Sifat-Sifat Katalis (Catalyst Properties)

(in CATALYST TECHNOLOGY Lecture)

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Instructor's Background

- BEng. (1995): Universitas Diponegoro
- Meng. (2000): Institut Teknologi Bandung
- PhD. (2006): Universiti Teknologi Malaysia

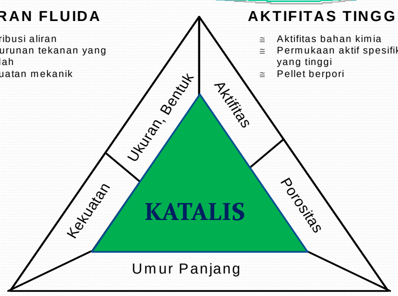
- Specialization:
  - Catalyst Design for Energy Conversion
  - Process Design for Energy Conversion
  - Combustion Engineering
  - Computational Fluid Dynamic (CFD)

ALIRAN FLUIDA

- Distribusi aliran
- Penurunan tekanan yang rendah
- Kekuatan mekanik

AKTIFITAS TINGGI

- Aktifitas bahan kimia
- Permukaan aktif spesifik yang tinggi
- Pellet berpori



STABILITAS

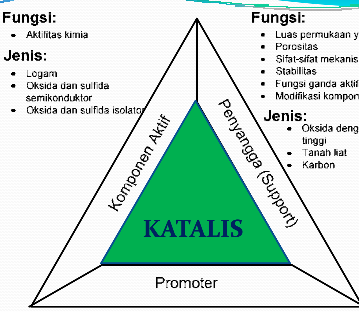
Tahan terhadap:
- sintering
- racun katalis
- fouling

Fungsi:
- Aktifitas kimia

Jenis:
- Logam
- Oksida dan sulfida semikonduktor
- Oksida dan sulfida isolator

Fungsi:
- Luas permukaan yang tinggi
- Porositas
- Sifat-sifat mekanis
- Stabilitas
- Fungsi ganda aktifitas
- Modifikasi komponen aktif

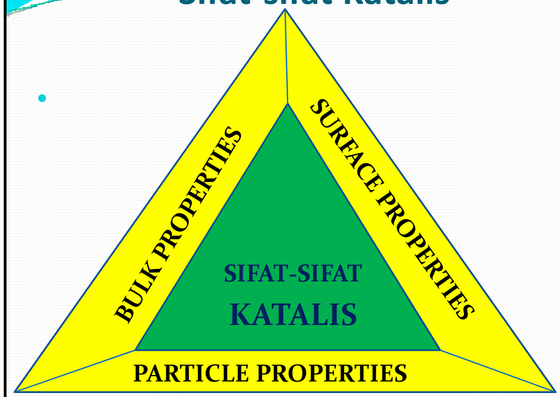
Jenis:
- Oksida dengan titik leleh tinggi
- Tanah liat
- Karbon



Fungsi pada support:
- Struktural
- Penghambat aktifitas
- Promosi aktifitas

Fungsi pada komponen aktif:
- Elektronik
- Morfologi
- racun

Sifat-sifat Katalis



BULK PROPERTIES

- **Bulk Properties** yang penting adalah:
  - Komposisi (composition)
  - Struktur Fase (phase structure)

Komposisi Katalis (*Catalyst Composition*)

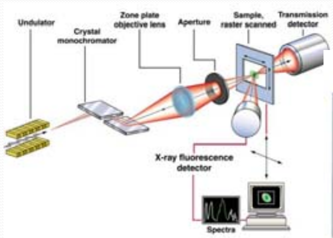
- **Identifikasi kualitatif dan kuantitatif** dari komponen-komponen **elemental** sebuah katalis adalah sesuatu yang penting
- Komponen-komponen penyusun tersebut termasuk juga kontaminan yang terdeposit selama pemakaian, misalnya:
  - Debu-debu
  - Racun dari umpan, misal: S, As, Pb, dan Cl
  - Kontaminan sekunder seperti Ni, Fe, V, Ca, dan Mg
  - dan karbon yang terdeposit selama pemakaian
- **Metode Penentuan**:
  - metode pelarutan
  - dan spektroskopi

Metode Pelarutan (*Solution Method*)

