Novel Application of Delafossite Materials

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Out Line

- What is delafossite
- p-type transparent semiconductor thin films
- The other functions of delafossite materials
  (Novel functions developed in our Lab.)
- Nanocomposite catalyst derivate from delafossite nanopowder
- Summary

What is delafossite (赤銅鐵礦)

RED COPPER IRON MINERAL

This sample of delafossite is displayed in the Smithsonian Museum of Natural History.
http://www.mwit.ac.th/~physicslab/hbase/minerals/delafossite.html

- Delafossite is an oxide of copper along with iron with the composition $CuFeO_2$.
- ABO_2
  - A=Ag, Cu, Pd, Pt
  - B= Al, Cr, Ga, Fe, Mn, Co, Rh, Ni, In, La, Nd, Sm, Eu, Y and Ti.
  - e.g. $CuAlO_2$, $CuCrO_2$

JOURNAL OF SOLID STATE CHEMISTRY 40, 170–174 (1981)

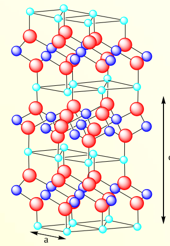
Single-Crystal Growth and Crystal Structure Refinement of $CuAlO_2$

T. ISHIGURO, A. KITAZAWA, N. MIZUTANI, AND M. KATO*

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Received April 6, 1981; in revised form July 9, 1981

Single crystals of the delafossite-type c
slow-cooling method from 1200°C. Three
columnar twin crystals with concave ang
the spinel-type twin. $CuAlO_2$ is rhombob
g/cm³ and *Dm* = 5.06 g/cm³. The crysta



Crystal structure of delafossite (Rhombohedral 3R)

35 石黒 隆ほか
窯業協会誌 92 [1] 1984 25

論 文・Paper

デラフォサイト型化合物における８面体層の変形

石黒　隆・石沢伸夫・水谷惟恭・加藤誠軌
（東京工業大学 工学部 無機材料工学科）

デラフォサイト（delafossite, $CuFeO_2$）型構造をとる約30種の $A^+B^{3+}O_2$ 化合物の格子定数か
ら結晶構造パラメーターを求め，BO_6 8面体の偏平度が B^{3+} イオンの半径 r_B とともに増加し，そ
の様子が r_B=0.8~0.9 Å 付近を境に大きく変わることなどの現象を見いだし，このような BO_6 8
面体層の異常な挙動をイオン結晶の格子エネルギーと A-O-B 結合の共有結合性とから議論した．

（1983年5月13日受付）

Transparent p-type conductive thin films

*H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, *Nature (London)*, **389** (1997) 939-942

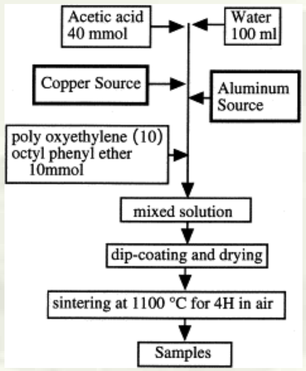
Materials	Transmittance (%)	Energy gap (eV)	Conductivity (S/cm)	Preparation method
$CuAlO_2$	70	3.5	0.34	PLD
$CuGaO_2$	80	3.6	0.063	PLD
$CuGa_{1-x}Fe_xO_2$	60	3.4	1.0	PLD
$CuIn_{1-x}Ca_xO_2$	70	3.9	0.028	PLD
$CuCrO_2$	40	3.1	1.0	PLD
$CuCr_{1-x}Mg_xO_2$	50	3.1	220	RF-sputtering
$CuYO_2$	60	3.5	0.025	PLD
$CuY_{1-x}Ca_xO_2$	50	3.5	1.05	PLD

