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Uncovering the deactivation mechanism of Au catalyst with *operando* high spatial resolution IR and X-ray microspectroscopy measurements

Elad Gross

Institute of Chemistry and The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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ABSTRACT

Detecting the reaction mechanism of multistep catalytic transformations is essential for optimization of these complex processes. In this study, the mechanism of catalyst deactivation within a flow reactor was studied under reaction conditions. Spectral mapping of the catalyst and the organic phase along a flow reactor were performed with micrometer-sized synchrotron-based X-ray and IR beams, respectively, with a spatial resolution of 15 μm. Heterogeneous Au catalyst was packed in a flow reactor and activated toward the cascade reaction of pyran formation. X-ray absorption microspectroscopy measurements revealed that the highly oxidized Au(III), which is the catalytically active species, was continuously reduced along the flow reactor. IR microspectroscopy measurements detected a direct correlation between the reduction of the Au catalyst and deactivation of the catalytic process. It was observed that within 1.5 mm from the reactor's inlet all the catalytic reactivity was quenched. Microspectroscopy measurements determined that the reduction of Au(III) was induced by nucleophilic attack of butanol, which is one of the reactants in this reaction. Slower deactivation rates were measured once the reactants concentration was decreased by an order of magnitude. Under these conditions the reaction path within the flow reactor was increased from 1.5 to 6 mm. These results demonstrate the molecular level understanding of reaction mechanism which can be achieved by high spatial resolution microspectroscopy measurements.

1. Introduction

Uncovering the complex factors that direct catalytic processes is a key element for optimizing chemical reactions and designing superior catalysts, which are based on a rational design [1–4]. Various methods were developed to elucidate the complex chemistry, which takes place on the surface of heterogeneous catalysts, from vibrational spectroscopy (UV-Vis, Raman, IR) [5,6] to magnetic resonance (ESR and NMR) [7] and X-ray spectroscopy (XPS) [8,9].

Vibrational spectroscopy is one of the most powerful techniques for analysis of catalytic processes since it provides direct chemical information, from which the determination of the chemical structure of reactants, intermediates, and products can be deduced [6,10,11]. A variety of vibrational spectroscopy methods were developed and utilized to detect the reactants into products transformation under reaction conditions. Among these methods are surface sensitive techniques such as sum frequency generation (SFG) vibrational spectroscopy [12,13] and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) [14,15] that can identify surface-adsorbed intermediates during catalytic reactions. In addition, high temporal resolution IR spectroscopy tools were developed and utilized to uncover the mechanism of catalytic processes [16–18].

However, the spatial resolution of these spectroscopic methods is not sufficient for analysis of catalytic reaction within a flow reactor. High spatial resolution IR spectroscopy can provide a detailed kinetic analysis of the progression of catalytic reactions within a flow reactor. The spatial resolution is dictated by the diffraction limit of the light and therefore the optimum resolution that can be gained in IR measurements is in the order of ~10 μm. The spatial resolution is mainly controlled by the spot size of the beam, which in most of the FTIR setups is wider than 0.1 cm. As a consequence, the spatial resolution of these techniques is lower by three orders of magnitude than the light diffraction limit, and they provide only averaged chemical information from the entire probed area [19,20].

High spatial resolution IR mapping can be achieved by using synchrotron IR light as a source for vibrational spectroscopy measurements [1,10,21,22]. The high photon flux of this source makes it possible to reduce the aperture down to a few micrometers with negligible decrease in the sensitivity, providing an IR beam spot size of ~10 μm. Several initial studies have demonstrated that synchrotron IR microspectroscopy measurements can track the progression of catalytic reactions in which zeolites and supported nanoparticles are used as catalysts [21,23–25].

For example, it was recently demonstrated that the catalytic reactivity within ZSM-5 crystals can be detected with IR microspectroscopy measurements [25]. The chemical structures of intermediates, which are formed during styrene oligomerization reaction, were monitored with synchrotron-based IR microspectroscopy.

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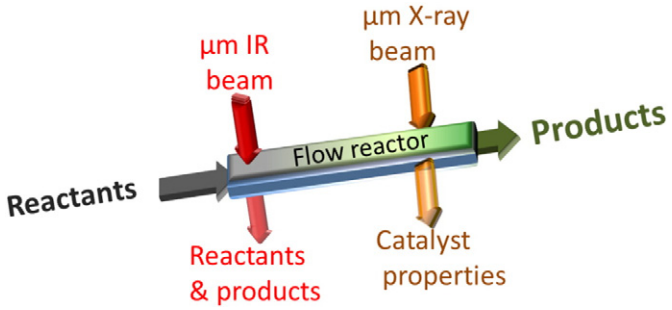

Fig. 1. Schematic representation of the experimental setup. Flow micro-reactor was packed with heterogeneous Au catalyst. Micrometer-sized IR and X-ray beams detected the vibrational spectra of organic molecules and the oxidation state of the catalyst, respectively, with a spatial resolution of 10 μm.

We have recently demonstrated that a detailed kinetic analysis of a multistep organic transformation can be achieved with synchrotron-based IR microspectroscopy measurements [21]. Heterogeneous Au catalyst was packed in a flow reactor and activated the cascade reaction of dihydropyran formation. High spatial resolution mapping of the reactants, intermediates and products along the flow reactor was performed with synchrotron-sourced IR beam. Full kinetic analysis of the catalytic reaction was accomplished by analyzing the IR microspectroscopy spectra at different points along the flow reactor.

