Results and Discussion

To demonstrate LITR-XAS technique for catalysis study in the ultrafast domain, we investigated a photo-catalytic reaction in a homogeneous system with [Pt(BINAP)₂] as the catalyst (BINAP = 2,2'-Bis(diphenylphosphino)-1,1'-binapthyl). [Pt(BINAP)₂] is known to catalyze the Diels-Alder reactions and has been used as a photosensitizer [4]. Nevertheless, little information is available regarding its electronic configuration and coordination structure in the excited state. In this experiment, a 5 picosecond laser pulse at a wavelength of 527 nm is used to excite [Pt(BINAP)₂] dissolved in an organic solvent. Our initial data indicate a clear change in the molecular structure of [Pt(BINAP)₂] upon electronic excitation. The Fourier transformed EXAFS data showed significant changes in the shell radial distribution function for the mixture containing fractionally converted excited state. A preliminary fits suggests an average first shell radius of 2.26 Å, which represents a contraction from that of the ground state.

Introduction

Catalysis plays a critical role in our nation’s economy from industrial manufacturing to environmental protection. Despite its importance, there is still a great lack of fundamental understanding of the dynamics of the active site at the molecular level. The key step of a catalytic process is the formation of a reaction intermediate through the interaction of the reactant and the active site. Knowledge about the intermediate or the “transitional state” can shed light on the energetic process and reaction pathway, which is crucial for the rational design of a catalyst. In most cases at present, such information can only be achieved through theoretical modeling. Conventional in situ X-ray absorption spectroscopy (XAS) can provide useful information on the catalyst structure under the operating conditions. It is often, difficult to decipher, however, if the observed changes are from the active site or the spectator species under the reactive environment. Capturing the catalytic intermediate in transit will provide the ultimate answer to the active site dynamics. It is, nevertheless, a very challenging proposition experimentally. In addition to the fact that the techniques must be able to probe within a short lifetime of a nanosecond or less, one has to be able to manipulate the catalytic process from the multiple sites simultaneously to gain a sufficient signal. Such study was deemed impossible until the recent success in developing a versatile laser-initiated, time-resolved X-ray absorption spectroscopic method (LITR-XAS). The technique was shown to be capable of capturing the excited state of transition metal complexes in transient at nanosecond time scales [1-3]. It is now possible to coherently control the catalytic reaction with laser induced photo or thermal pulses and to follow the active site with progression of time with XAS. Experimental setup and examples of photo-initiated catalytic reaction will be discussed in this presentation.

Materials and Methods

Shown in Figure 1 is the schematic of the experimental setup. It consists of an ultrafast pump/probe system and a movable catalyst system (MCS). The former contains a pulsed laser and an XAS detection scheme. The latter can be a liquid jet or a rotating disk, depending on whether the catalyst system is homogeneous or heterogeneous. A Nd:YLF laser with picosecond pulse duration is used to provide light from visible to UV. The light pulse can initiate a photo-catalytic reaction in a homogeneous system. Alternatively, it can trigger thermally stimulated catalysis by converting the laser pulse to a heat spike at the surface for a heterogeneous system. The X-ray pulse from the synchrotron storage ring strikes the sample at an adjustable delay and the fluorescence signal is collected by a multi-element detector. The design of the MCS provides a fresh, unperturbed sampling space between each laser pulse to ensure coherent change from the catalytic sites.

Figure 1. The experimental setup of LITR-XAS detection method.

Significance

This study represents the first experimental investigation of the catalytic transitional state by time-resolved X-ray absorption spectroscopy in the nanosecond time domain.

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References