

English Version

中国化学会第29届学术年会

2014年8月4日-7日 北京·北京大学

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会议注册：2013年12月1日-2014年6月30日

论文征集：2013年12月1日-2014年6月15日

会前缴费：2013年12月1日-2014年6月30日



41 parallel sessions

11 special topic forum

896 Invited Lectures

1230 Oral Lectures

3056 Posters

~ 8000 intendees



Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR

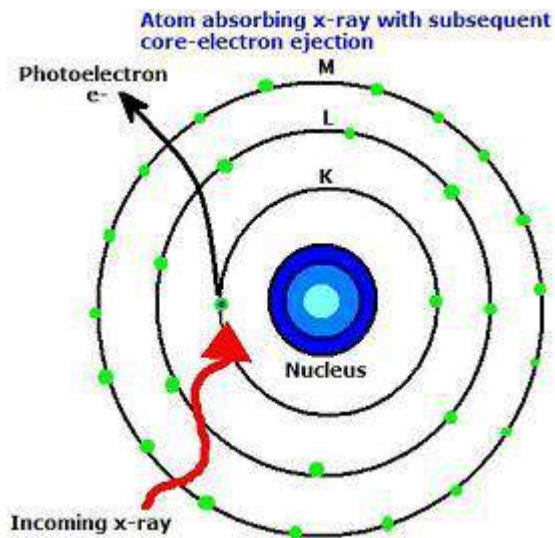
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Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR



XAS (X-ray absorption spectroscopy) is an element specific method to investigate the **bond angles**, **bond lengths** and **coordination numbers**.



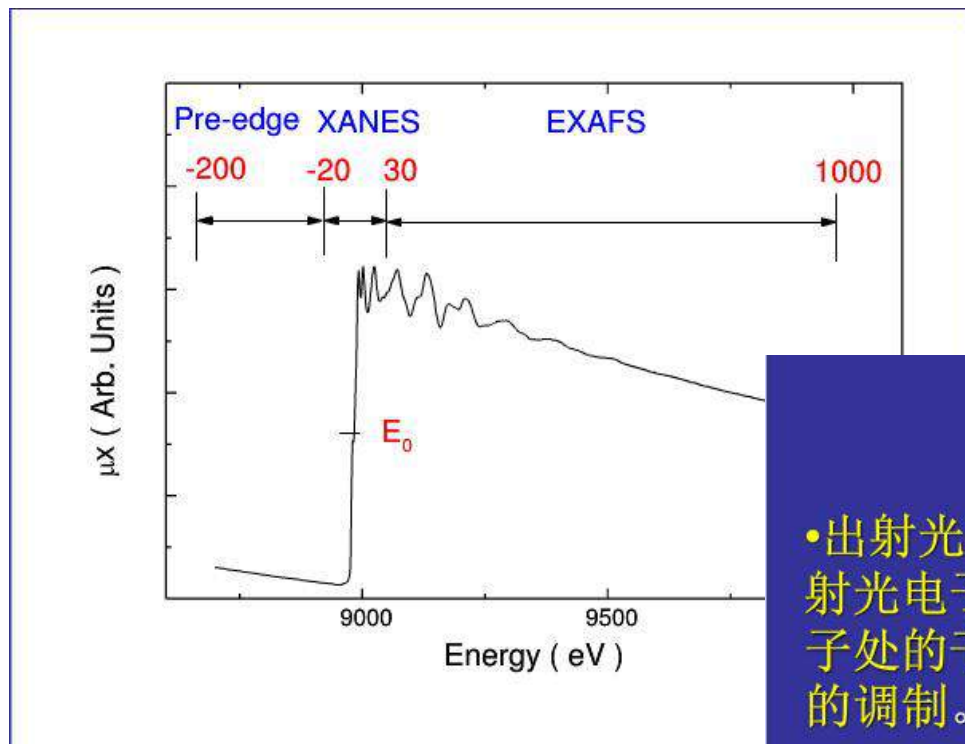
Absorption edges: they correspond to the binding energies of the inner-shell electrons (K, L, M..).

Each chemical element has specific, well-defined binding energies

XAS spectrum can be divided into different parts based on the energy range of the X-ray beam compared to the absorption edge

1. Pre-edge: no ionisation occurs
2. XANES (X-ray Near Edge Structure): $E < E^0 + 10$ eV
3. NEXAFS (Near-Edge X-ray Absorption Fine Structure): $E^0 + 10 < E < E^0 + 50$ eV
4. EXAFS (Extended X-ray Absorption Fine Structure): $E > E^0 + 50$ eV

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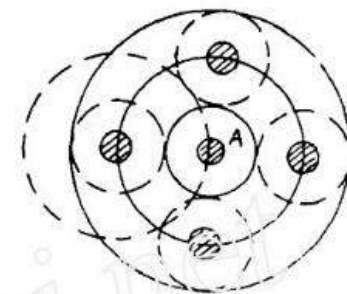


According to the fine structure of the spectrum, XAFS can get the information about the neighboring atoms.

产生的物理机制

• 出射光电子波与背散射光电子波在吸收原子处的干涉对吸收谱的调制。

干涉是由出射波与散射波的相位差引起的，与入射波的强弱、近邻原子的种类及数目 N 、以及吸收原子到近邻原子的距离 R 有关。所以，通过XAFS可得到近邻原子的信息。



图二 表示光电子末态 $|f\rangle$ 的组成。阴影圆表示原子，实线圆表示原子A吸收X光子产生光电子的出射波，虚线圆表示邻近原子的散射波。


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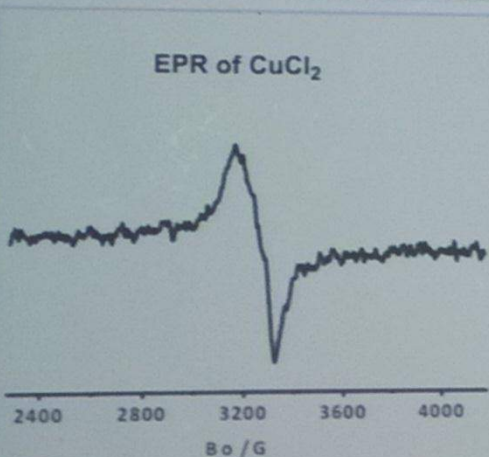
Electron paramagnetic resonance (EPR)

A technique for studying materials with **unpaired electrons**.

