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**Characterization of Mono- and
Bimetallic Nanoparticles synthesized
via Microemulsions**

Characterization of Mono- and Bimetallic Nanoparticles synthesized via Microemulsions

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Ramona Y. G. König

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Variables and Abbreviations

a	lattice constant / Å
a	activity / $\mu\text{mol g}^{-1} \text{s}^{-1}$
a_0	extrapolated intensity at zero scattering angle
a_i^0	lattice parameter of the component i
A	active
A	polar phase
A	reactant (MR)
A*	intermediate reactant
A	frequency factor (SAXS)
A	absorbance (MR) / a.u.
A_0	absorbance at the start of the reaction / a.u.
AB	allylbenzene
Amp	4-aminophenol
AMS	α -methyl styrene
B	non-polar phase
B	reactant (MR)
c	lattice constant / Å
c	curvature / m^{-1}
c_0	initial concentration of the substrate / M
$c_{\text{COD},0}$	initial concentration of COD / M
$c_{\text{COD},t}$	concentration of COD at time t / M
$c_{\text{COE},t}$	concentration of COE at time t / M
c_{Nip}	concentration of 4-nitrophenol / mM
c_{NaBH_4}	concentration of NaBH_4 / mM
C	amphiphilic phase
C	monomer
C_{O}	concentration of oxidized species / M
C_{R}	concentration of reduced species / M
COD	1,5-cyclooctadiene
COA	cyclooctane
COE	cyclooctene

cp_{α}	upper critical point
cp_{β}	lower critical point
CV	cyclic voltammogram
d	lattice spacing / Å
d	diameter / nm
D	size / nm
E	potential / V
$E^{0'}$	formal potential of an electrode / V
E^0	standard reduction potential / V
E_a	apparent activation energy / kJ mol^{-1}
E_i	initial potential / V
EDX	energy dispersive X-ray spectroscopy
efb	emulsification failure boundary
<i>et al</i>	et alii
F	Faraday constant, $96485.336 \text{ C mol}^{-1}$
G	Gibbs free energy / J
GC	glassy carbon
GC	gas chromatography
h	Planck's constant, $6.626 \cdot 10^{-34} \text{ J s}$
H	curvature
ΔH_R	reaction enthalpy / kJ mol^{-1}
HRTEM	high-resolution transmission electron microscope
I	inactive
I	current / A
I	intensity
I_{CO}	current of the oxidation of CO to CO_2 / A
$I_{FA,f}$	current of the oxidation of formic acid to CO_2 in the forward sweep / A
$I_{FA,b}$	current of the oxidation of formic acid to CO_2 in the backward sweep / A
I_{Pt}	current of the oxidation of Pt to PtO / A
$\Delta I(q)$	detected intensity / a.u.
$I(q)$	intensity / a.u.
ICPS	inductively coupled plasma spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
k	kinetic rate constant / s^{-1}
8	

k'	pseudo kinetic rate constant / s^{-1}
k_i	kinetic rate constant of the respective reaction / s^{-1}
K	adsorption equilibrium constant (MR) / s^{-1}
K	constant containing information about the particle contrast, the volume and the concentration inside the sample (SAXS)
m_A	mass of the polar component / g
m_B	mass of the non-polar component / g
m_C	mass of the amphiphilic component / g
m_{metal}	amount of metal / g
m_{total}	total mass of the system / g
MR	model reactions
n	integer
n	number of electrons
n	stirrer speed / rpm
n_{product}	number of moles of the product
Nip	4-nitrophenol
NPs	nanoparticles
o/w	oil-in-water
p	momentum / N s
p	pressure / Pa
p_A	partial pressure of the species A / Pa
p_B	partial pressure of the species B / Pa
p_{H_2}	hydrogen pressure / MPa
P	product
P*	intermediate product
$P(q)$	form factor
PEIP20EO	polyethylene imine ethoxylated
PEM	polymeric electrolyte membrane
p-XRD	powder X-ray diffraction
q	magnitude of the scattering vector / nm^{-1}
r	reaction rate / mM min^{-1}
r_0	initial rate / mM min^{-1}
r_{ads}	reaction rate of the adsorption
r_{des}	reaction rate of the desorption

r_r	reaction rate of the reaction
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
R/r	radius / nm
R_G	radius of gyration / nm
$S(q)$	structure factor
S_{COE}	selectivity of the catalyst towards the hydrogenation of COD to COE
SAED	small angle electron diffraction
SAXS	small angle X-ray scattering
t	time / s, min
t_c	time of conversion
T	temperature / °C, K
V	volume / mL
$V(\text{H}_2)_t$	volume of hydrogen at time t / mL
$V(\text{H}_2)_{t=0}$	initial volume of hydrogen / mL
w_A	weight fraction of aqueous phase
w_B	weight fraction of oil phase
w/o	water-in-oil
w_{efb}	water emulsification failure boundary
X	conversion
X_{AMS}	conversion of AMS
X_{AB}	conversion of AB
X_B	mole fraction of the component B
X_{COD}	conversion of COD
XRD	X-ray diffraction
Z_i	amount of species A (or P) adsorbed at a given pressure and temperature
Z_{tot}	total amount of available surface sites at a given pressure and temperature