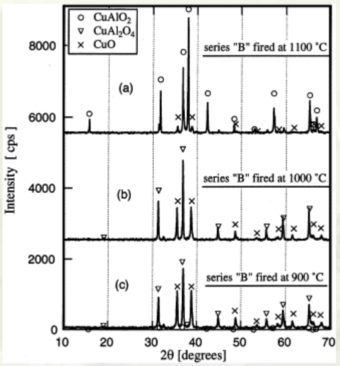
Preparation of $CuCrO_2$ thin films by chemical solution method

NSC-98-2218-E-027-004 (2009.1-2009-10)

- PLD is difficult to prepare on wide area.
- Vacuum system is expensive for industrial application.
- Challenge in wet chemical process
  - Difficult to obtain pure delaffosite phase (easy to form spinel phase $CuCr_2O_4$ and residue CuO)
  - Thin film quality always lower than prepared by vacuum method.
  - High process temperature

Properties of copper–aluminum oxide films prepared by solution methods





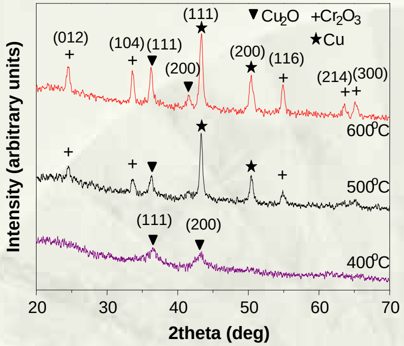
K. Tonooka et. al, Thin solid films, 411, 2002, p129

Preparation of p-type conductive transparent $CuCrO_2$:Mg thin films by chemical solution deposition with two step annealing

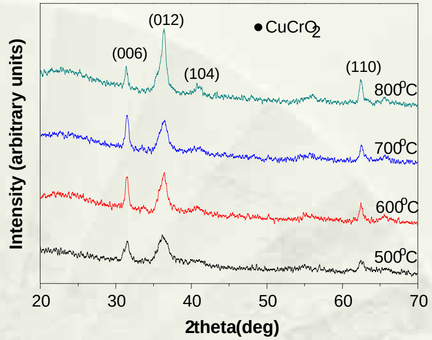
- Solid state reaction :
- $2CuO + 2Cr_2O_3 \rightarrow CuCr_2O_4 + CuO$ 700 °C
- $CuCr_2O_4 + CuO \rightarrow 2CuCrO_2 + 1/2O_2$ 1050 °C

- ***Strategies of two step annealing***
- $2CuO + H_2 \rightarrow Cu_2O + H_2O$ 400 °C
- $Cu_2O + Cr_2O_3 \rightarrow CuCrO_2$ 500 °C

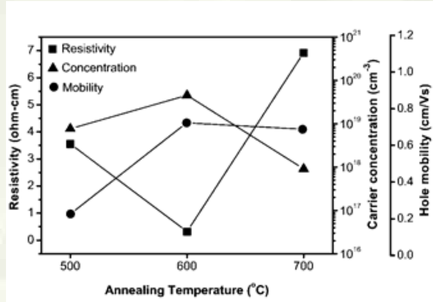
Two-step Annealing



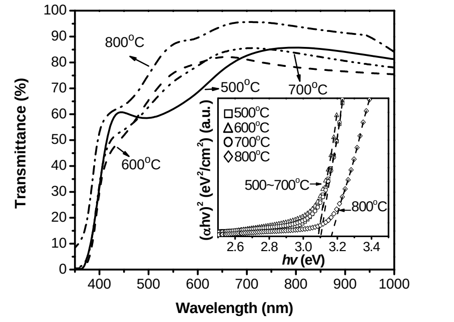
GIXRD pattern of Cu-Cr-O thin films annealed at various temperatures under forming gas ambient



GIXRD patterns of the $CuCrO_2$:Mg thin films prepared with two-step annealing.



Resistivity, Hall mobility, and carrier concentration of $CuCrO_2$:Mg thin films prepared with two-step annealing, annealing



Optical transmittance spectra of $CuCrO_2$:Mg thin films prepared with two-step annealing. The inset shows the absorption edge of $CuCrO_2$:Mg thin films.

