アークプラズマ法によって調製した高分散担持金属触媒の局所構造解析

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Introduction

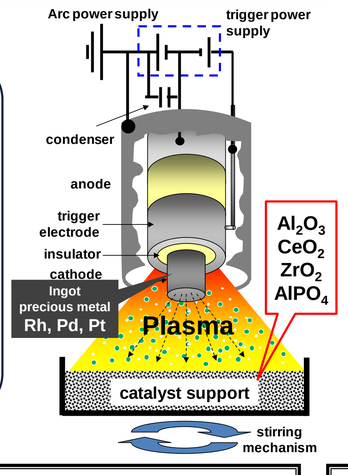
Conventional catalyst preparation (Impregnation) = Multistage process

Ingot precious metal → Loss → Powder → Loss → Water-soluble salt → Loss → Supported catalyst

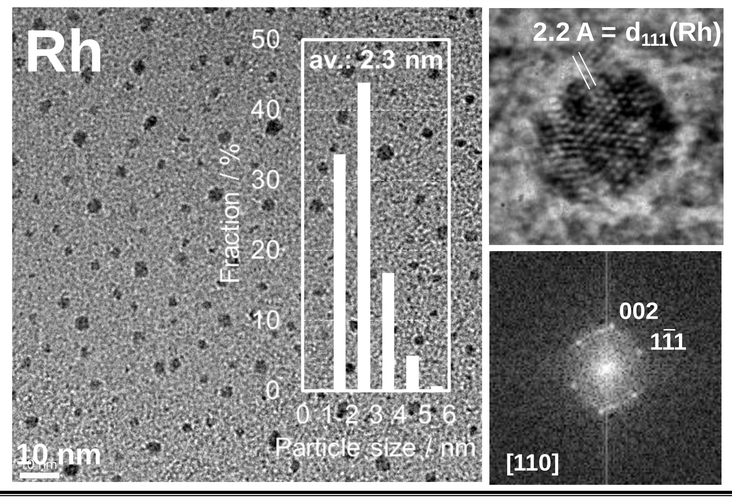
Arc-plasma (AP) preparation = Directly deposition

(1) enhanced catalyst activation, selectivity and lifetime
(2) a highly dispersed active species
(3) reduced energy requirements
(4) shortened preparation time

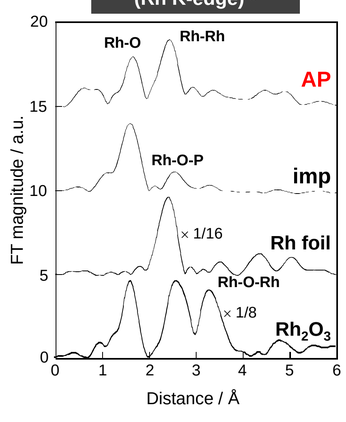
C.-j. Liu et al., *Catal. Today* 72, 173 (2002).



Unsupported Rh nanoparticles prepared by arc-plasma process

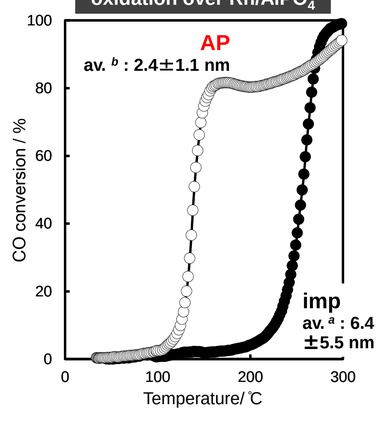


EXAFS of $Rh/AlPO_4$ (Rh K-edge) [a]



[a] Interval of *k*-space to *r*-space of FT is 3.0-13.8 Å^{-1}.
[b] Average size of Rh nanoparticles on $AlPO_4$.