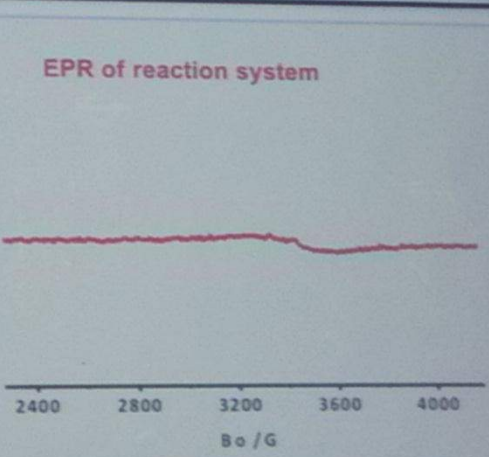
$$20 \text{ } t\text{BuONa} + \text{CuCl}_2 \xrightarrow[\text{?}]{\text{DMF}} \text{Cu}^{\text{II}}(\text{OtBu})_2$$



EPR of CuCl₂



EPR of reaction system



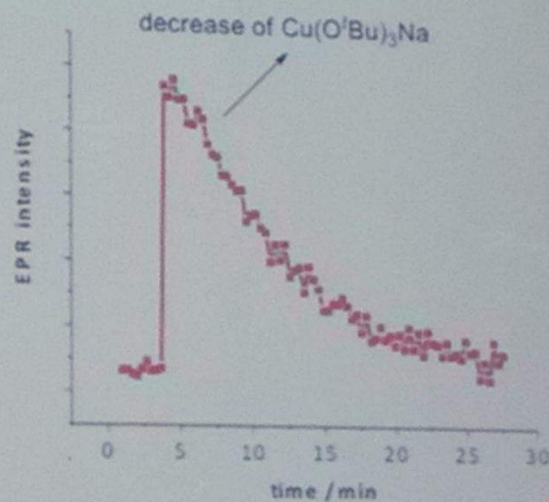
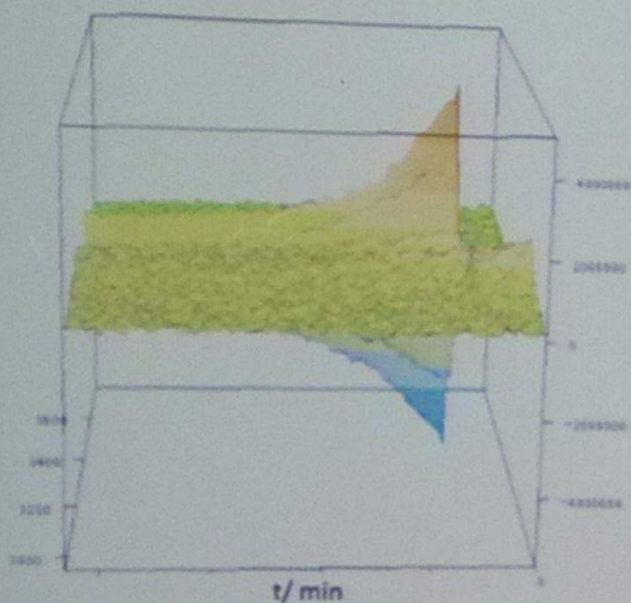
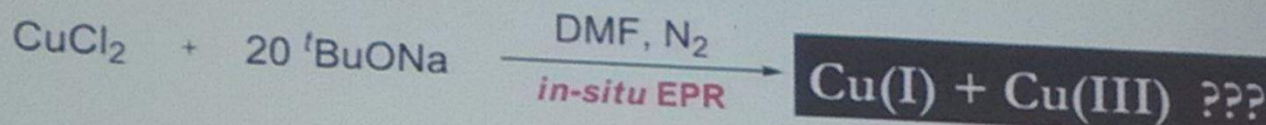
No EPR signal after the reaction of *t*BuONa and CuCl₂. Strange!!!

Cu^{II}: d⁷

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In situ EPR Study

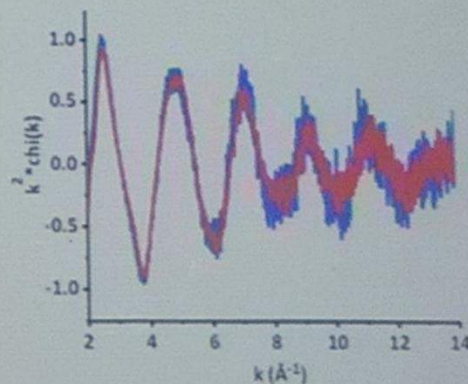
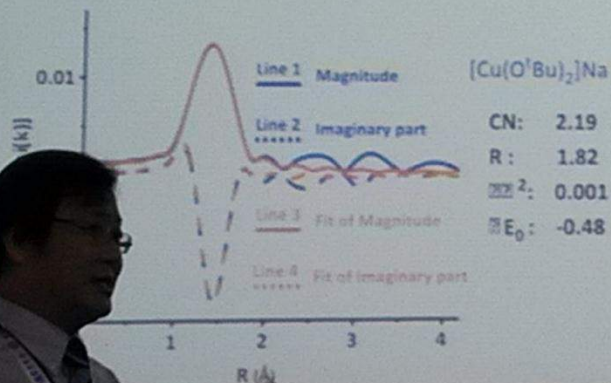
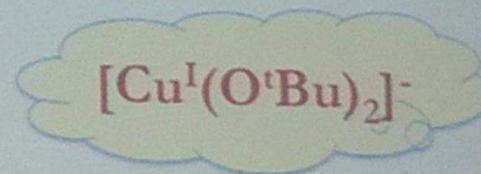
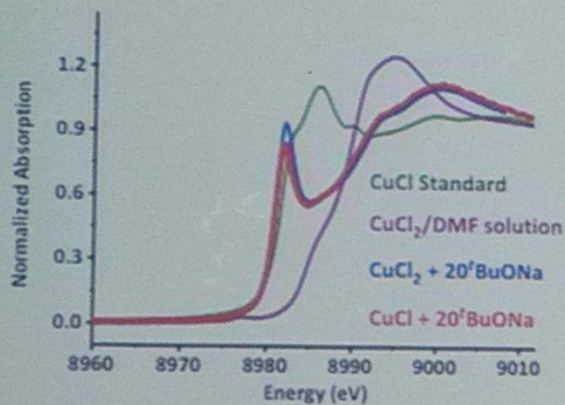
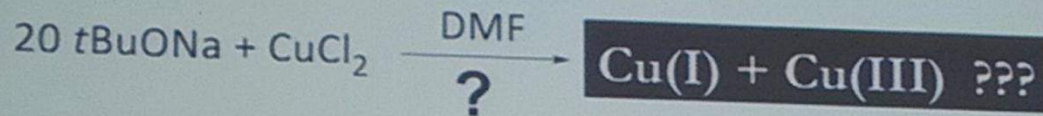


