

XAFS Characterization for SiO₂-Encapsulated Ag/WO₃ CatalystRajaram Bal^{1,*} and Takehiko Sasaki²¹ Light Stock Processing Division, CSIR- Indian Institute of Petroleum, Dehradun-248005, India² Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8561, Japan

1 Introduction

Direct oxidative dehydrogenative coupling of aniline to azobenzene (and azoxybenzenes) has been greatly explored, as the latter are ubiquitous motifs and serve as valuable intermediates to dyes, pigments, food additives, reducing agents, chemical stabilizers, therapeutic agents, polymerization inhibitors, photochemical switches, and as precursors in natural product synthesis. We examined the catalytic activity of our previously reported 2D-type Ag/WO₃ nanoplates [1] and nanoflowers catalysts [2]; however, these highly reactive catalysts produced CO₂ apart from other byproducts, leading to lower selectivity for azoxybenzenes. Therefore, in order to overcome this situation, we tried to adopt the confinement effect concept by using porous silica, which possesses short channels of highly accessible active sites that actually provide a protective shield to stabilize the oxygenated reactive species [3]. In an attempt to develop a novel catalyst system, we have synthesized nanoarchitectures of Ag/WO_x embedded within the silica channels with 2D morphology by a simple surfactant-assisted method. This catalyst is denoted as the 2D-type Ag/WO₃/SiO₂^{ENC}, that exhibited excellent catalytic properties for the production of azoxybenzene with a very high yield (~78.0%) under base-free reaction conditions [4].

2 Experiment

The Ag/WO₃ nanolayer (NL) catalyst was synthesized by the modified procedure in ref. [2]. Synthesis of the 2D-type Ag/WO₃/SiO₂^{ENC} was prepared by a wet chemical method [4]. XANES measurements at the Ag-K edge were carried out in transmission mode at room temperature at the AR NW10A station of the Photon Factory Advanced Ring at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF).

3 Results and Discussion

To analyze the molecular reactions in silver ions of the respective Ag-W-based catalysts, we conducted XANES measurements (Figure 1), which allows not only the determination of the valence of an excited atom but also gives information about the type of neighboring atoms. The different XANES features for silver species in the Ag/WO₃/SiO₂^{ENC} catalyst and Ag₂O basically reflect the different coordination environments surrounding Ag⁺ in these two compounds. As the numbers of oxygens increase around Ag⁺ (during oxidation), the

Ag K-edge step sharpens, and the edge peak (white line) becomes more prominent, which can be ascribed unambiguously to a dipole allowed 2p_{3/2} → 4d transition. Its intensity is directly related to the deoccupation of states derived from Ag 4d orbitals. The degree of depletion and thereby the increment in intensity demonstrate the degree of covalent bonding (highly directional orbitals) in the catalyst compared to the Ag(I) in AgNO₃.

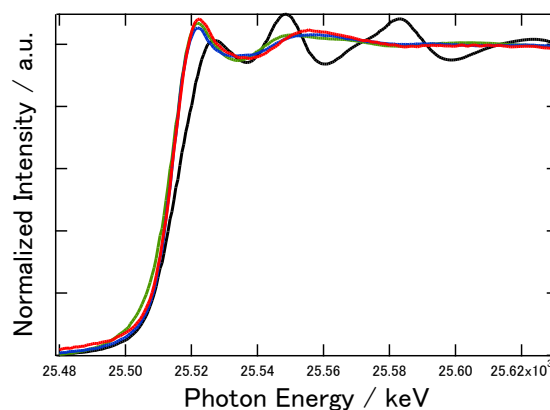


Fig. 1: Ag K-edge XANES spectra for Ag-WO₃/SiO₂^{ENC} (Red), Ag/WO₃^{NL} (Blue), AgNO₃ (Green) and Ag foil (Black).

In conjunction with other methods such as TEM, XPS, TPD, DFT calculations as well as reaction studies, we could successfully fabricate nanocomposites of Ag/WO₃ intercalated within the channels of the silica network using a surfactant-assisted hydrothermal process. The advanced catalytic activity of the present catalyst is due to its smaller size (2-5 nm), presence of twinned defect, activation of molecular oxygen effectively at the surface and electronic effect from two different metals [4].

References

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* raja@iip.res.in