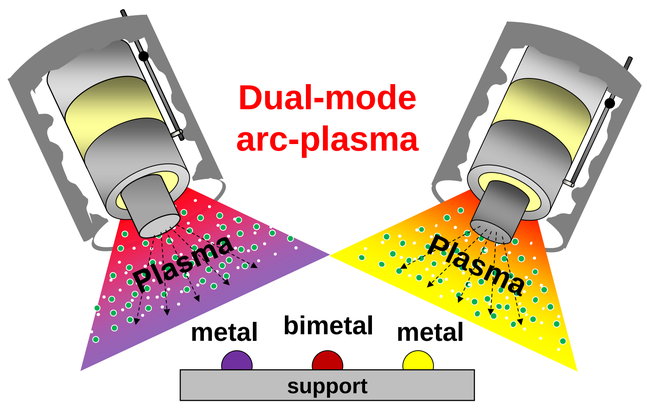
Catalytic activity for CO oxidation over $Rh/AlPO_4$



S. Hinokuma et al., *Top. Catal.*, 52, 2108 (2009).
S. Hinokuma et al., *Catal. Today*, 175, 593 (2011).
S. Hinokuma et al., *Bull. Chem. Soc. Jpn*, in press.

In this work

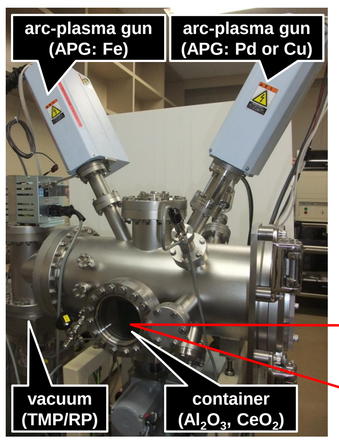
previous research



1. to clarify effects of synchronous and asynchronous pulse deposition
2. to evaluate a local structure and catalytic performance
3. to compare with catalytic properties of wet-impregnation (imp) catalysts

Experimental

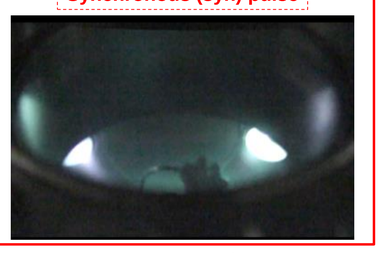
Experimental setup of dual arc-plasma



Preparation condition

- Supports : Al_2O_3, CeO_2
- Cathodes : Fe and M (M=Pd, Cu)
- Pressure : 1.0×10^{-3} Pa
- Discharge voltage: 125 V
- Condenser capacity: 360 μF

Synchronous (syn) pulse



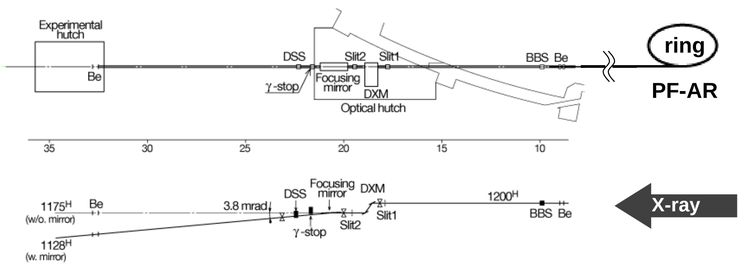
Fe-M/Al_2O_3 or CeO_2 syn asyn (fresh) → 900 ˚C, 25 h, 10% H_2O/air → (aged)

Characterization

- XRD
- XRF
- XPS
- Specific surface areas (S_{BET})
- FT-IR
- Metal dispersion (CO chemisorption)
- HRTEM
- CO oxidation catalytic activity test (0.1% CO, 1.25%O_2, He balance, W/F=5.0×10^{-4} g·min·cm^{-3})