- A new Cu(II) species was quickly formed
- The consumption of Cu(II)-species was observed via the in situ EPR

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XANES/EXAFS Studies



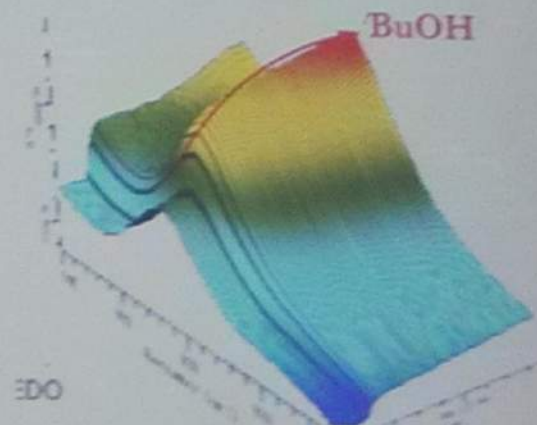
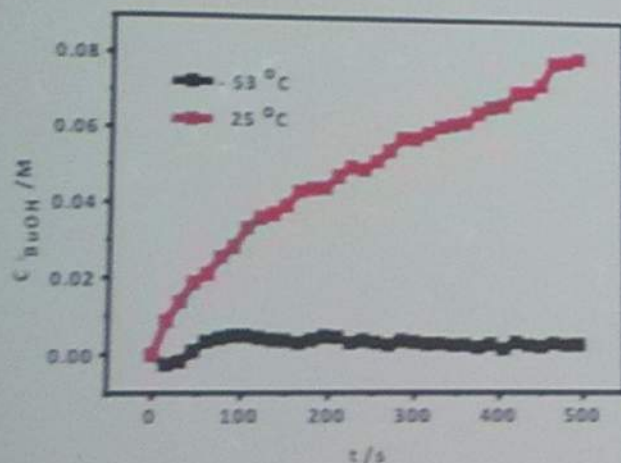
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Operando IR Study



Kinetic profiles of the reduction



The kinetic profiles of 25 °C and -53 °C were shown. No reduction occurs at -53 °C

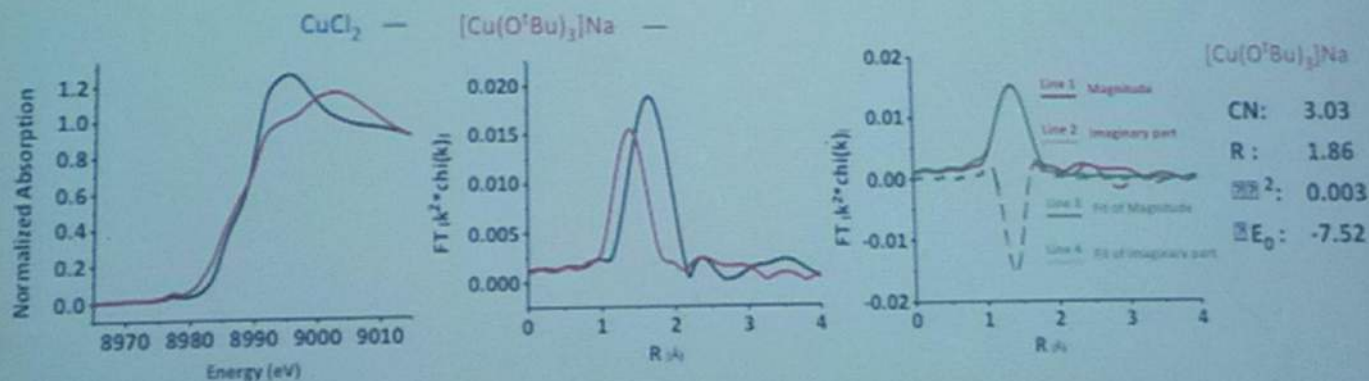
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The Determination of $\text{Cu}(\text{O}^t\text{Bu})_3\text{Na}$



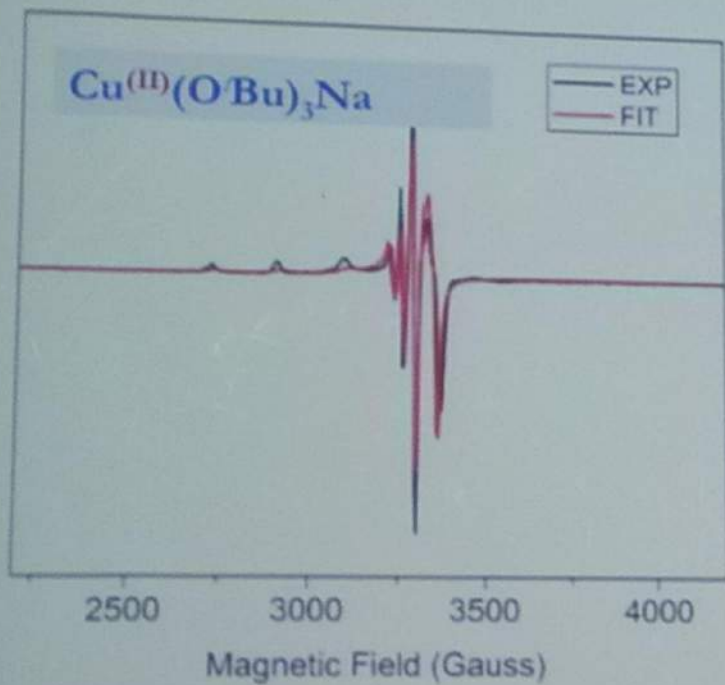
A good chance to study the structure of $\text{Cu}^{\text{II}}(\text{O}^t\text{Bu})_3\text{Na}$



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Low-temperature (160k) EPR Spectrum



Spin Hamiltonian parameters of Cu(II) species:

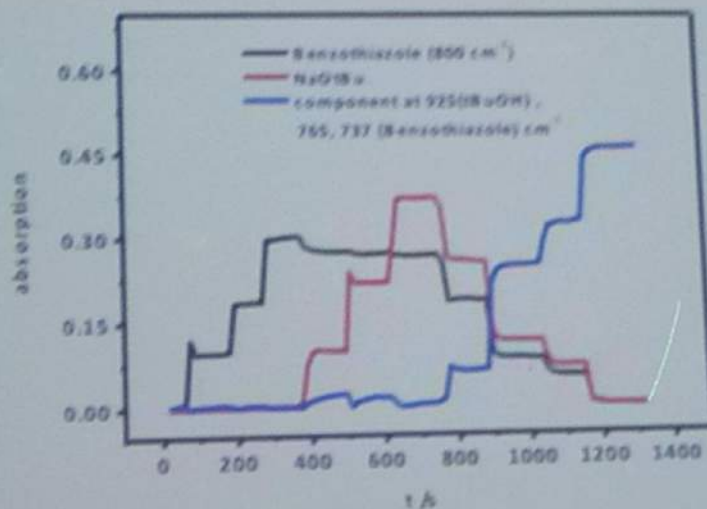
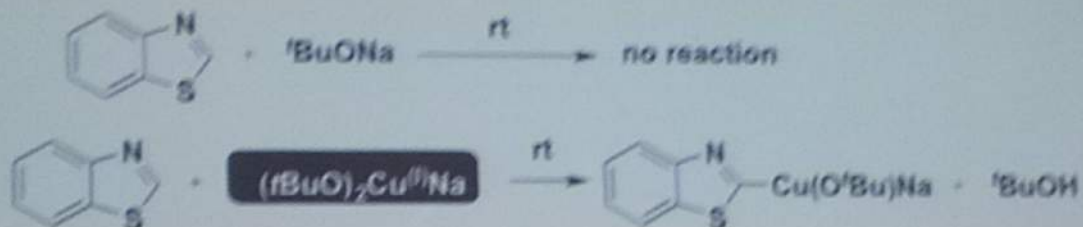
$$g = 2.00, 2.00, 2.24;$$
$$A = 37, 25, 197$$

The g and hyperfine A values indicate coordination by weak-field oxygen ligands

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C-H Activation on the Cu(I)-Complex

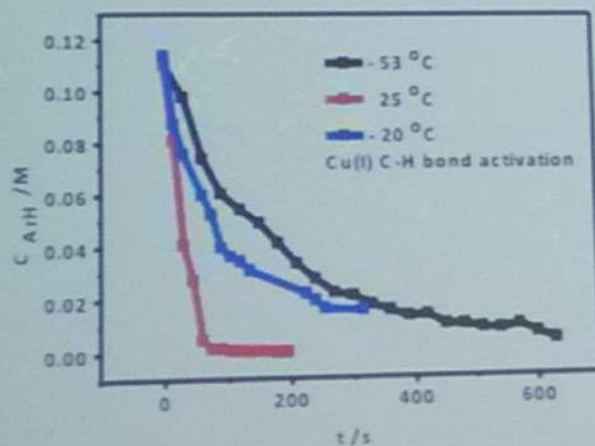


The C-H activation of ArH by $\text{Cu}^{\text{I}}(\text{O}^t\text{Bu})_2\text{Na}$ is very fast at rt

Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR



Kinetic Profiles



$$v = k[\text{Cu}^{\text{I}}(\text{O}^t\text{Bu})_2\text{Na}][\text{ArH}]$$

$$k = 3.2 \cdot 10^{-2} \text{ mol}^{-1}\text{Ls}^{-1}$$

@ -53 °C

$$k = 4.8 \cdot 10^{-2} \text{ mol}^{-1}\text{Ls}^{-1}$$

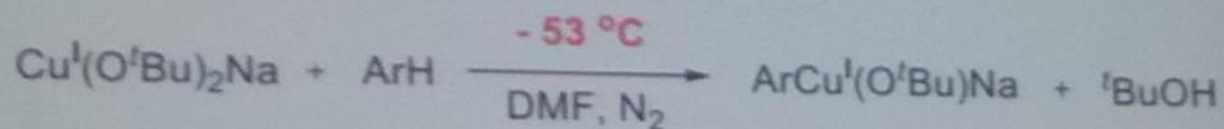
@ -20 °C

The C-H activation could be completed within 10 mins @ -53 °C

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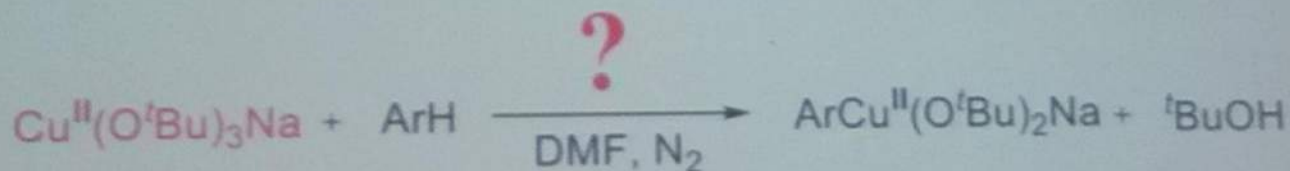


C-H activation by Cu(I)



$$k = 3.2 \cdot 10^{-2} \text{ mol}^{-1}\text{Ls}^{-1}$$

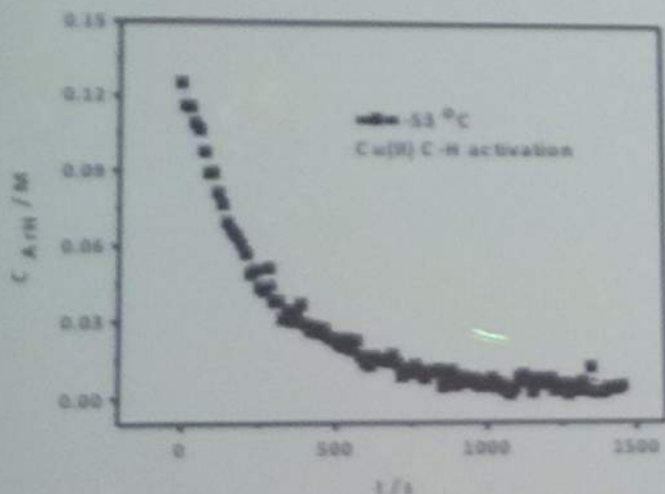
C-H activation by Cu(II)



Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR



C-H Activation on the Cu(II)-Complex



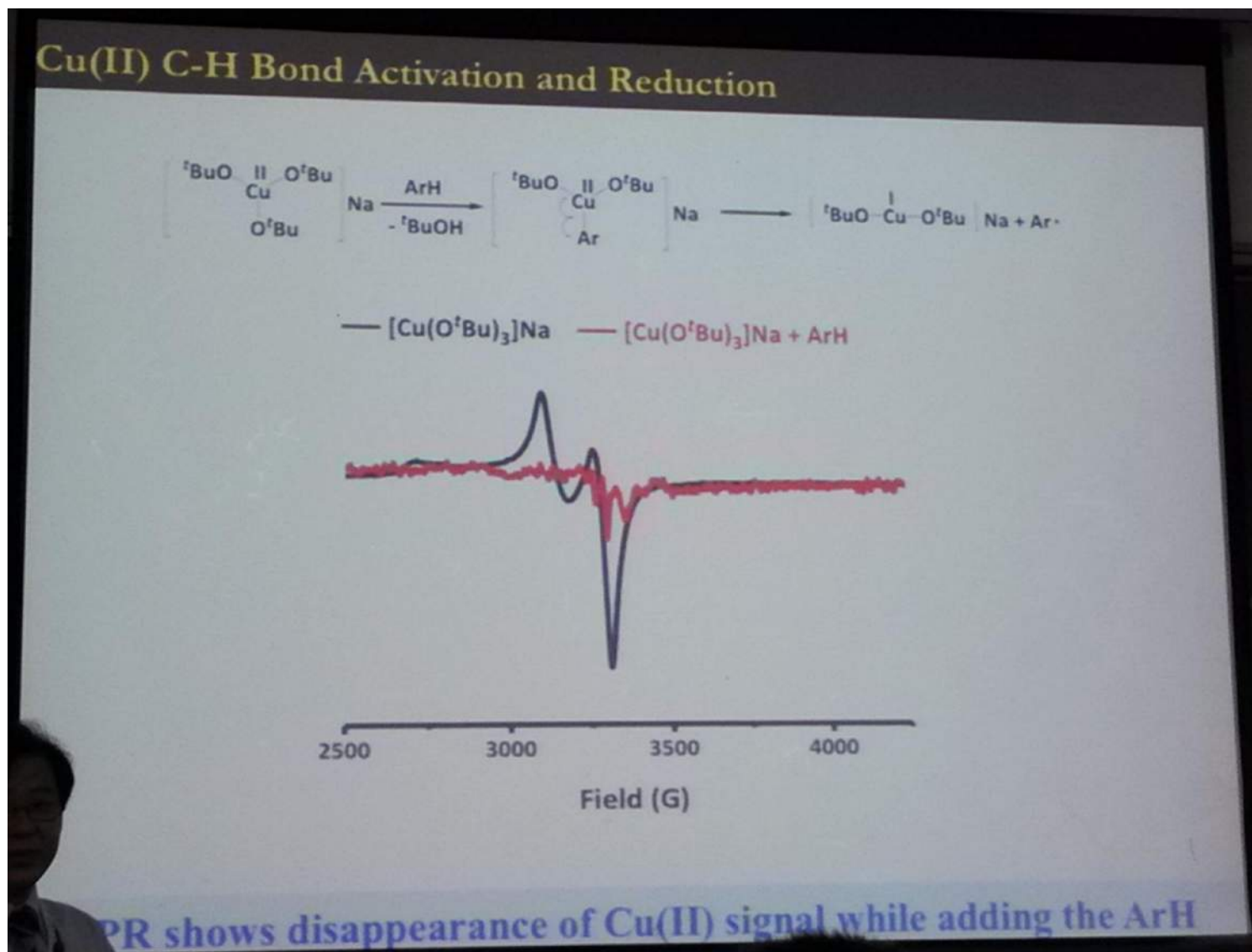
$$v = k[\text{Cu}(\text{O}^t\text{Bu})_3\text{Na}][\text{ArH}]$$