Symbols

δ	weight fraction of co-surfactant
ε	cell efficiency
γ_b	weight fraction of surfactant
λ	wavelength / nm / Å
μE	microemulsion
θ	angle / °
10	

θ_i	fractional surface coverage
θ_1	fractional surface coverage of A
θ_2	fractional surface coverage of P
θ_v	fraction of vacant sites
ω	full-width half-maximum
ω	angular velocity
*	active sites of a catalyst

Numbers

1	1-phase region
<u>2</u>	lower 2-phase region
2upper	upper 2-phase region

Abstract

Research in the field of heterogeneous catalysis often focuses on the search for highly active and cheap catalysts in order to find possible substitutes for expensive but efficient base materials such as platinum. In this thesis mono- and bimetallic platinum-based nanoparticles (NPs) were synthesized via water-in-oil microemulsions. The resulting Pt, PtBi and PtPb nanoparticles were then characterized.

By means of high resolution transmission electron microscopy (HRTEM) it was found that the resulting nanoparticles have an average diameter of 4.3 ± 1.5 nm. The structural characterization via powder X-ray diffraction (XRD) and inductively coupled plasma spectroscopy (ICPS) showed that the bimetallic nanoparticles consist of mixtures of phases including oxides.

The catalytic properties of the bimetallic PtBi and PtPb nanoparticles were studied and compared with the monometallic platinum nanoparticles in various reactions. In the industrially relevant electrochemical oxidation of formic acid carbon monoxide is formed which is known to block the active sites of platinum catalysts. In this work, the resistance of the PtBi and PtPb nanoparticles against the catalyst-poisoning carbon monoxide was found to be significant. Furthermore, the bimetallic PtBi and PtPb nanoparticles have shown good stability in the electrochemical environment.

A comparison of the catalytic activity of the three different nanoparticles was possible via different model reactions. For the reduction of 4-nitrophenol to 4-aminophenol, as well as for the hydrogenations of both α -methyl styrene to cumene and allylbenzene to propylbenzene, it was found that the monometallic Pt NPs are the most active catalysts, followed by the PtPb and the PtBi NPs. The activity of the bimetallic PtPb nanoparticles was found to be significantly higher than that of the PtBi NPs. For the selective hydrogenation of 1,5-cyclooctadiene the same selectivity towards the hydrogenation of cyclooctene was found for all three nanoparticles.

The experimental findings in this work underline the great potential that the bimetallic PtPb nanoparticles synthesized in water-in-oil microemulsions have for catalytic applications.

Kurzzusammenfassung

Forschung im Bereich der heterogenen Katalyse konzentriert sich oft auf die Suche nach hochaktiven und zugleich günstigen Katalysatoren, um teure Materialien, wie zum Beispiel Platin als Grundmaterial zu ersetzen. In der vorliegenden Arbeit wurden monometallische Platin sowie bimetallische Platin-Bismuth und Platin-Blei Nanopartikel charakterisiert, die in Wasser-in-Öl Mikroemulsionen dargestellt wurden. Aufnahmen mit einem hochauflösenden Transmissionselektronenmikroskop (HRTEM) zeigten, dass die Nanopartikel einen mittleren Durchmesser von 4.3 ± 1.5 nm haben. Die Zusammensetzung der bimetallischen Nanopartikel wurde mit Pulverdiffraktometrie (XRD) und induktiv gekoppelter Plasmaspektroskopie (ICPS) bestimmt. Hierbei wurde festgestellt, dass die dargestellten Partikel nicht aus einer reinen bimetallischen Phase, sondern aus einem Phasengemisch bestehen.

Die katalytischen Eigenschaften der dargestellten Pt, PtBi und PtPb Nanopartikel wurden mit verschiedenen Techniken bestimmt. Die elektrochemische Oxidation von Ameisensäure ist eine industriell relevante Reaktion, bei der reine Platin Katalysatoren vom entstehenden Kohlenmonoxid vergiftet werden. In dieser Arbeit wurde gezeigt, dass die dargestellten bimetallischen PtBi und PtPb Nanopartikel eine hohe Toleranz gegenüber dem entstehenden Kohlenmonoxid besitzen. Des Weiteren konnte die gute Stabilität der bimetallischen Nanopartikel in der elektrochemischen Umgebung gezeigt werden.

Anhand verschiedener Modelreaktionen wurde nunmehr die katalytische Aktivität der drei verschiedenen Nanopartikeln bestimmt und verglichen. Sowohl für die Reduktion von 4-Nitrophenol zu 4-Aminophenol, als auch für die Hydrierungen von α -Methylstyrol zu Cumol und von Allylbenzol zu Propylbenzol, sind die monometallischen Pt Nanopartikel die Katalysatoren mit der höchsten Aktivität. Die Aktivität der bimetallischen PtPb Nanopartikeln ist zwar geringer als die der monometallischen Partikel, jedoch ist sie signifikant höher als die Aktivität der PtBi Nanopartikel. Bei der selektiven Hydrierung von 1,5-Cyclooctadiene konnte kein Unterschied in der Selektivität zwischen den drei verschiedenen Nanopartikeln festgestellt werden.

Zusammenfassend wurde in dieser Arbeit das große Potential für katalytische Anwendungen der in Wasser-in-Öl Mikroemulsionen dargestellten Platin-Blei Partikeln gezeigt.