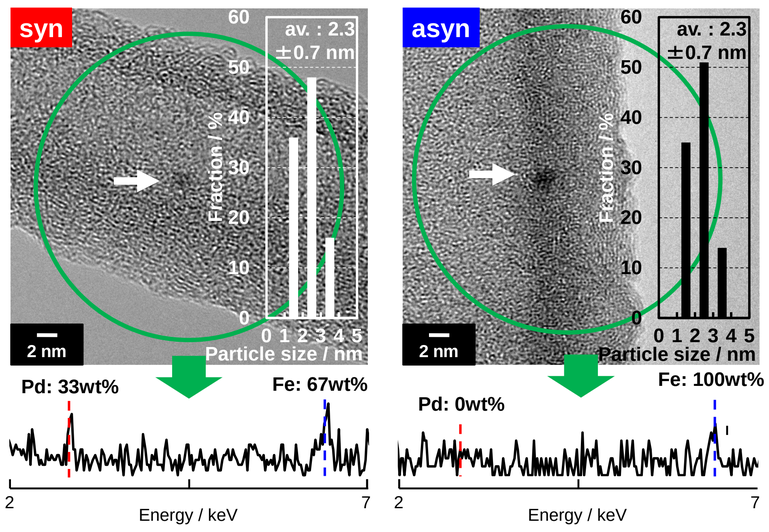
XAFS (BL9C, NW10A, KEK) Proposal No. 2012G749

Light source: Bending magnet, Double-crystal monochromator: Si(111) or (311)



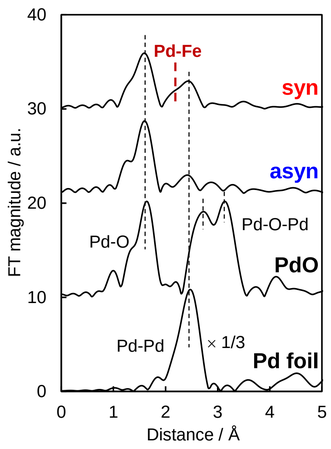
Results and Discussion

TEM images and EDX spectra of Fe-Pd



Pd K-edge EXAFS and fitting parameters

1.2wt% Fe-1.0wt% Pd/Al_2O_3(fresh)



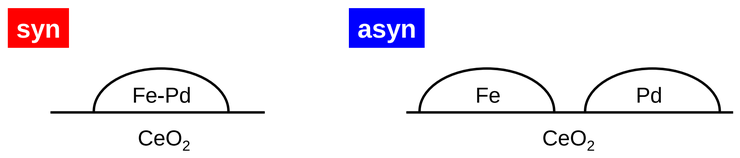
	shell	CN[a] (±0.2)	r/Å[b] (±0.03)	σ^2/10^{-2} Å^2[c] (±0.05)	R/%
syn	Pd-O	2.7	2.01	0.45	2.0
	Pd-Fe	0.5	2.70	0.65	
	Pd-Pd	0.8	2.73	0.59	
asyn	Pd-O	2.7	2.01	0.27	2.5
	Pd-Pd	0.6	2.71	0.59	
PdO	Pd-O	4.0	2.02	0.27	0.5
	Pd-O-Pd	4.0	3.05	0.52	
	Pd-O-Pd	8.0	3.43	0.55	
Pd foil	Pd-Pd	12.0	2.74	0.59	0.1

Interval of k-space to r-space of FT is 3.0-16.0 Å^{-1}.
[a]Coordination number. [b]Interatomic distance. [c]Debye-Waller factor.

Catalytic properties of CeO_2-supported catalysts

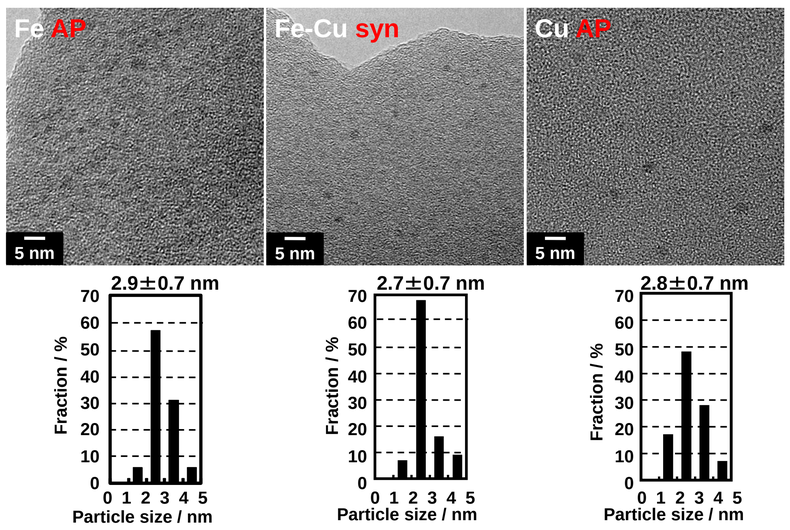
	Fe / wt%	Pd / wt%	S_{BET} / m^2·g^{-1}	CO/Pd[a] / %	Fe[0b] / %	Pd[0b] / %	T_{10}[c] / °C
Fe-Pd (fresh) syn	0.43	0.25	166	74	77	51	98
Fe-Pd (fresh) asyn	0.31	0.22	167	57	65	36	105