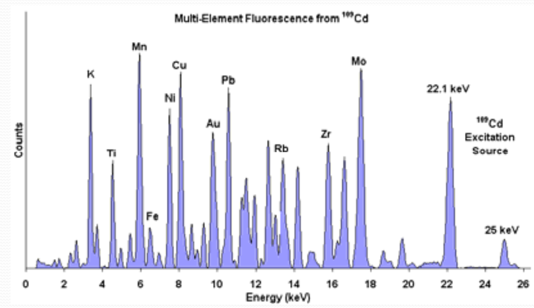
- Unsur yang akan diketahui dilarutkan dalam larutan tertentu sehingga menghasilkan warna larutan tertentu
- Kuantitas unsur tersebut dapat diukur melalui **ABSORPSI FOTOMETRIC (photometric absorption)**.
- Sebagai contoh : (pengukuran cobalt)
  - Baca buku Richardson halaman 137
- Standard-standar yang sudah ada; cobalt, nickel, molybdenum, dan platinum

Metode Spektroskopi

- Begin with ➔ **Atomic Emission Spectroscopy**
- The most versatile and often-used technique is: **X-RAY FLUORESCENCE (XRF)**.



Peaks Sample of XRF



Metode Spektroskopi Lainnya

- Atomic Absorption Spectroscopy (AAS)
- Inductively Coupled Plasma Spectroscopy (ICP MS)
- Analytical Electron Spectroscopy

Struktur Fase (*Phase Structure*)

- Struktur fase menjelaskan **identifikasi komponen** dengan membandingkan antara hasil karakterisasi dengan sampel senyawa murninya
- Beberapa metode yang umum dipakai adalah;
  - Metode Difraksi ➔ **X-RAY DIFFRACTION (XRD)**
    - Kristal atau non kristal (amorf)
    - Berapa persen kristalinitasnya
    - Komponen /komponen oksida per peak
  - Metode *Temperature Programmed* ➔ DTA, TGA dan TPR
    - DTA: Differential Thermal Analyzer ➔ measures energy change
    - TGA: Thermal Gravimetric Analysis ➔ measures energy change
    - TPR: Temperature Programmed Reduction

PARTICLE PROPERTIES

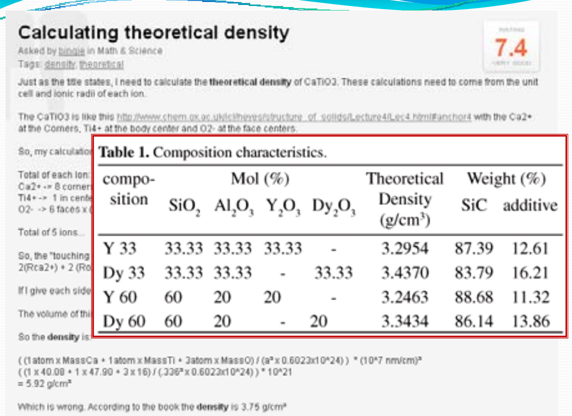
- Particle propesties untuk katalis terdiri dari:
  - *Densities*
  - *Particle size*
  - *Mechanical properties*
  - *Surface area*
  - *Pore size distribution*
  - *diffusivity*

Densities

- **Densities: mass per unit volume**
- Pertanyaan: **Volume yang mana ????**
- Ada **empat jenis Densities**:
  - *Theoretical Densities*
  - *Skeletal Densities*
  - *Particle Densities*
  - *Packing Densities*

Theoretical Densities

- Is ratio of the mass of a collection of discrete pieces of solid to the sum of the volumes of each pieces ➔ just one cell
- Ditentukan berdasarkan **karakteristik XRD**
- Maka disebut juga: **x-ray / unit cell density** atau **crystal densities**



Calculating theoretical density

Asked by bingie in Math & Science

Tags: density, theoretical

7.4

Just as the title states, I need to calculate the **theoretical density** of CaTiO3. These calculations need to come from the unit cell and ionic radii of each ion.

The CaTiO3 is like this http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/Lecture4/Lec4.html#anchor4 with the Ca2+ at the Corners, Ti4+ at the body center and O2- at the face centers.

So, my calculatio

Total of each ion:
Ca2+ -> 8 corner
Ti4+ -> 1 in cent
O2- -> 6 faces x

Total of 5 ions...