Reported electrical and optical properties of $CuCrO_2$:Mg thin films

Composition	Method	Process temperature (°C)	Resistivity (Ω-cm)	Transmittance (%)	Thickness (nm)	Ref.
$CuCr_{0.95}Mg_{0.05}O_2$	Sputtering	600	0.045	30	250	R. Nagarajan, et. al, J. Appl. Phys., 89 (2001) 8022
$CuCr_{0.95}Mg_{0.05}O_2$	PLD	500	0.1	60	100	My work in AIST Thin solid films, 516 (2008) 5941
		600	0.5	60	100	
$CuCr_{0.93}Mg_{0.07}O_2$	Splay Pyrolysis, Ar annealing	800	1	80	155	S. H. Lim et. al, J. Phys Chem., 69 (2008) 2047
$CuCr_{0.95}Mg_{0.05}O_2$	Sol-gel, Ar annealing	600	16	21	210	S. Götzendörfer et. al, J. Sol-Gel Sci Technol 52 (2009) 113
		700	210	32	200	
$CuCr_{0.95}Mg_{0.05}O_2$	CSD, Two-step annealing	500	3.55	50	197	This work Te-Wei Chiu et. al, Ceramics International, accepted
		600	0.32	70	195	
		700	6.92	70	195	

The other functions of $CuCrO_2$

- Transparent p-type conductive thin films
- Antibacterial — New! We are the first to demonstrate this function
- Photo catalyst for Hydrogen generation
- Photo catalyst for environmental applications
- Ozone gas detector
- Gas purification catalyst
- Additives for the catalytic combustion
- Thermoelectric materials

Surface area

Antibacterial properties (*E. coli*)

Incubated with glass substrate.

Incubated with $CuAlO_2$/glass substrate.

Potential application of transparent antibacterial thin films

- Touch panel
- Artificial-tooth, glasses
- Antifouling
  - Sightseeing submarine
  - Aquarium box

Photo catalyst for Hydrogen generation

Comparative study of $CuMO_2$ synthesized via solid state reaction

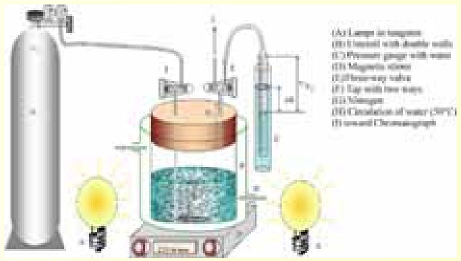
	$\sigma \times 10^6$ $(\Omega cm)^{-1}$	ΔE (eV)	s (μV/K)	$\mu \times 10^6$ ($cm^2 V^{-1} s^{-1}$)	V_{fb} (V/sce)	E_g (eV)	VH_2 (cm^3)	η (%)
$CuFeO_2$	78.74	0.18	600	5.6	0.1	1.30	2.05	0.125
$CuCrO_2$	4.176	0.22	660	5.6	−0.02	1.32	1.70	0.081
$CuAlO_2$	40	0.17	2035	4	−0.11	1.34	1.45	0.088
$CuMnO_2$	20	0.50	550	80	0.15	1.25	1.20	0.057

All oxides are prepared from solid state reaction.

The main physical properties of p-$CuCrO_2$ synthesized through SSR[a] and NR[b]

Oxide	$\sigma \times 10^6$ $(\Omega cm)^{-1}$	s (μVK^{-1})	ΔE (eV)	L (nm)	S_{sp} (m^2/g)	N_A/N_D (%)	$\mu \times 10^6$ ($cm^2 V^{-1} s^{-1}$)	E_g (eV)	V_{fb} (V/sce)
$CuCrO_2$	4.176	660	0.22	38	28.70	0.05	2.46	–	−0.02
$CuCrO_2$	6.412	520	0.25	32	34.09	0.24	0.74	1.32	–