[a] Determined by pulsed CO chemisorption at 50 °C. Reduction by H_2 at 200 °C.
[b] Determined by Fe2p and Pd3d XPS.
[c] Temperature at which CO conversion reached to 10%



S. Hinokuma et al., *Catal. Today*, 201, 92 (2013).

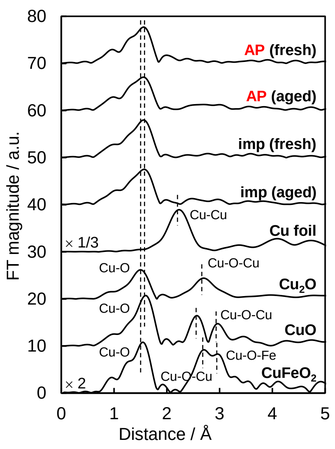
TEM images and size distributions



X-ray absorption spectra (XAFS) of Al_2O_3-supported catalysts

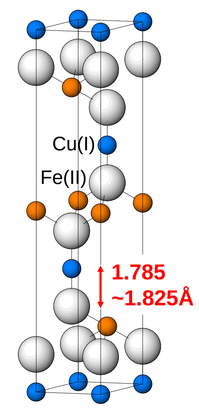
2.4wt% Fe-3.1wt% Cu/Al_2O_3

Cu K-edge EXAFS



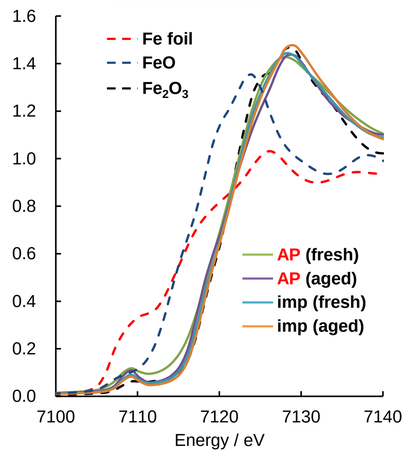
	Shell	CN[a] (±0.2)	r/Å[b] (±0.03)	σ^2/10^{-2} Å^2[c] (±0.05)	R/%
AP (fresh)	Cu-O ($CuFeO_2$)	0.6	1.83	0.10	0.1
	Cu-O (CuO)	2.6	1.95	0.26	
AP (aged)	Cu-O ($CuFeO_2$)	0.5	1.81	0.19	0.01
	Cu-O (CuO)	3.4	1.95	0.55	
imp (fresh)	Cu-O (CuO)	3.2	1.94	0.60	0.5
imp (aged)	Cu-O (CuO)	3.1	1.95	0.60	0.7
Cu foil	Cu-Cu	12.0	2.54	0.95	0.4
Cu_2O	Cu-O	2.0	1.84	0.46	3.9
CuO	Cu-O	4.0	1.96	0.52	1.9
$CuFeO_2$	Cu-O	2.0	1.83	0.58	2.2

Interval of k-space to r-space of FT is 2.0-15.0 Å^{-1}.
[a]Coordination number. [b]Interatomic distance. [c]Debye-Waller factor.