$$k = 2.1 \cdot 10^{-2} \text{ mol}^{-1}\text{Ls}^{-1}$$

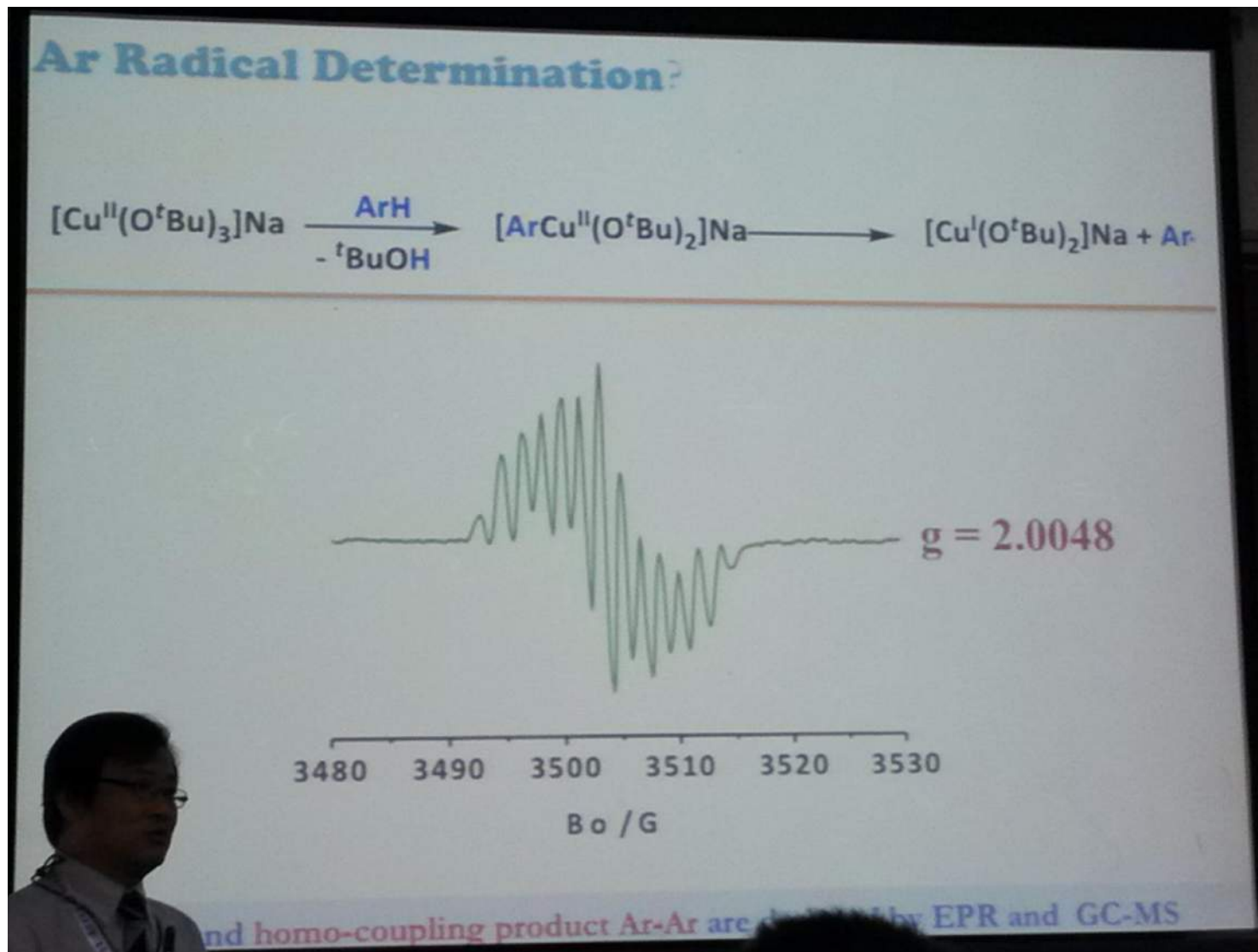
@ -53 °C

The C-H activation could be completed within 15 mins @ -53 °C

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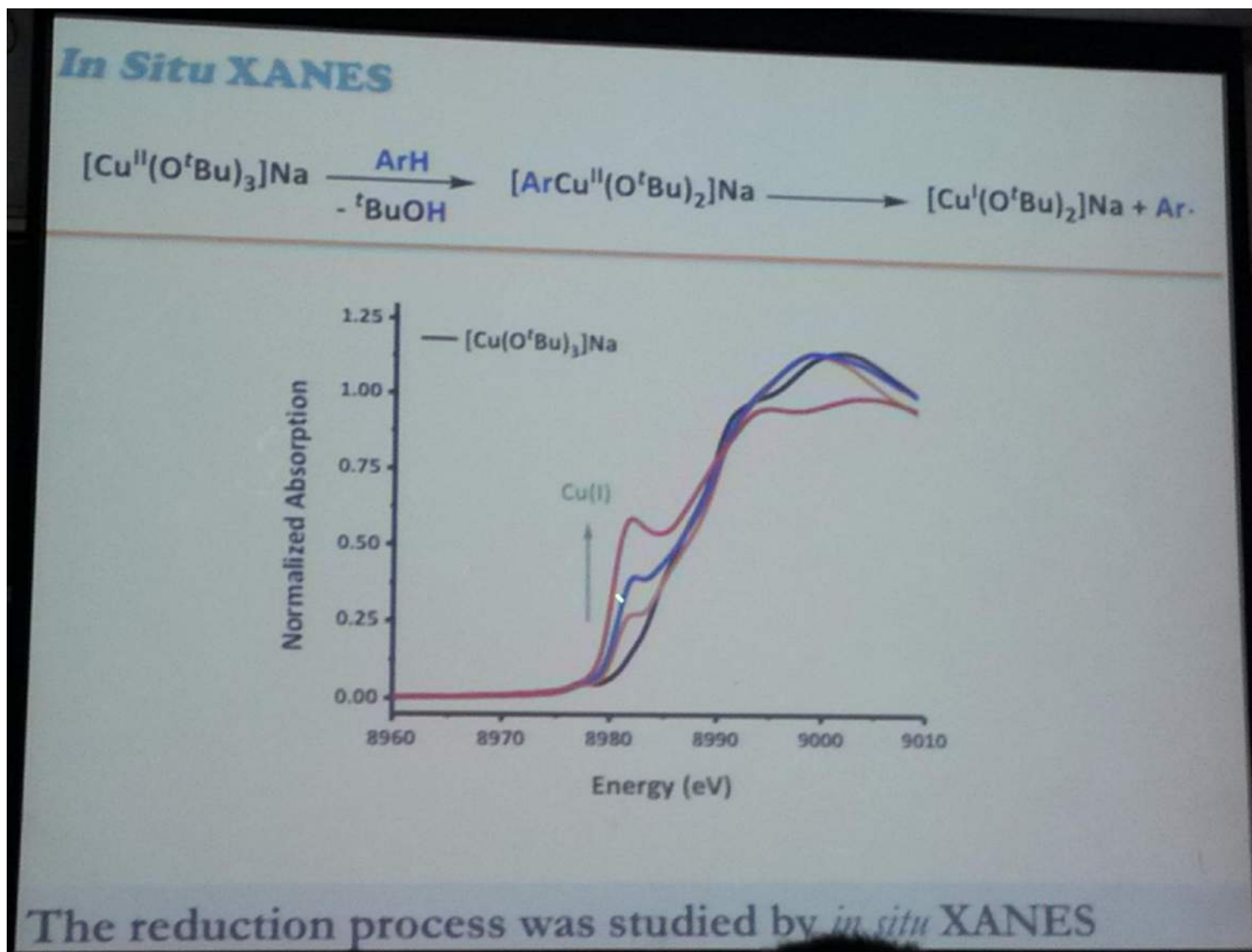


