

RuO₂ Clusters within LTA Zeolite Cages: Consequences of Encapsulation on Catalytic Reactivity and Selectivity**

Bi-Zeng Zhan and Enrique Iglesia*

The consequences of cluster size and spatial constraints are critical for the design of selective catalysts. Zeolites and other microporous solids provide essential scaffolds for controlling the size and accessibility of active structures and the nature of spatial constraints around such sites.^[1,2] The size-dependent redox properties of oxide nanoclusters lead to diverse catalytic properties for a given composition,^[3–5] but the synthesis and stability of such structures remain significant challenges. Encapsulation in zeolite cages or channels is an attractive route to control and maintain cluster size, but it has been confirmed in only a few cases.^[6–9] RuO₂ clusters of uniform size (ca. 1 nm) were deposited predominantly in FAU-X (faujasite-X zeolite, 1.3 nm) during hydrothermal synthesis and showed high reactivity for aerobic alcohol oxidation.^[6] A similar strategy led to RuO₂ clusters within MFI (ZSM-5) channels,^[7] which after reduction catalyzed 1-hexene hydrogenation with higher rates than for 2,4,4-trimethyl-1-pentene, a larger molecule that diffuses slowly in MFI channels. Coating Pt–Fe/SiO₂ with LTA (zeolite-A) films led to selective oxidation of CO in the presence of larger butane molecules.^[10]

Herein, we report the encapsulation of RuO₂ clusters within sodium-LTA cages during hydrothermal synthesis, producing a caged catalyst that will be referred to as Na(RuO₂)A, and the catalytic consequences of encapsulation. In situ X-ray absorption spectra (XAS) were used to probe the ruthenium oxidation state in LTA-encapsulated clusters after treatment with H₂ or O₂. Na(RuO₂)A and RuO₂/SiO₂ samples gave identical near-edge spectra (Figure 1), suggesting that RuCl₃ precursors were fully converted to RuO₂ during hydrothermal synthesis, as in the case of RuO₂ clusters

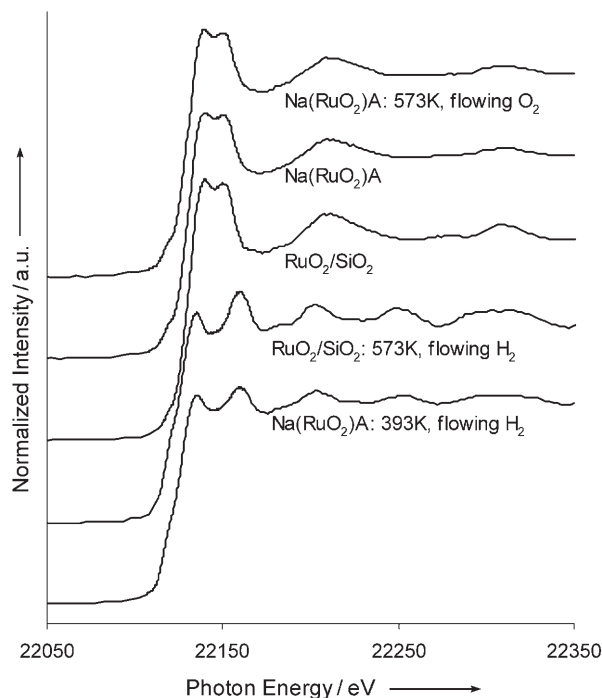


Figure 1. Near-edge X-ray absorption spectra for Na(RuO₂)A and RuO₂/SiO₂ (as-synthesized) and after treatment in O₂ (Praxair, UHP) and H₂ (Praxair, UHP). For clarity, traces are shifted vertically.

within FAU^[6] and MFI.^[7] Treatment of Na(RuO₂)A in O₂ up to 673 K for 1 h did not cause detectable changes in the near-edge spectra. Na(RuO₂)A treated in H₂ at 393 K gave near-edge (Figure 1) and fine-structure (Figure S1 in the Supporting Information) spectra similar to those for reduced Ru/SiO₂ (treated in H₂ at 573 K)^[11] and for Ru metal powders (not shown). Thus, RuO₂ nanoclusters within LTA cages are reduced from Ru⁴⁺ to Ru⁰ in H₂ below 393 K, consistent with H₂ consumption rates measured during this treatment (Figure 2).