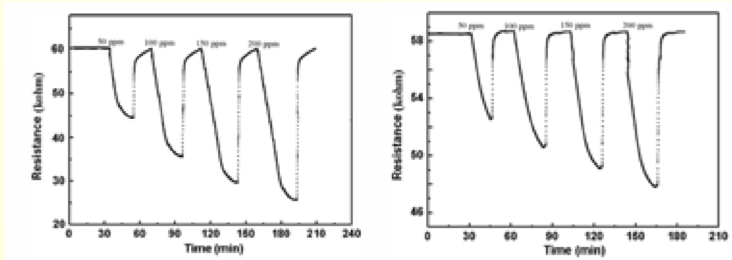
[a] Solid state reaction.
[b] Nitrate route.



Apparatus for measuring H_2 generation efficiency

S. Saadi, A. Bouguelia, M. Trari, *Solar Energy*, **80** (2006) 272

Room temperature ozone senser



Electrical resistance changes at room temperature of $CuCrO_2$ (a)nano crystal and (b)micro crystal due to successive increases in O_3 concentration.

S. Zhou, X. Fang, Z. Deng, D. Li, W Dong, R. Tao, G. Meng, T. Wang, *Sensors and Actuators B*, **143** (2009) 119.

EXHAUST GAS PURIFICATION CATALYST

- Japanese Patent: No.2008-156130
- DELAFOSSITE TYPE OXIDE, METHOD FOR MANUACTURING THE SAME AND EXHAUST GAS PURIFICATION CATALYST
- PROBLEM TO BE SOLVED: To provide a delafossite type oxide having high oxygen storage capacity from a low temperature range without requiring the presence of a noble metal, a method for manufacturing the same and an exhaust gas purification catalyst.
- SOLUTION: the delafossite type oxide of 3R type is represented by the general formula：ABOx, wherein A represents at least one selected from the group consisting of Cu, Ag, Pd and Pt; and B represents at least one selected from the group consisting of Al, Cr, Ga, Fe, Mn, Co, Rh, Ni, In, La, Nd, Sm, Eu, Y and Ti.

THERMOELECTRIC MATERIAL

- Japanese Patent: 2007-149996
- LAYERED OXIDE THERMOELECTRIC MATERIAL HAVING DELAFOSSITE STRUCTURE
- PROBLEM TO BE SOLVED: To develop p-type and n-type oxide thermoelectric materials being chemically stable at a high temperature and having a dimensionless figure of merit ZT close to 1.
- SOLUTION: The P-type thermoelectric conversion material is composed of a layered oxide having a delafossite structure shown in general formula $CuCr_{1-x}$ Mgx O_2 ($0.03 \leq x \leq 0.05$). Mg^{2+} with an ion radius near that of Cr^{3+} is substituted for Cr^{3+} of $CuCrO_2$ and carriers are introduced, and a figure of merit Z ($Z=S^2 \sigma/\kappa$) can be enhanced by improving an electric conductivity σ. The excellent electric conductivity is obtained at the high temperature of 600 to 1,100 K, and a Seebeck coefficient reaches 200 to 350 μV/K. The dimensionless figure of merit ZT exceeds 0.2 at 1,100 K, and the p-type thermoelectric conversion material is available as a high-temperature thermoelectric power-generation material.

Additives for the catalytic combustion

- Cu-Cr-O nanocomposites that can be used as additives for the catalytic combustion of AP(ammonium perchlorate)-based solid-state propellants.
- The Cu-Cr-O composites in recent years are found great promising in application as burning rate catalysts (ballistic modifier) for solid propellants used in defense (ballistic missiles) and space vehicles (rocket propellants).
- Addition of the Cu-Cr-O nanocomposites as catalysts obviously enhances the burning rate as well as lowers the pressure exponent of the AP-based solid-state propellants.