So, the "touching
2(Rca2+) + 2 (Ro

If I give each side

The volume of thi

So the **density** is:

((1atom x MassCa + 1atom x MassTi + 3atom x MassO) / (a^3 x 0.6023x10^24)) * (10^7 nm/cm)^3
((1 x 40.08 + 1 x 47.90 + 3 x 16) / (.336^3 x 0.6023x10^24)) * 10^21
= 5.92 g/cm^3

Which is wrong. According to the book the **density** is 3.75 g/cm^3

Table 1. Composition characteristics.

composition	Mol (%)				Theoretical Density (g/cm^3)	Weight (%)	
	SiO_2	Al_2O_3	Y_2O_3	Dy_2O_3		SiC	additive
Y 33	33.33	33.33	33.33	-	3.2954	87.39	12.61
Dy 33	33.33	33.33	-	33.33	3.4370	83.79	16.21
Y 60	60	20	20	-	3.2463	88.68	11.32
Dy 60	60	20	-	20	3.3434	86.14	13.86

Skeletal Densities

- Volume didefinisikan sebagai **jumlah volume solid material dan semua pori-pori tertutup di dalam padatan**
- Pori-pori ini tidak dapat dimasuki oleh fluida apapun
- Dinamakan juga dengan **Helium Density**

TABLE 7.1. Example of Densities 7 wt % NiO/Al_2O_3

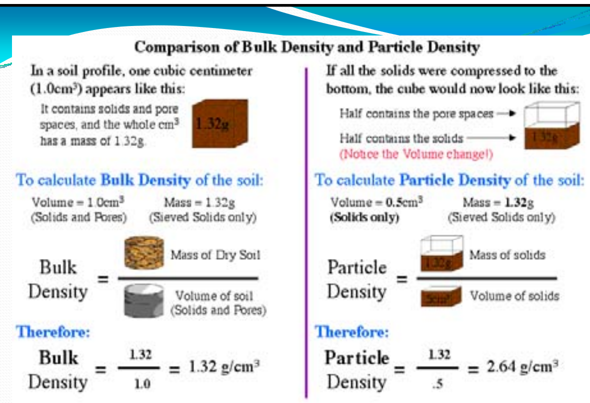
Density	Value
Theoretical, d_t	3.89 g cm^{-3} (crystal)
Skeletal, d_s	2.39 g cm^{-3} (solid + closed pores)
Particle, d_p	1.22 g cm^{-3} (pellet)
Packing, d_b	0.732 g cm^{-3} (bed)
	ε = 0.40
	θ = 0.49

Particle Densities

- Volume didefinisikan sebagai **jumlah volume padatan, pori-pori tertutup, dan pori-pori yang dapat diakses di dalam partikel**
- Atau dinamakan juga Volume Partikel
- Disebut juga **Mercury Density** atau **True Density**
- Persamaan:

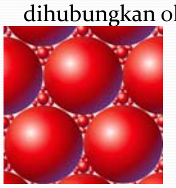
$$\theta = \left(1 - \frac{d_p}{d_s}\right)$$

- θ : porosity; d_p: particle densities; and d_s: skeletal densities

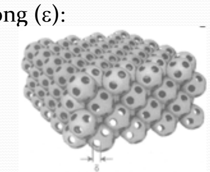


Packing Density

- Volume didefinisikan sebagai **jumlah volume padatan, pori-pori tertutup, dan pori-pori yang dapat diakses di dalam partikel, serta volume ruang kosong antar partikel**
- Dinamakan juga **Bulk Density** atau **Bed Density**
- Packing Density (d_b) dan Particle Density dihubungkan oleh fraksi ruang kosong (ε):



$$\varepsilon = \left(1 - \frac{d_b}{d_p}\right)$$



Ukuran Partikel

- Metode pengukuran: sieving, optical and electrical imaging, light scattering, light shadowing, elutriation, sedimentation, electrical resistance, impaction, dan nozzle pressure drop

TABLE 7.2. Typical Results for a Particle Size Distribution Silica-Alumina Cracking Catalyst

Size range (μm)	Distribution (wt%)
0-20	3
20-45	35
45-60	25
60-90	25
90+	12

Mechanical Properties

- **Crushing Strength** ➔ kekuatan mekanik dari katalis, tahan tekanan atau tidak

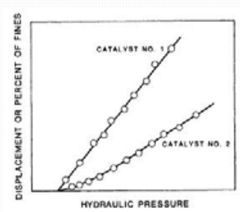


Figure 7.7. Results of bulk crushing strength tests.