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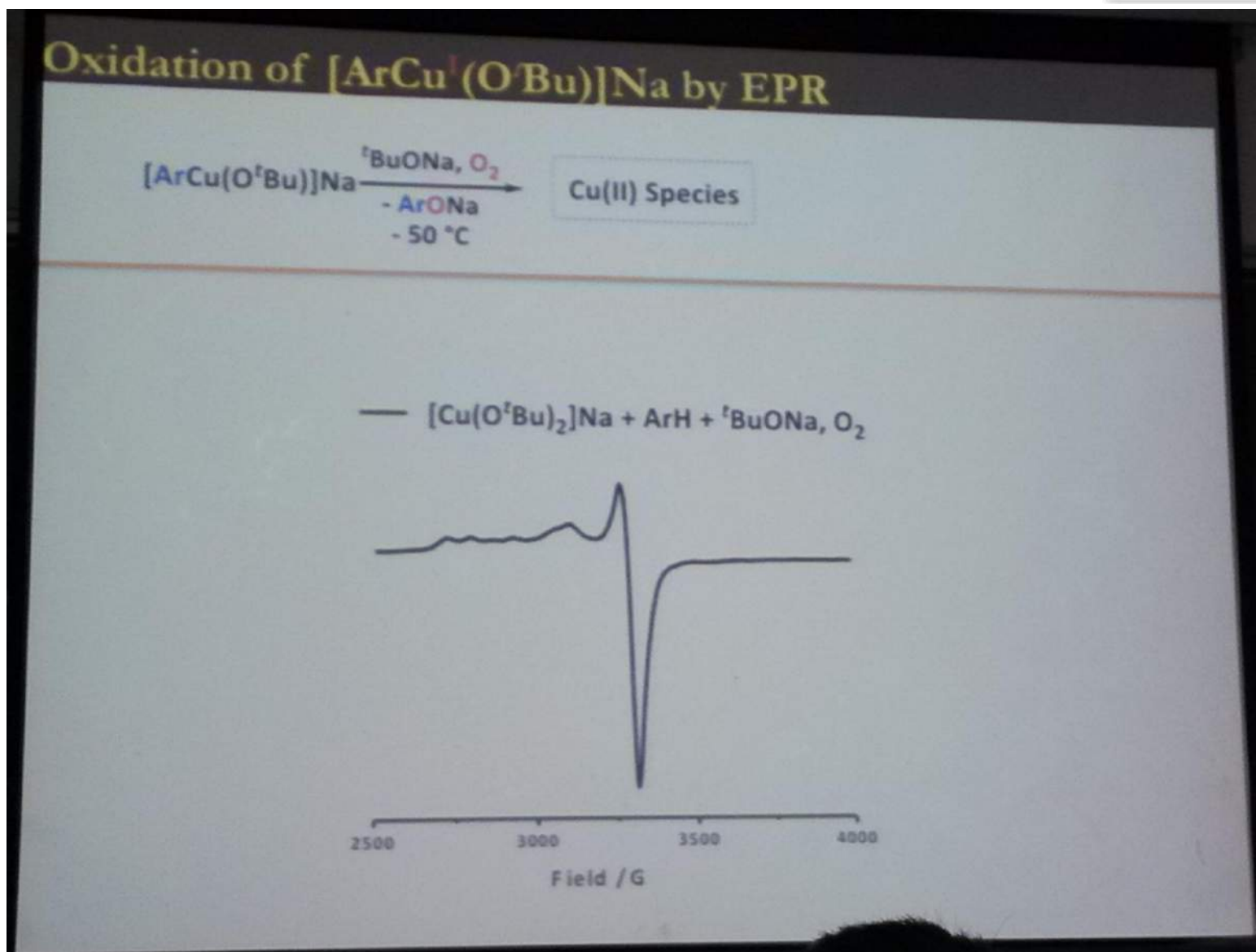


Picture from Aiwen Lei

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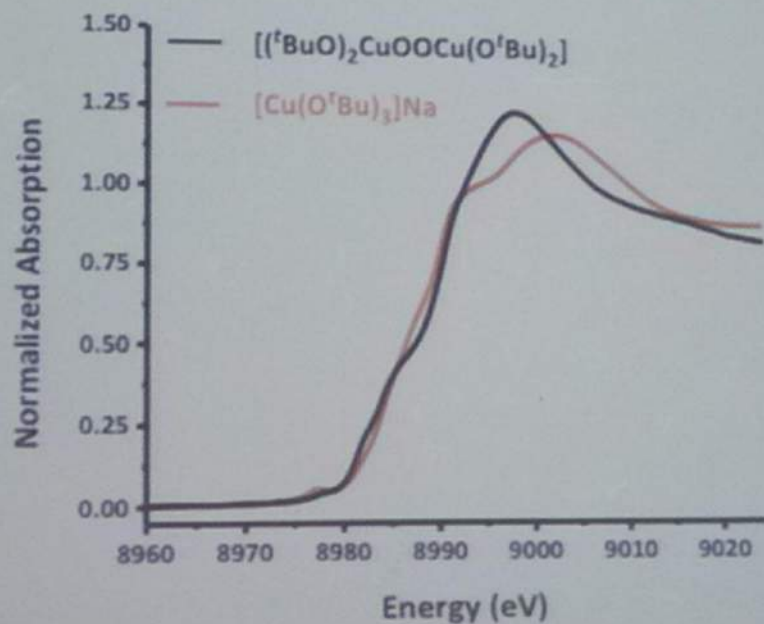
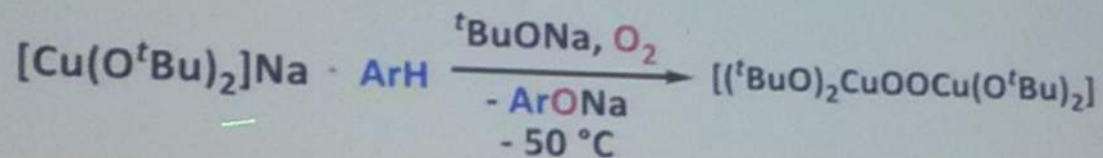


Picture from Aiwen Lei

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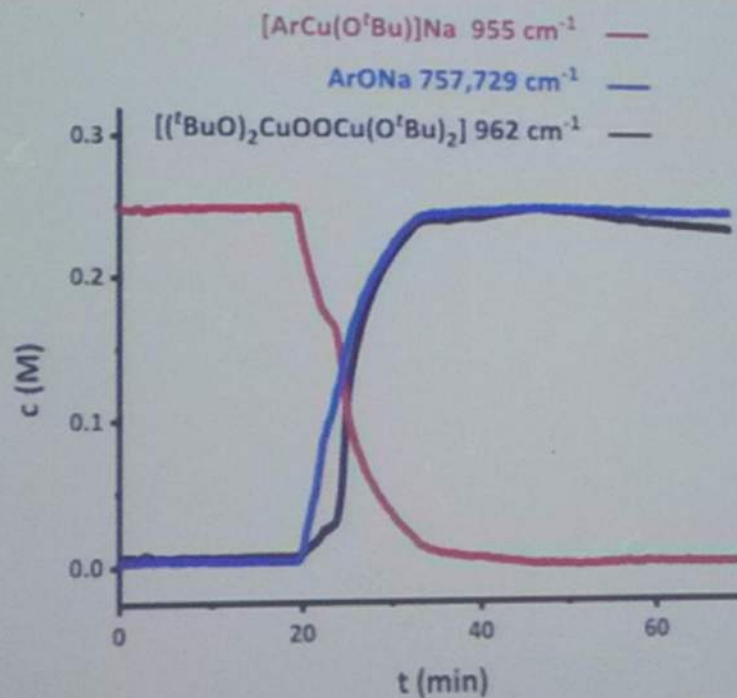
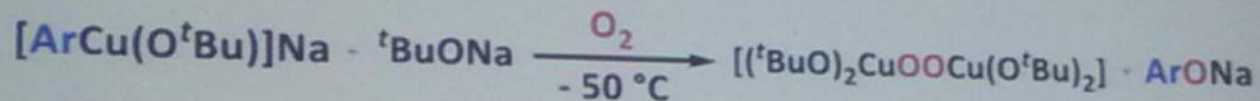
Oxidative process by *In Situ* XANES