LI Wei, CHENG Hua J. Cent. South Univ. Technol. (2007)03−0291−05

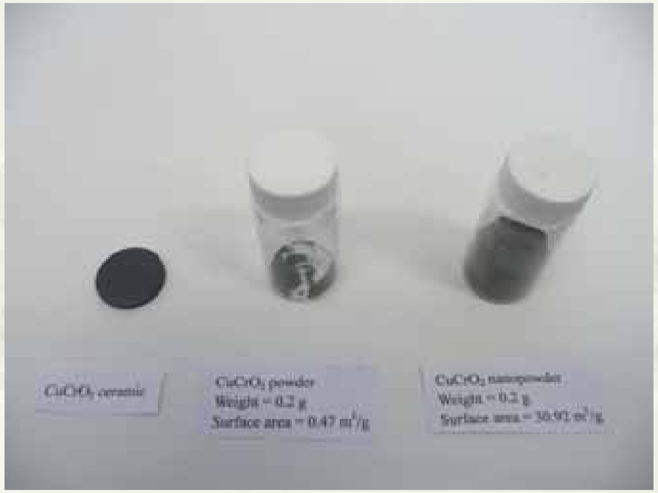
Various type of sugar

Rock candy

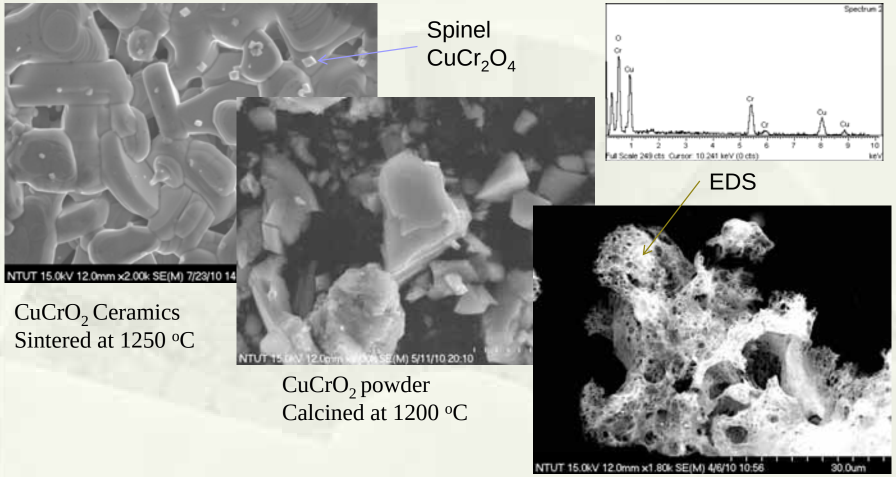
Granulated sugar

Cotton candy

Various type of $CuCrO_2$



Microscopic view



$CuCrO_2$ Ceramics
Sintered at 1250 ^oC

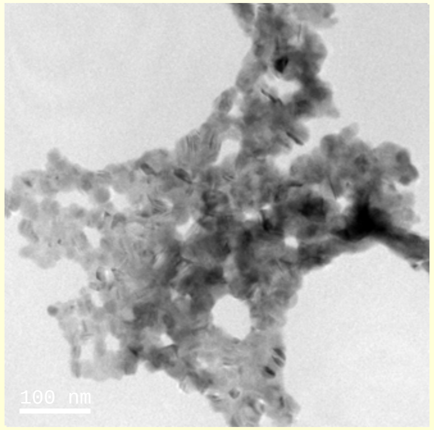
$CuCrO_2$ powder
Calcined at 1200 ^oC

Porous $CuCrO_2$ powder

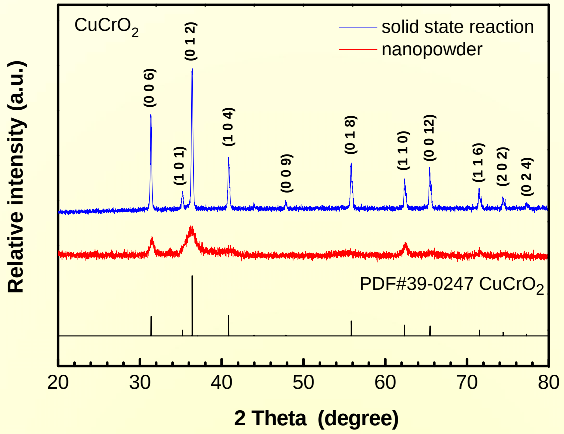
Synthesis of $CuCrO_2$ powder

- Solid state reaction
  - The particle size of $CuCrO_2$ powder prepared by traditional solid state reaction is in micro order
  - Easy to contain spinel impurities ($CuCr_2O_4$)
  - In order to obtain pure derafossite phase :High calcination temperature and controlled atmosphere was required (High energy consumption)
- Our method
  - Burning the raw material by ignition (self combustion)
  - With out high temperature furnace
  - Just under air

Porous $CuCrO_2$ powder

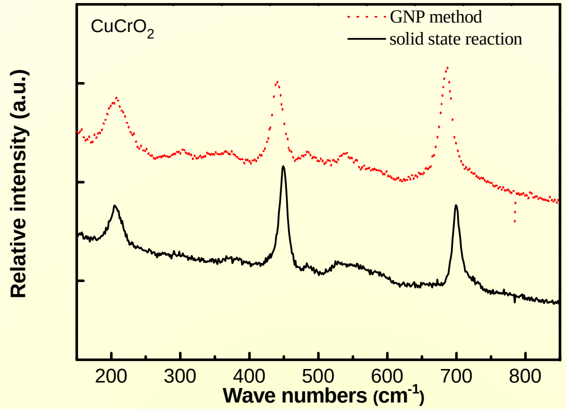


XRD

