal array of the cylindrical region of atom exclusion

MD calculation of SiO_2 melt under NVT ensemble

Relaxation 2500K ⇒ 300K

MD cell volume Number of atoms ⇨ 4 times

MD cell : a = 8.8 nm, b = 10.4 nm, c = 3.0 nm

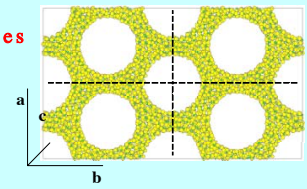
Removal of the region of atom exclusion

NPT ensemble (300 K, 0.1MPa) 200000 steps (40 ps)

Detail of the Initial Structure III

MD cell volume Number of atoms ⇨ 4 times

MD cell : a = 8.8 nm, b = 10.4 nm, c = 3.0 nm



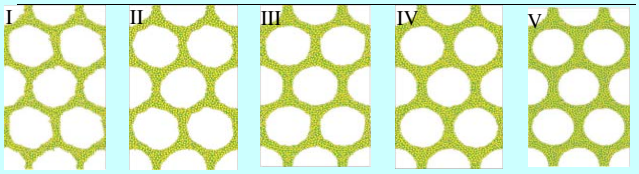
Removal of the region of atom exclusion

MD calculation: NPT ensemble (300 K, 0.1MPa)

200000 step (40 ps)

Modeling Conditions and Results

model	Initial Condition: Number of SiO_2 unit	Initial Condition: Density /g cm^{-3}	Final structure (after the MD calculation): Density /g cm^{-3}	a axis /nm	b axis /nm	c axis /nm
I	653	0.65	0.69	8.65	14.89	2.93
II	784	0.78	0.81	8.59	15.06	2.95
III	849	0.84	0.89	8.63	15.00	2.93
IV	996	0.99	1.00	8.66	15.28	2.98
V	1246	1.42	1.20	8.87	15.29	3.04



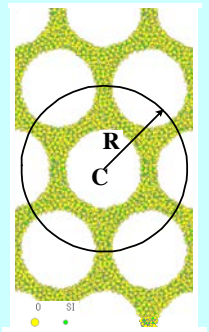
Cross-section shapes of mesopore

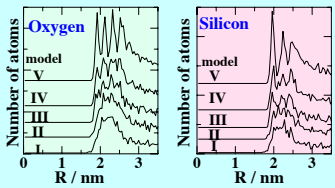
Model I, Model II, Model III — Hexagon

Model IV, Model V — Circle

Increasing the number of atom (Wall thickness)

Distribution of Si and O atoms



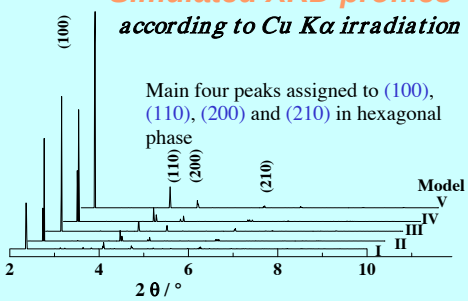


Oxygen : < 4 layers Silicon : < 3 layers

Pore wall < 3 SiO_4 layers

Simulated XRD profiles

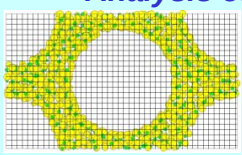
according to Cu Kα irradiation



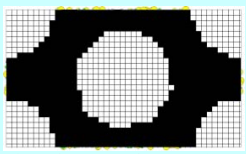
Main four peaks assigned to (100), (110), (200) and (210) in hexagonal phase

Relative peak intensity of (110) or (200), to (100) model II or III > model V.

Analysis of Pore Structure



Formation of 3D grid in the MD cell



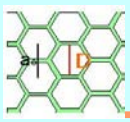
Determination of nature of each grid point

atomic cell — included in the Van der Waals sphere (Si:41 pm O:140 pm)

pore cell

Surface Area: Sum of Interfacial area between atomic cell and pore cell

Mean pore diameter: Estimated by pore volume and length of c-axis



Wall thickness $= a_0 - D$

Results of pore structure analysis and simulated XRD

Model	I	II	III	IV	V
Surface area / $m^2 g^{-1}$	1626	1181	1072	870	686
Pore volume / $cm^3 g^{-1}$	0.78	0.63	0.55	0.46	0.36
Pore diameter / nm	3.33	3.26	3.19	3.15	3.08
Wall density / g cm^{-3}	1.50	1.70	1.76	1.91	2.15
a_0 / nm	4.32	4.32	4.32	4.36	4.42
Wall thickness / nm	0.99	1.06	1.13	1.21	1.34

MCM-41 Sonwane et al., (1999)

Pore diameter/ nm	3.8
Surface area / $m^2 g^{-1}$	1240
Pore volume / $cm^3 g^{-1}$	0.93

$a_0 = 2 / \sqrt{3} \times d(100)$

Wall thickness

Experimental value by TEM (Kruk et al.,2000) ca. 1 -1.3 nm

Pore Volume

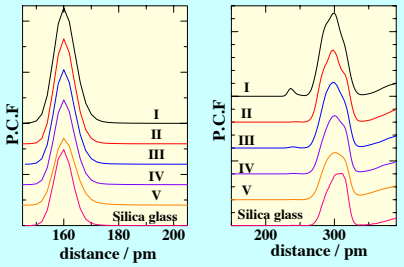
Simulation < Experiment

Calculation of pore volume will need to an improved program

Surface Area

Model I, II, III > 1000 $m^2 g^{-1}$

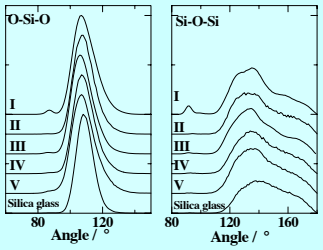
Pair correlation functions(PCF) of Si-O and Si-Si



Si-O : almost the same Si-Si : MCM-41 < silica glass

These results support strongly our experimental results

Distribution of bond angle of O-Si-O and Si-O-Si



O-Si-O angle

Internal angle of SiO_4 tetrahedra

Angle: MCM-41 < silica glass
Width of distribution: MCM-41 > silica glass

SiO_4 tetrahedra in the pore wall ⇒ strained

Si-O-Si angle

Angle between neighboring two SiO_4 tetrahedra

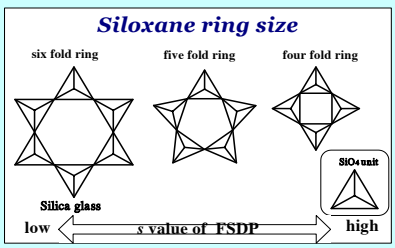
Distribution shift to low angle region compared to silica glass

Model I

Si-O-Si	87°
O-Si-O	92°
Si-Si (from PCF)	236 pm

⇒ No realistic model

Medium range order of amorphous silica



Summary

Modeling of MCM-41 type porous silica was performed by molecular dynamics simulation.

Some models have reproduced ca. 3 nm diameter and more than 1000 $m^2 g^{-1}$ surface area.

It is clear that MCM-41 type silica model have same Si-O interatomic distance and shorter Si-Si interatomic distance compared to silica glass.

MD calculation revealed that the mean Si-O-Si bond angle in MCM-41 type silica is smaller than that in silica. This result supports our experimental results.

喜望峰