Na(RuO₂)A diffractograms showed only crystalline LTA (Figure S2 in the Supporting Information). The absence of RuO₂ lines (ca. 28.4 and 35.5°) suggests that RuO₂ domains are small or amorphous. High-resolution transmission electron micrographs of Na(RuO₂)A (Figure S3 in the Supporting Information) confirmed the predominant presence of RuO₂ clusters with diameters of about 1 nm, similar to the size of the cages in LTA (1.1 nm). This result is consistent with preferential encapsulation, as also found in FAU^[6] and MFI^[7] and as supported by N₂ adsorption uptakes.^[12] Energy-dispersive X-ray spectra (EDS; Figure S4 in the Supporting Information) showed uniform Ru distributions among and

[*] Dr. B.-Z. Zhan,^[†] Prof. E. Iglesia
Department of Chemical Engineering
University of California at Berkeley
Berkeley, CA 94720 (USA)
Fax: (+1) 510-642-4778
E-mail: igation@berkeley.edu

[†] Current address:
Chevron Research and Technology Company
Richmond, CA 94802 (USA)

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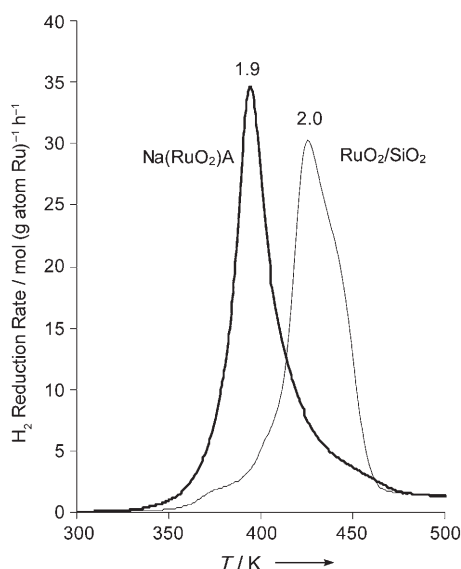


Figure 2. H_2 uptake on $\text{Na}(\text{RuO}_2)\text{A}$ and $\text{RuO}_2/\text{SiO}_2$ during reduction treatments (H_2/Ru ratios shown above each peak).

within LTA crystals, but also detected a few crystallites containing mostly Ru; their size and location suggest that they are present outside LTA crystals and that they do not contribute significantly to the surface area of Ru or RuO_2 structures. Treatment with dilute (0.005 M) oxalic acid removed some of these larger clusters and decreased their contribution to catalytic reactions (Figure S5 in the Supporting Information).

The dynamics of RuO_2 reduction were measured from H_2 consumption rates during thermal treatment. Reduction rates (Figure 2) and Arrhenius plots of incipient reduction rates (Figure S6 in the Supporting Information) showed that RuO_2 domains in $\text{Na}(\text{RuO}_2)\text{A}$ were reduced more rapidly than in $\text{RuO}_2/\text{SiO}_2$ (ca. 6 nm; 18% dispersion, Table 1). The temper-

atures required to achieve reduction rates of 4 mol (g atom Ru) $^{-1}$ h $^{-1}$ were 368 K and 396 K for $\text{Na}(\text{RuO}_2)\text{A}$ and $\text{RuO}_2/\text{SiO}_2$, respectively. These trends are unusual, because smaller oxide domains dispersed on mesoporous supports are typically harder to reduce than larger domains.^[5,14,15] The remarkable reducibility of encapsulated RuO_2 clusters may reflect their weak interactions with Na-terminated walls in LTA cages, in contrast with the strong Ru-O-Si linkages formed upon grafting RuO_2 onto hydroxylated SiO_2 surfaces.