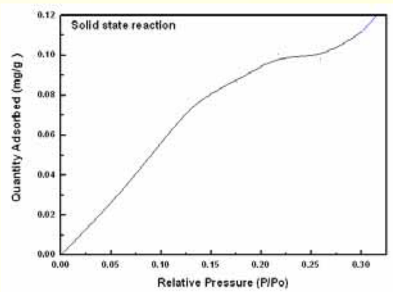


Depend on Scheller Eq. the crystalline size of $CuCrO_2$ are 45.65 and 10.2 nm, respectively.

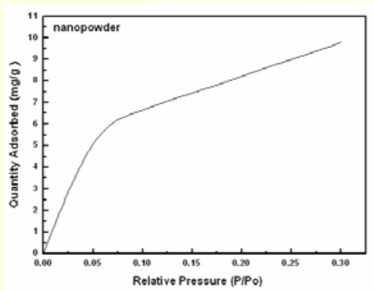
Raman spectra



Absorption isotherms



Absorption isotherms of $CuCrO_2$ power prepared by solid state reaction.
Surface area = 0.47 m^2/g



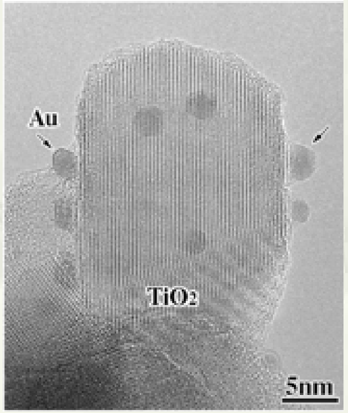
Absorption isotherms of $CuCrO_2$ nano powder
Surface area = 30.92 m^2/g

Composite catalyst derived from Delafossite

- Use delafossite it-self as a catalyst
  - Photo catalyst
  - Gas purification
  - Combustion catalyst
- Cu-base catalyst derived from delafossite
  - Steam reforming
  - CO oxidation
- **Supported metal cluster**
  - Using delafossite as a supporter materials
  - CO selective oxidation
  - Preparation method
    - Co-precipitation
    - Deposition-precipitation
    - Chemical vapor deposition
    - Laser vaporization
    - Modified wet impregnation
    - Photo-deposition

Au nano particle catalyst

Developed by Prof. Haruta (U. of Metro. Tokyo)



