Catalytic Reactivity and Selectivity on LTA Encapsulated RuO₂

Bi-Zeng Zhan¹ and Enrique Iglesia*¹
¹Department of Chemical Engineering, University of California at Berkeley, CA 94720, (US)
*iglesias@berkeley.edu

Introduction

Size-dependent redox properties of oxide nanoclusters have attracted great interest because they allow diverse catalytic behavior for a given elemental composition [1], but the synthesis and stability of clusters of uniform size remain significant challenges. Zeolites and related microporous materials provide essential scaffolds for controlling size, accessibility, and spatial constraints. [2-3] RuO₂ clusters of uniform size (~1 nm) have been deposited during synthesis within cages of FAU-X (faujasite-X zeolite, 1.3 nm) using hydrothermal crystallization without organic templates. [2] These encapsulated RuO₂ clusters showed high reactivity for aerobic oxidation of alcohols to aldehydes and ketones at near-ambient temperatures. A similar synthetic strategy has been reported for the synthesis of RuO₂ clusters within MFI (ZSM-5) channels [3], which upon reduction hydrogenate 1-hexene selectively over 2,4,4-trimethyl-1-pentene, which diffuses much more slowly within MFI channels. Here, we report the encapsulation of RuO₂ clusters within LTA (zeolite-A) cages (Na(RuO₂)A) during hydrothermal synthesis and the effect of LTA frameworks on the catalytic reactivity and selectivity for alcohol oxidation and alkene hydrogenation probe reactions on encapsulated RuO₂ and Ru clusters, respectively.

Materials and Methods

Encapsulation of RuO₂ in LTA was carried out using hydrothermal crystallization. Ru chloride hydrate was added to an aluminoisolate gel without an organic template. Hydrothermal crystallization was carried out at 373 K for 18-24 h under stirring conditions (400 rpm). Black solids were separated and washed with deionized water to reach a pH value of 7-8 and then dried at 393 K for 8 h in ambient air. Silica-supported RuO₂ was prepared as a reference sample by incipient wetness impregnation with Ru(NO)(NO₃)₃; thus, AlNMR spectra showed only lines for framework Al species in Na(RuO₂)A, because of reduced impurities. Solid-state magic-angle spinning (MAS) ²⁷Al NMR spectra showed only lines for framework Al species in Na(RuO₂)A. RuO₂ diffraction lines were not detected on Na(RuO₂)A (~28.4 and 35.5° on RuO₂/SiO₂); thus, RuO₂ domains were small or amorphous. Transmission electron microscopy and energy dispersive X-ray spectra (TEM-EDS) showed high dispersion of RuO₂ throughout the LTA crystallites in Na(RuO₂)A. High-resolution TEM images on Na(RuO₂)A showed RuO₂ clusters ~1 nm in diameter, consistent with their encapsulation within 1.1 nm cages in LTA. Thus, the hydrothermal synthesis protocols used led to significant RuO₂ encapsulation, as also found for zeolites with larger channel apertures (RuO₂/FAU [2] and RuO₂/MFI [3]).

The redox properties of supported RuO₂ domains were probed by using H₂ as stoichiometric reductant during thermal treatment. Reduction profiles for RuO₂/SiO₂ are similar to those reported previously [4]. Reduction temperatures for RuO₂ domains in Na(RuO₂)A were ~25 K lower than for RuO₂/SiO₂, indicating more reducible RuO₂ domains formed within LTA, consistent with their different oxidative dehydrogenation (ODH) rates on methanol oxidation to mixtures of formaldehyde, methyl formate, and dimethoxyethane. The ODH turnover rate on RuO₂/SiO₂ agrees with those previously reported (32 h⁻¹ at 393 K) [4], but ODH turnover rates were four-fold higher (121 h⁻¹) on Na(RuO₂)A.

We have also explored the competitive oxidation of methanol (C₃H₆O) and 2-methyl-1-propanol (C₆H₁₄O) co-reactants to test reactant shape-selectivity and the specificity of the encapsulation synthetic protocols, C₅ diffuses very slowly through 8-ring windows in LTA. The ratio of C₅/C₃ values (0.33) consistent with the predominant presence of RuO₂ cluster within cages. The detectable oxidation rates of C₅ absorptions (1.7 h⁻¹) reflect traces of RuO₂ clusters on accessible external surfaces or channel entrances in Na(RuO₂)A. The LTA frameworks also provide reactant shape-selectivity in the hydrogenation of ethylene in the presence of thiophene on Na(Ru)A, formed by reduction of Na(RuO₂)A with H₂ (Figure 1), because of encapsulated Ru clusters only accessible to ethylene. Thus, the 8-ring windows inhibit competitive adsorption or sulfidation of Ru by thiophene, which leads to rapid deactivation on unprotected Ru clusters in Ru/SiO₂ and traces of Ru clusters on external surfaces in Na(Ru)A (Figure 1a). These encapsulated Ru clusters provide a route for the protection of active sites from titration by organosulfur compounds and for retaining their reactivity for H₂ activation, hydrogenation, and hydrotreating reactions in mixed feedstocks containing these titrants as demonstrated in Figure 1b, in which steady ethylene hydrogenation rates remain only in Na(Ru)A.

References


Figure 1. Hydrogenation of ethylene and thiophene mixture on supported Ru clusters. Conditions: 0.1-0.3 g catalysts, 2 kPa ethylene, 1 kPa thiophene, 10 kPa H₂, balance He, 333 K. Prior to hydrogenation, RuO₂/SiO₂ was reduced at 573 K in flowing H₂ (100 cm³/min) for 1 h, while the reduction temperature for Na(RuO₂)A was 353 K.