Magic angle spinning ^{27}Al NMR spectra (Figure S7 in the Supporting Information) for $\text{Na}(\text{RuO}_2)\text{A}$ and $\text{Na}(\text{RuO}_2)\text{A}$ were identical, suggesting that RuO_2 clusters did not perturb framework aluminum centers. The amount of H_2 consumed (per Ru atom) was 1.9 ± 0.2 on $\text{Na}(\text{RuO}_2)\text{A}$ and 2.0 ± 0.2 on $\text{RuO}_2/\text{SiO}_2$ (Figure 2), consistent with the full reduction of Ru^{4+} to Ru^0 , as is also evident from XAS data (Figure 1) and from previous studies on SiO_2 supports.^[11]

Table 1 shows methanol oxidative dehydrogenation (ODH) turnover rates (TOR_{ODH} ; per surface Ru atom) and selectivities on $\text{Na}(\text{RuO}_2)\text{A}$ and $\text{RuO}_2/\text{SiO}_2$. ODH reaction rates are limited by C–H bond activation of chemisorbed methoxide species on RuO_2 domains.^[11] This step requires reduction of Ru^{4+} centers within Mars–vanKrevelen redox cycles. Initial HCHO products then react with methanol to form methoxymethanol ($\text{CH}_3\text{OCH}_2\text{OH}$) intermediates that dehydrogenate to methylformate (MF) or condense to form dimethoxymethane (DMM). HCHO also reacts to form HCOOH and CO_x . These sequential pathways require one oxidative CH_3OH dehydrogenation (ODH) event for each HCHO, MF, DMM, and CO_x molecule formed. Methanol ODH turnover rates on $\text{RuO}_2/\text{SiO}_2$ agreed with those in previous studies (32 h^{-1} at 393 K),^[11] but ODH turnover rates were significantly higher on $\text{Na}(\text{RuO}_2)\text{A}$ (121 h^{-1}). These reactivity differences reflect the highly reducible nature of RuO_2 clusters in LTA, which are evident from their H_2 reduction rates (Figure 2).

Competitive oxidation of methanol (C_1) and 2-methyl-1-propanol (C_4) was used to probe the selectivity of the encapsulation synthetic protocols and the potential for reactant-shape selectivity using LTA-encapsulated clusters. 2-Methyl-1-propanol does not diffuse through eight-membered ring windows in LTA.^[13] The ratio of C_1 and C_4 alcohol ODH rates was much higher on $\text{Na}(\text{RuO}_2)\text{A}$ (2.1) than on $\text{RuO}_2/\text{SiO}_2$ (0.33; Table 2), consistent with RuO_2 surfaces residing predominantly within LTA cages and being inaccessible to 2-methyl-1-propanol. Measured C_4 alcohol ODH rates (1.7 h^{-1} ; Table 2) reflect trace concentrations of large RuO_2 clusters on external surfaces of $\text{Na}(\text{RuO}_2)\text{A}$. Methanol ODH rates on $\text{Na}(\text{RuO}_2)\text{A}$ were much lower in competitive reactions than when methanol was used as the sole alcohol reactant (3.5 vs. 117 h^{-1} , Table 2); 2-methyl-1-propanol ODH rates, however, were unaffected by the presence of methanol co-reactants.

Thus, the ratio of C_1 and C_4 alcohol ODH rates was much higher with individual reactants (65) than in competitive reactions (2.1), because 2-methyl-1-propanol at channel entrances or external surfaces interferes with methanol diffusion into zeolite channels.