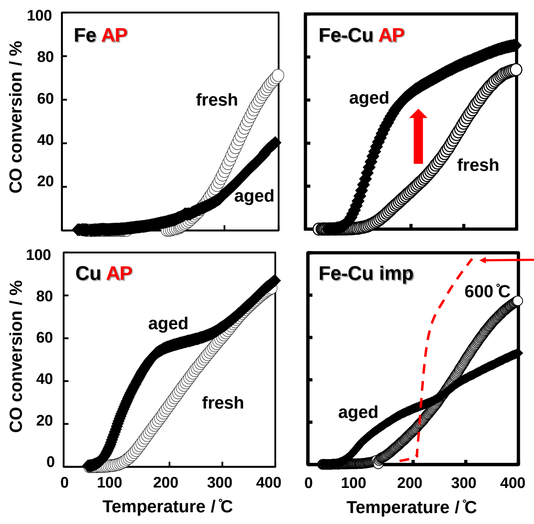


$CuFeO_2$

Fe K-edge XANES



Catalytic activity over CeO_2-supported catalysts

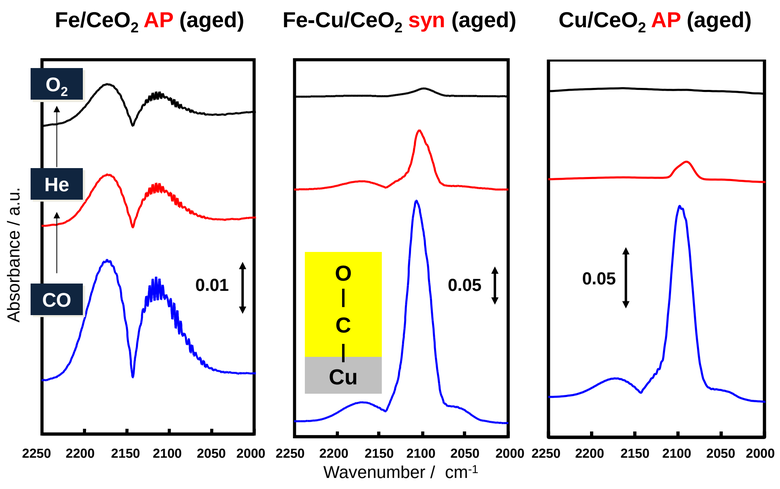


Fe-Cu AP	S_{BET} / m^2·g^{-1}
fresh	169
aged	6

0.4% Pt/Al_2O_3 imp (aged)

0.1% CO, 1.25% O_2, He balance. 10 ˚C·min^{-1}, W/F=5.0×10^{-4} g·min·cm^{-3}.

CO adsorption (in situ FT-IR at 50 ˚C)



The amount of CO adsorption on Cu

Fe / wt%	Cu / wt%		Cu^+/Cu	CO_{ads} / μmol·g^{-1}	CO/Cu	CO/Cu^+
0.20	-	AP (aged)	-	0.3	-	-
-	0.15	AP (aged)	0.89	5.7	0.24	0.27
0.18	0.11	AP (aged)	0.79	10.7	0.62	0.79
0.17	0.11	imp (aged)	0.66	1.9	0.11	0.17
-	0.13	imp (aged)	0.84	3.7	0.18	0.21

Conclusions

- ◆パルス放電を同期した多元系AP法によって平均粒子径2～3 nmの均一なFe-PdおよびFe-Cuナノ粒子を調製し、大型研究施設（KEK, PF）を利用して局所構造を測定した。
- ◆XAFS測定によって、AP法により調製したFe-Pd触媒ではFe_3Pd_1、Fe-Cu触媒ではデラフォサイト型$CuFeO_2$に類似の局所構造を有する表面化合物が生成していることが明らかになった。
- ◆高分散の複合金属ナノ粒子の形成によって、活性な低酸化状態の金属が安定化した。これが要因となって、単独金属および湿式含浸法で調製した触媒より高いCO酸化活性を示した。
- ◆CO吸着量およびin situ FT-IR測定から、Fe-Cu/CeO_2のCO吸着サイトは低酸化状態のCuである。熱処理によるCeO_2のシンタリングにも関わらず、$CuFeO_2$は高分散状態を保持することが分かった。

本研究は文部科学省の委託（元素戦略プロジェクトおよび元素戦略拠点形成型プロジェクト）を受けて実施した。