In this study, we further analyzed the Au-catalyzed dihydropyran formation reaction, determining the deactivation mechanism of the catalyst under flow conditions. The chemical and electronic properties of the organic phase and the Au catalyst along the flow reactor were determined under reaction conditions with μm-sized, synchrotron-sourced, IR and X-ray beams (Fig. 1). These measurements clarified the reasons for deactivation of the Au catalyst. NEXAFS microspectroscopy measurements revealed that under flow reaction conditions the Au catalyst is reduced from the catalytically active species, Au(III), into non-active species. Accordingly, IR microspectroscopy measurements detected that the reduction of the Au catalyst was followed by quenching of the catalytic reactivity. Kinetic measurements determined that the presence of butanol, which is one of the reactants in this reaction, can either directly or indirectly reduce the catalytically active Au(III) species into its catalytically inert metallic state. Different approaches to minimize and delay the deactivation process are discussed in the paper.

2. Experimental setup

Au nanoparticles with a diameter of 2.0 ± 0.3 nm were prepared by encapsulating Au ions in a G4-PAMAM (Polyamidoamine) dendrimer matrix. Following their encapsulation, the Au ions were reduced into Au nanoparticles by the addition of $NaBH_4$ into the reaction mixture (Fig. 2a) [26,27]. The encapsulated nanoparticles were loaded on a mesoporous silica support (SBA-15) with a surface area of 760 $m^2\ g^{-1}$. The pore diameter of the mesoporous silica was 7 ± 1 nm and therefore the dendrimer-encapsulated Au nanoparticles were easily deposited in the pores of the mesoporous support with high distribution and without aggregation. The dendrimer-encapsulated Au nanoparticles were anchored onto the walls of the mesoporous support by hydrogen bonds which were formed between the OH-terminated G4-PAMAM dendrimer (G4-OH) and the SiO_2 surface [28]. This interaction prevented the detachment of dendrimer-encapsulated Au nanoparticles from the mesoporous SiO_2 support, even under liquid phase reaction conditions [29].

The small size of the encapsulated metallic nanoparticles enabled their oxidation from Au(0) into Au(III) by the addition of an inorganic oxidizer, $PhICl_2$, into the solution phase (Fig. 2b). No leaching of Au ions was detected following the oxidation of the Au nanoparticles into Au ions. The high stability of the Au ions is due to their encapsulation within the dendrimer matrix [30,31]. The oxidation process is reversible and the Au ions can be reduced back to Au(0) following an exposure to H_2. It was previously demonstrated that the oxidation of Au into Au(III) activates the Au catalyst toward a variety of π-bond activation reactions which are mainly activated by homogenous Au catalysts [30–32].

The Au@G4-OH/SBA-15 catalyst was deposited in a designated IR flow cell. The cell was constructed of two CaF_2 windows, which were separated by a 0.2 mm thick Teflon sheet. Prior to the X-ray microspectroscopy measurements, the catalyst was packed inside a quartz rod (ID 250 μm). Each reactor was connected to a syringe pump for continuous delivery of solvents into the flow reactor. These two reactors, that were specifically designed for in situ synchrotron-sourced IR and the X-ray measurements, have similar inner volume and diameter, ensuring comparable residence time of the reactants. No leaching of metal ions to the solution phase was detected during the catalytic reaction. The supernatant was collected and analyzed by GC and NMR. GC analysis verified that the catalytic yield and products selectivity in the IR and X-ray reactors were comparable (with variations of up to ±15%).

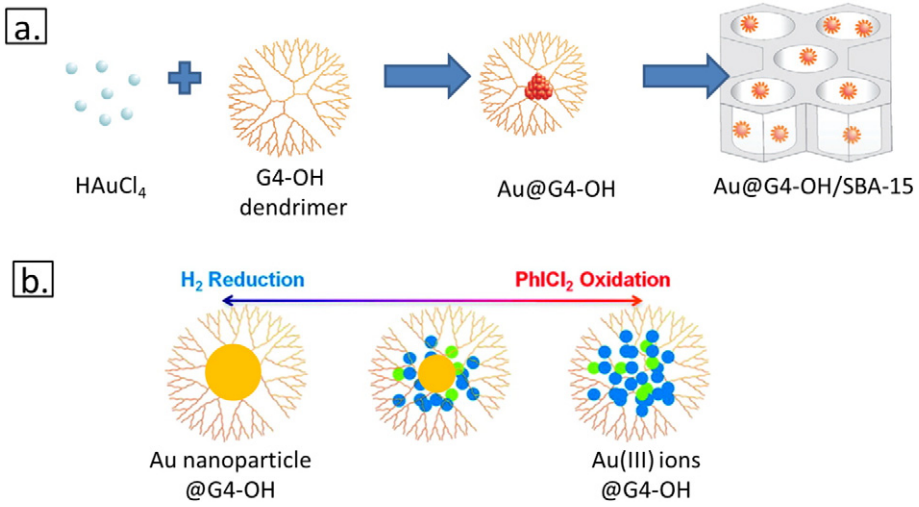

Fig. 2. (a) Preparation scheme of dendrimer-encapsulated Au nanoparticles and their deposition within the pores of mesoporous silica (SBA-15). (b) The dendrimer-encapsulated Au nanoparticles (marked in yellow circle) can be oxidized into the catalytically active Au(III) ions (green circles) along with formation of chloride ions (blue circles) by the addition of an inorganic oxidizer, $PhICl_2$, to the solution. The Au ions can be reduced back to their metallic state by exposure to H_2. The oxidation–reduction process is reversible. No leaching of Au ions to the solution phase was detected throughout the oxidation and reduction cycles.