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# Pd/Cu-Oxide Nanoconjugate at Zeolite-Y Crystallite Crafting the Mesoporous Channels for Selective Oxidation of Benzyl-Alcohols

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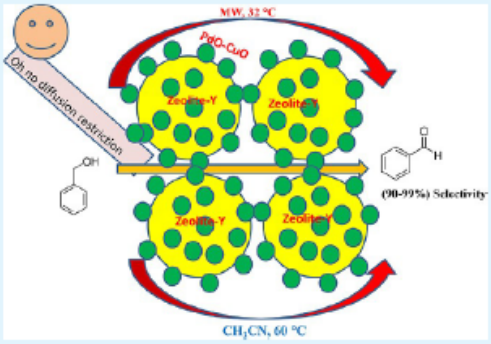
Supporting Information

**ABSTRACT:** Solid-state grinding of palladium and copper salts allowed the growth of palladium/copper oxide interface at the zeolite-Y surface. The hybrid nanostructured material was used as reusable heterogeneous catalyst for selective oxidation of various benzyl alcohols. The large surface area provided by the zeolite-Y matrix highly influenced the catalytic activity, as well as the recyclability of the synthesized catalyst. Impregnation of PdO-CuO nanoparticles on zeolite crystallite leads to the generation of mesoporous channel that probably prevented the leaching of the metal-oxide nanoparticles and endorsed high mass transfer. Formation of mesoporous channel at the external surface of zeolite-Y was evident from transmission electron microscopy and surface area analysis. PdO-CuO nanoparticles were found to be within the range of 2−5 nm. The surface area of PdO-CuO-Y catalyst was found to be much lower than parent zeolite-Y. The decrease in surface area as well as the presence of hysteresis loop in the $N_2$-adsoprtion isotherm further suggested successful encapsulation of PdO-CuO nanoparticles via the mesoporous channel formation. The high positive shifting in binding energy in both Pd and Cu was attributed to the influence of zeolite-Y framework on lattice contraction of metal oxides via confinement effect. PdO-CuO-Y catalyst was found to oxidize benzyl alcohol with 99% selectivity. On subjecting to microwave irradiation the same oxidation reaction was found to occur at ambient condition giving same conversion and selectivity.




**KEYWORDS:** *PdO-CuO, zeolite-Y, solid-state dispersion, benzyl alcohol, oxidation, microwave irradiation*

## 1. INTRODUCTION

Nanoparticles (NPs) with smaller size distribution have recently been of high focus due to their exceptional catalytic performance compared to their bulk and large-size counterparts.[1−15] Ultrafine NPs usually within the range of 2−5 nm or more appropriately <2 nm appeared to be atom-efficient catalyst because of their high surface to-volume ratio.[1−4,13,15] Such narrow size NPs also possess highly dense catalytic active sites that are available for effective catalysis.[5,6] In comparison to the monometallic NPs, bimetallic nanoclusters or metal oxides shows better activity due to the symbiosis existed between two different metals.[3,5,6,8] Because of such synergistic interaction the properties of the individual metal or metal oxides gets altered by virtue of charge and energy transfer resulting in the change in catalytic activities. So synthesis of mixed-metal oxides nanoparticle in smaller dimension is highly demanded because of their unique catalytic behavior governed by synergistic effect, as well as by the size.[16−20]

One of the disadvantages associated with these ultrafine or low dimension NPs is that they frequently suffer from agglomeration because of their high instability and thereby affect the catalytic efficiency.[4,7,9,16] Apart from stability, reusability of a nanocatalyst is an important factor that validates the usefulness of synthesizing a particular catalyst. So to improve the stability and reusability of these small and highly active particles, different techniques have been developed. Immobilizations into solid support like MOF, COF, silica, and graphene sheets are few of the conventional techniques to support such nanomaterials.[21] For example, Cao et al. designed conjugated microporous polymer to support ultrafine silver NPs (<3.7 nm).[21] Shang et al. fabricated graphene sheets with Pd and Ru ultrafine NPs and encapsulated into mesoporous $SiO_2$ for various catalytic oxidation−reduction reaction.[22] Zhao et al. synthesized ultrafine platinum/iron oxide nanoconjugates in silica nanoshells for CO oxidation.[23] Growth of such smaller range NPs into these solid matrixes are usually done by wet deposition technique, photo deposition,

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