Reactant-shape selectivity was also observed in competitive oxidation of methanol (C_1) and isopropyl alcohol (IPA) (Figure S5 in the Supporting Information). The ratio of ODH rates for methanol and IPA was 1.5 on $\text{RuO}_2/\text{SiO}_2$ and 3.0 on $\text{Na}(\text{RuO}_2)\text{A}$. This value further increased to 3.7 after treating

Table 1: Methanol oxidation rates and selectivities on RuO_2 catalysts.^[a]

Catalysts	Ru dispersion [%]	TOR_{MeOH} [mol (g atom $\text{Ru}_{\text{surface}})^{-1}$ h $^{-1}$]	TOR_{ODH} [mol (g atom $\text{Ru}_{\text{surface}})^{-1}$ h $^{-1}$]	Production selectivity [%]			
				HCHO	MF	DMM	CO_2
$\text{RuO}_2/\text{SiO}_2$ (4.3 wt% Ru)	18	61	32	21	71	4	4
$\text{Na}(\text{RuO}_2)\text{A}$ (4.7 wt% Ru)	48	171	121	35	52	6	7

[a] 4 kPa MeOH, 9 kPa O_2 , 1 kPa N_2 , balance He, 393 K. Catalysts treated in 20% O_2 in He ($100 \text{ cm}^3 \text{ min}^{-1}$) at 423 K for 2 h before reactions; TOR_{ODH} is the oxidative dehydrogenation rate per surface Ru atom at 20% conversion. No dimethyl ether detected.

Table 2: ODH rates and rate ratios for methanol (C₁) and 2-methyl-1-propanol (C₄) oxidation on RuO₂ catalysts.^[a]

Catalyst	ODH rates [mol (g atom Ru _{surface}) ⁻¹ h ⁻¹]		C ₁ /C ₄ ODH rate ratio
	C ₁	C ₄	
RuO ₂ /SiO ₂ (4.3 wt % Ru)	2.2	6.7	0.33
Na(RuO ₂)A (4.7 wt % Ru)	3.5	1.7	2.1
Na(RuO ₂)A ^[b] (4.7 wt % Ru)	117	1.8	65

[a] 2 kPa MeOH, 2 kPa 2-methyl-1-propanol, 9 kPa O₂, 1 kPa N₂, balance He, 413 K. Catalysts treated in 20% O₂ in He (100 cm³ min⁻¹) at 423 K for 2 h before reactions. [b] MeOH and 2-methyl-1-propanol reactions carried out separately.

Na(RuO₂)A with 0.005 M aqueous oxalic acid at ambient temperature, a treatment that partially removes RuO₂ clusters on external zeolite surfaces. X-ray photoelectron spectra (XPS) showed that Ru/Si atomic ratios decreased from 0.054 to 0.040 after oxalic acid treatment; this value is much lower than expected from the bulk compositions (0.098), suggesting that exposed Ru surfaces lie predominantly within LTA crystallites.

Encapsulated Ru clusters hydrogenate alkenes in the presence of organosulfur compounds that typically inhibit such reactions by competitive coadsorption or sulfidation.^[16–18] Eight-membered ring windows in LTA prevent thiophene access to encapsulated Ru clusters and maintain active Ru surfaces in the presence of poisons that deactivate unprotected Ru clusters. Thiophene hydrogenation rates decreased with time on both Ru/SiO₂ and Na(Ru)A (reduced from RuO₂). The hydrogenation products (2,3-dihydrothiophene, 3,4-dihydrothiophene, tetrahydrothiophene) became undetectable after 3 h (Figure S8 in the Supporting Information), indicating that all Ru sites accessible to thiophene in both catalysts are poisoned by thiophene-derived species.^[16,17] Ethene and thiophene hydrogenation rates decreased in parallel on Ru/SiO₂. Ethene hydrogenation rates (per surface Ru atom) decreased from 5.3 h⁻¹ to 3.4 h⁻¹ within 3 h. The residual ethene hydrogenation rates reflect the hydrogenation reactivity of sulfided Ru species, as also detected on [bis(tetramethylthiophene)Ru⁰]^[16] [(thiophene)Ru(Cp)]^[17] (Cp = C₅H₅), and RuS_x.^[18] In contrast, Na(Ru)A gave stable ethene hydrogenation rates (ca. 21 h⁻¹) after an initial decrease (from 25 to 21 h⁻¹), apparently caused by the poisoning of Ru sites at external surfaces or channel entrances. Thus, LTA frameworks provide significant protection from thiophene adsorption and poisoning in Ru nanoclusters and lead to ethene hydrogenation rates much higher than on unprotected Ru clusters.