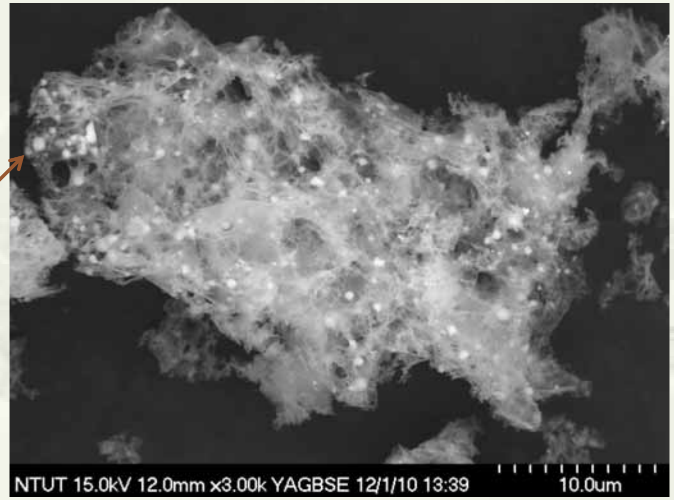
Au/TiO_2

Co-precipitated
Calcined at 400°C

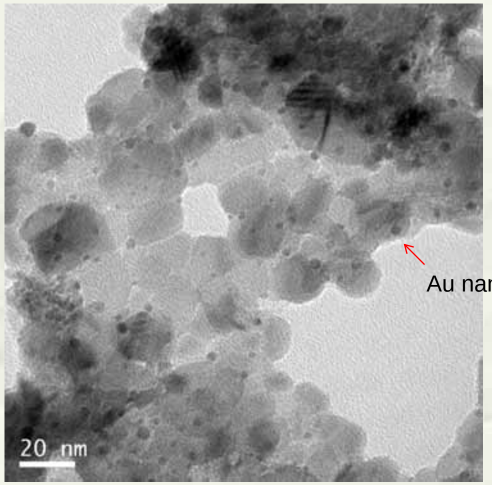
Semispherical Au particle supported on TiO_2

Failed experiment?

Very large Au Cluster



$Au/CuCrO_2$ nano composite

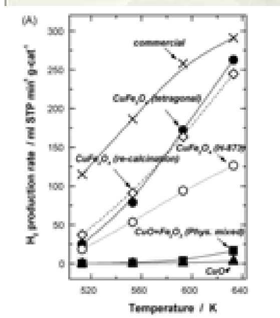


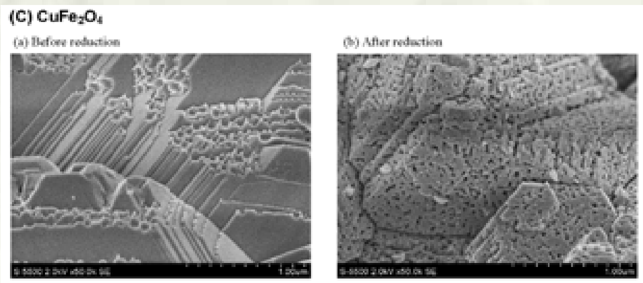
Application on steam reforming

Self-assembled porous nano-composite with high catalytic performance by reduction of tetragonal spinel $CuFe_2O_4$

Satoshi Kameoka[a,*], Toyokazu Tanabe[a], An Pang Tsai[a,b]

[a] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] National Institute of Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, Japan





Applied Catalysis A: General 375 (2010) 163–171

Results of catalytic reaction test for nano $CuCrO_2$

Reported by Satoshi Kameoka IMRAM, Tohoku University

◎ Catalyst pretreatment

- $CuCrO_2$: [I] H_2 treatment 300ºC for 1h.
  [II] H_2 treatment 600ºC for 1h.