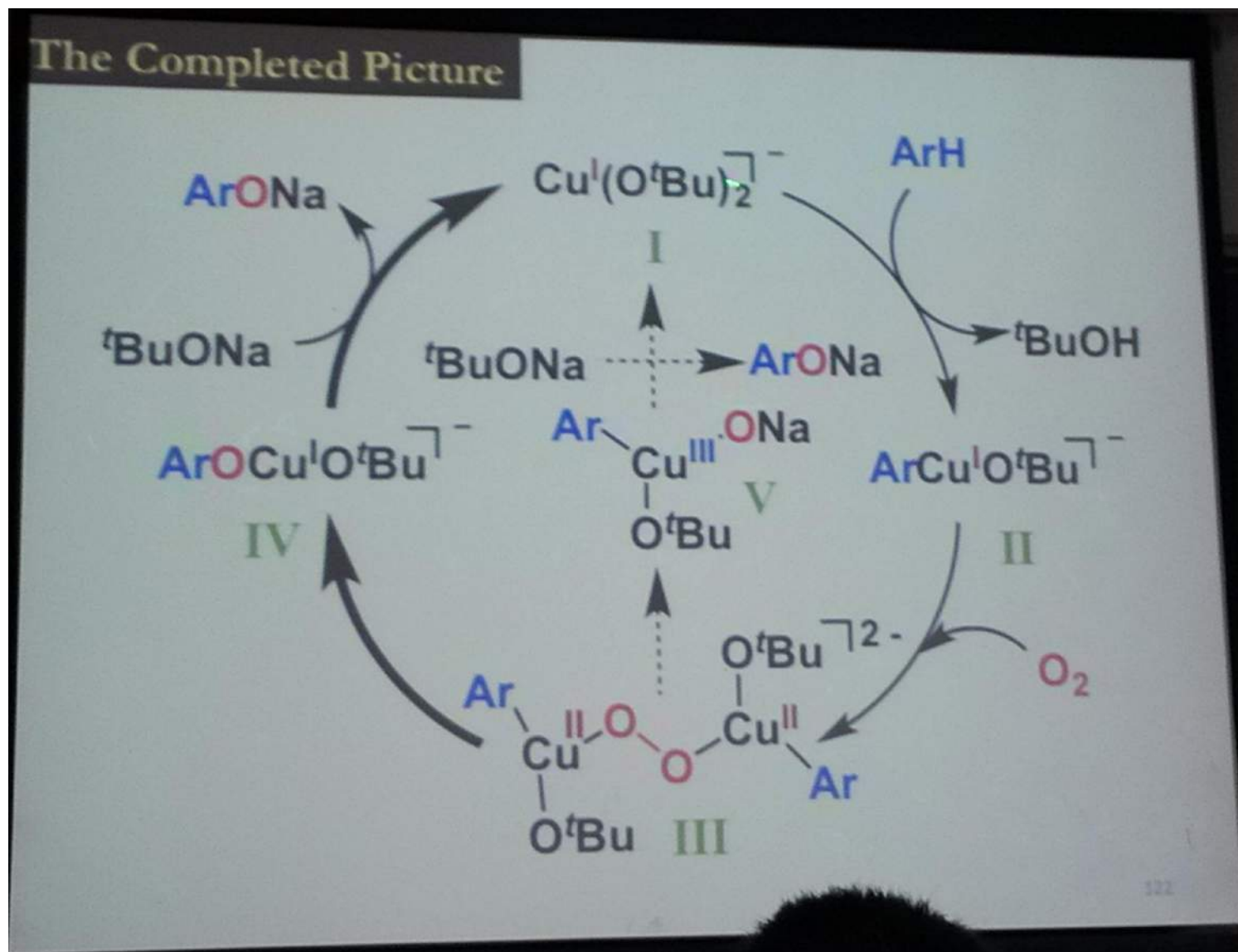
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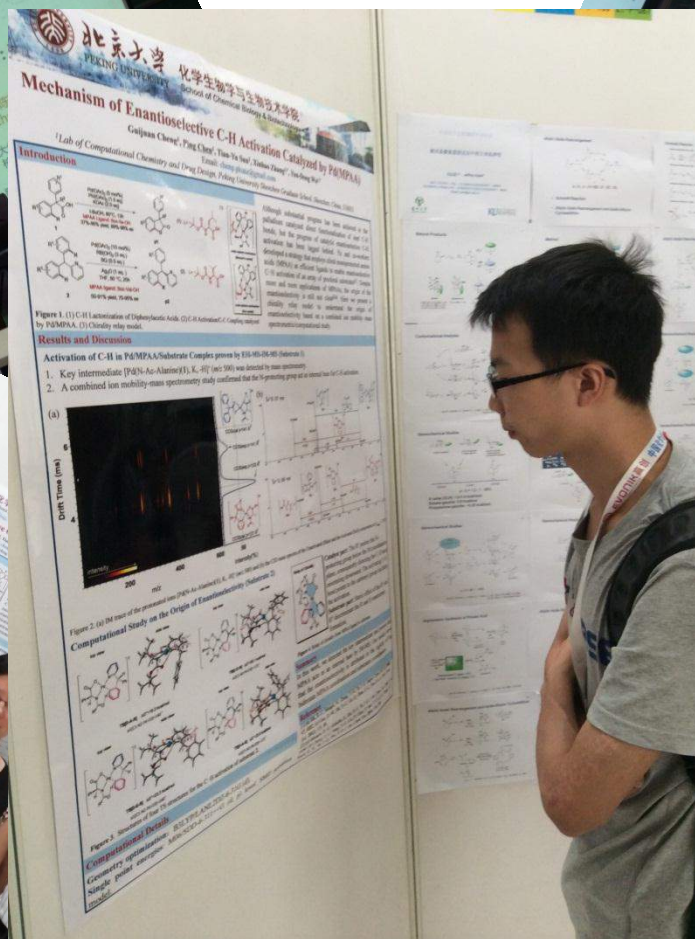
Kinetic Profiles by Operando IR



Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR



Pictures





Thanks for you attention!