- **Loss on Attrition** ➔ seberapa besar yang lolos pada screening dengan ukuran tertentu. Kehilangan kurang dari 1 persen berat dapat diterima

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- **Loss on Ignition (LOI)**
  - The loss on ignition is reported as part of an elemental or oxide analysis of a mineral.
  - The volatile materials lost usually consist of "combined water" (hydrates and labile hydroxy-compounds) and carbon dioxide from carbonates.
  - It may be used as a quality test, commonly carried out for minerals such as iron ore.
  - For example, the loss on ignition of a fly ash consists of contaminant unburnt fuel.

Surface Area

- Texture dari katalis termasuk: **surface area**, **pore size distribution**, dan **bentuk**.
- Metode pengukuran ➔ **physical adsorption**
- Baca Richardson halaman 146 – 151
- **Persamaan Langmuir** ➔ low pressure monolayer

$$\frac{V}{V_M} = \frac{Kp/p_0}{(1 + Kp/p_0)}$$

- **Persamaan BET** (Brunauer, Emmett, Teller):

$$\frac{V}{V_M} = \frac{cp}{[p_0 - p][1 + (c-1)p/p_0]}$$

TABLE 7.3. Differences between Physical and Chemisorption

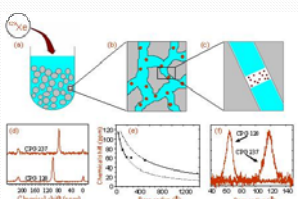
Property	Physical adsorption	Chemisorption
1. Forces responsible	Physical van der Waals electrostatic forces	Chemical bonds, ionic, covalent
2. Heat of adsorption (exothermic)	Low (<10 kcal mole^{-1}) similar to liquefaction	Moderate to high (10–50 kcal mole^{-1}) similar to reactions
3. Activation energy	None	Low (<15 kcal mole^{-1}) to moderate (25 kcal mole^{-1})
4. Specificity	None	Specific adsorbate-adsorbent interactions
5. Reversibility	Complete, rapid	Slow
6. Extent	Multilayers	Monolayer saturation

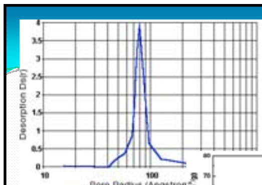
TABLE 7.4. Typical Surface Areas for Catalysts

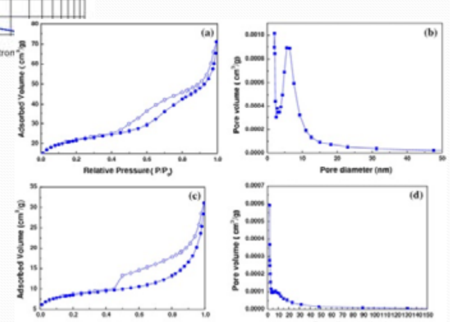
Catalyst	Use	S_g (m^2 g^{-1})
REHY zeolite	Cracking	1000
Activated carbon	Support	500–1000
SiO_2–Al_2O_3	Cracking	200–500
CoMo/Al_2O_3	Hydrotreating	200–300
Ni/Al_2O_3	Hydrogenation	250
Fe–Al_2O_3–K_2O	Ammonia synthesis	10
V_2O_5	Partial oxidation	1
Pt gauze	Ammonia oxidation	0.01

Pore Size Distribution

- Pengukuran:
  - Macropores ➔ mercury porosimeters
  - Mesopores ➔ nitrogen adsorption-desorption isotherm
- Baca Richardson halaman 151 - 155







Diffusivity

- Merupakan sifat katalis yang paling sulit diukur

SURFACE PROPERTIES

- **Katalis adalah surface-active agent**, oleh karena itu pengukuran fenomena-fenomena di permukaan katalis adalah sangat krusial
- Sifat-sifat permukaan katalis meliputi:
  - **Morphology** (shape and size, crystallite size) and **composition**
  - **Structure**
  - **Dispersion** (fraksi atom aktif di permukaan katalis) ➔ chemisorption isotherm, reaction titration, poison titration
  - **Acidity** ➔ jenis *acidity, acid strength, distribution of acid strength*
  - **Activity** ➔ kinetics and practical in reactor system

Deskripsi Tugas Kuliah Teknologi Katalis