$CuCrO_2$ → Cu* + Cr_2O_3 (reductive decomposition)

($2CuCrO_2$ + H_2 → 2Cu + Cr_2O_3 + H_2O)

◎ Reaction

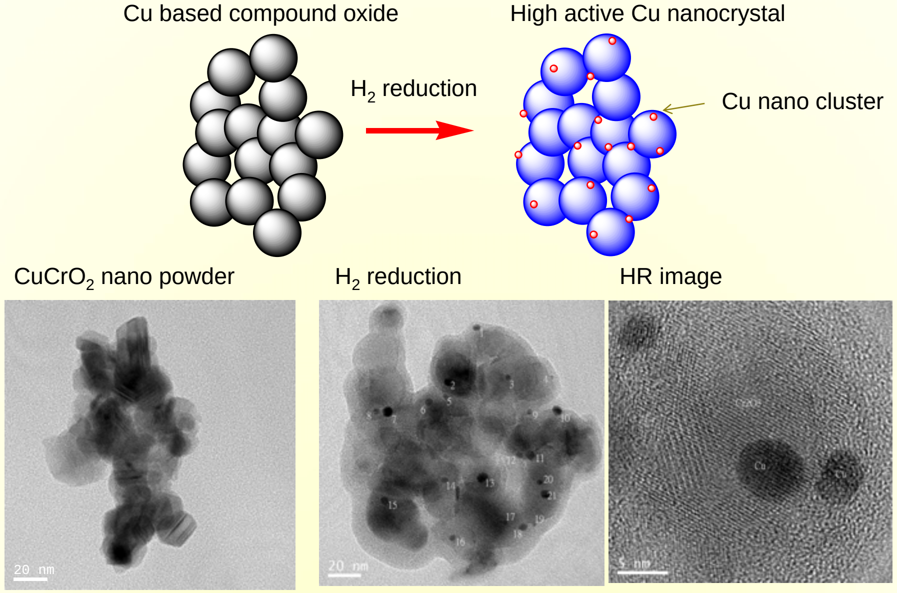
- Reactor : a conventional fixed bed flow reactor
- Reaction : Steam reforming of methanol (SRM)

$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$

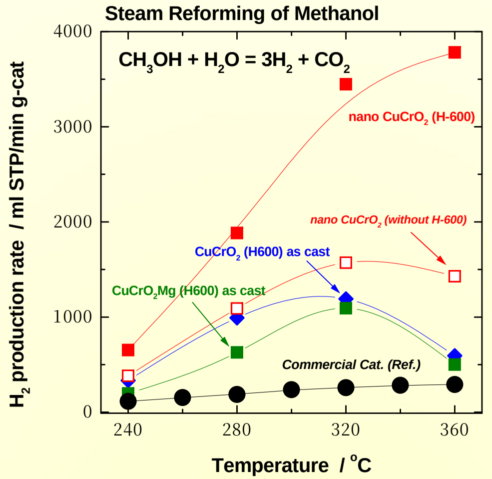
CH_3OH/H_2O = 2/3 (mol ratio)

LHSV= 15 h^{-1} (SV=85000 h^{-1}, F/W=7000 mlg-1h^{-1})

- pretreatment: at 300 ºC with H_2 for 1h.
- analysis : an on-line GC (Shincarbon: H_2, CO_2, CO, CH_4)



Ref: http://www.nedo.go.jp/informations/events/190710/shiryou/oral14-1.pdf



Ref: commercial Cu/Al/Zn catalyst

S. Kameoka, et. al, Applied Catalysis A: General 375 (2010) 163–171

Summary

- Conductive and transparent p-type $CuCrO_2$:Mg thin films were prepared by chemical solution deposition with two step annealing.
- Antibacterial properties of delafossite thin films such as $CuAlO_2$ and $CuCrO_2$ were demonstrated
- Highly porous $CuCrO_2$ nanopowder were performed by self-combustion process in air.
- High performance steam reforming catalyst were derived from $CuCrO_2$ nanopowder.
- $CuCrO_2$ supported Au nano cluster were synthesized by photo catalytic reduction.