In conclusion, RuO₂ nanoclusters (ca. 1 nm diameter) were predominantly encapsulated within LTA cages during hydrothermal crystallization of LTA. These RuO₂ clusters are more easily reduced than comparable clusters on mesoporous supports and give much higher turnover rates for reactions involving reduction–oxidation cycles, such as methanol oxidation. RuO₂ clusters encapsulated on Na-LTA oxidize methanol preferentially over 2-methyl-1-propanol. Further-

more, Ru clusters formed by reduction of RuO₂-LTA hydrogenate ethene in the presence of organosulfur compounds, which poison Ru clusters on SiO₂. These results represent the first report of encapsulation within zeolites with eight-membered ring channels and demonstrate the marked catalytic consequences of encapsulation for reactivity, reactant selectivity, and protection of active sites against sintering and poisons.

Experimental Section

Encapsulation of RuO₂ within LTA cages was carried out using hydrothermal crystallization.^[19] The hydrothermal synthesis was conducted at 373 K for 16 h while stirring (400 rpm; see also the Supporting Information). The sample contained 4.7 wt % Ru and a Si/Al atomic ratio of 1.3 after drying at 393 K for 8 h in ambient air. Silica-supported RuO₂ was prepared by incipient wetness impregnation with [Ru(NO)(NO₃)₃] using methods reported previously.^[11] RuO₂/SiO₂ (4.3 wt %) was treated at 673 K for 2 h in flowing dry air before characterization and catalytic measurements.

In situ X-ray absorption spectra were recorded at the Stanford Synchrotron Radiation Laboratory using beamline 6–2. Samples (10 mg, 80–120 mesh) were held within a quartz capillary (0.8 mm inner diameter, 0.1 mm wall thickness).^[8] Spectra were recorded at ambient temperature and on samples heated from ambient to the target temperature at 0.167 K s⁻¹ and held for 1 h. XPS spectra were measured with a Kratos (Axis HS) instrument. The dispersion of Ru clusters was determined from H₂ uptakes at 313 K, assuming a 1:1 H/Ru_{surface}^[11] stoichiometry (Autosorb-1, Quantachrome). H₂ reduction rates of supported RuO₂ domains were measured during thermal treatment with H₂ (Praxair, 20% H₂/Ar; 1.33 cm³ s⁻¹) and heated from 243 to 873 K at 0.167 K s⁻¹. The complete reduction of CuO powder (Sigma-Aldrich, 99.995%) was used for calibration. Catalytic rates and selectivities were measured in a packed-bed quartz micro-reactor using samples (60–120 mesh, 0.03–0.3 g) diluted with quartz powder to prevent temperature gradients. Reactant and product concentrations were measured by on-line gas chromatography (Hewlett-Packard 6890GC).

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- [12] Uptake (Autosorb-6, Quantachrome) of N₂ at its boiling point gave a BET surface area of 11.2 m²g⁻¹ for Na(RuO₂)A. This value reflects only the external area of zeolite crystals (LTA micropores are inaccessible to N₂ under these conditions^[13]), consistent with the size of LTA crystals (ca. 500 nm by scanning electron microscopy), which would have a surface area of 10 m²g⁻¹ (for cubic crystals). The RuO₂ clusters (ca. 2 nm diameter; 48% dispersion, Table 1) alone would give a surface area of about 50 m²g⁻¹ if they were present at external surfaces and accessible to N₂. Thus, BET data are consistent with preferential encapsulation of RuO₂ clusters within LTA cages in these samples.
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