

60 °C. Chromatography on a 12 × 1 in. silica gel column have a crude yellow product which was purified by preparative thin-layer chromatography. Benzene-hexane (1:1) developed a yellow band which yielded 0.03 g of a semicrystalline yellow material, which was not successfully purified, and an orange band. The latter was rechromatographed with use of pure benzene to give 0.1 g (18%) of the desired product as orange crystals, mp 202-205 °C. Anal. Calcd: C, 56.3; H, 3.5; Cl, 3.9. Found: C, 56.5; H, 3.5; Cl, 4.4. IR (KBr): 3060 (w), 1962 (s, Ru-CO), 1620 (s), 1545 (w), 1485 (m), 1475 (s), 1440 (s), 1260 (s), 1210 (s), 1155 (s), 1145 (s), 1095 (m), 785 (w), 745 (m), 690 (s), 515 (s), 320 (m, RuCl) cm⁻¹. ¹H NMR (CDCl₃): 4.87 ppm. ¹⁹F NMR (CDCl₃): 74.31, 74.76 ppm. ³¹P NMR (CDCl₃): 27.4 ppm. Electronic spectrum (CHCl₃) [λ_{max} (log ε)]: 239 (4.44), 260 (4.38), 280 (sh) nm.

Rh(F₆acac)(CO)(Ph₃P) (4). A solution of 0.46 g (0.5 mmol) of Rh(CO)H(Ph₃P)₃ and 0.26 g (0.5 mmol) of Pd(F₆acac)₂ in 20 mL of toluene was heated for 12 h at 50 °C and then chromatographed on a silica gel column as before. Dichloromethane eluted a yellow compound which was further purified by preparative TLC (silica, benzene). Recrystallization from acetone-ethanol gave 0.065 g (22%) of the product as orange flakes, mp 164-165.5 °C. Anal. Calcd: C, 48.0; H, 2.7. Found: C, 47.8; H, 2.6. IR (KBr): 3060 (w), 1999 (s, Rh-CO), 1630 (m), 1610 (s), 1560 (w), 1530 (w), 1460 (s), 1490 (m), 1485 (m), 1260 (s), 1200 (m), 1150 (s), 1100 (s), 805 (s), 750 (s), 745 (sh), 690 (s), 675 (m), 580 (m), 535 (m), 535 (m), 525 (m), 505 (m) cm⁻¹. ¹H NMR (CDCl₃): 6.24 ppm. ¹⁹F NMR (CDCl₃): 75.52, 75.71 ppm. ³¹P NMR (CDCl₃): 47.7 ppm (*J*_{Rh-P} = 178). Electronic spectrum (CHCl₃) [λ_{max} (log ε)]: 240 (4.29), 264 (3.98), 270 (3.98), 325 (3.90) nm.

Rh(F₆acac)(CO)(Ph₃P)₂ (5). A mixture of 0.20 g (0.22 mmol) of RhH(CO)(Ph₃P)₃ and 0.05 g (0.22 mmol) of hexafluoroacetylacetone in 10 mL of toluene was heated for 30 min at 80 °C and then evaporated onto 5 g of silica gel. This was placed atop a 6 × 1/2 in. column made up in hexane. Benzene-hexane (1:1) eluted a trace of unidentified orange material. Pure benzene eluted (Ph₃P)₂Rh(CO)(F₆acac), 0.03 g (16%), as yellow needles, mp 147-148 °C, after recrystallization from ethanol. Anal. Calcd: C, 58.5; H, 3.6. Found: C, 58.8; H, 3.6. IR (KBr): 3060 (w), 1980 (s, Rh-CO), 1670 (s), 1535 (m), 1520 (m), 1480 (w), 1440 (s), 1255 (s), 1200 (s), 1140 (s), 1095 (s), 785 (w), 740 (m), 690 (s), 660 (m), 520 (s), 505 (s) cm⁻¹. ¹H NMR (CDCl₃): 4.66 ppm. ¹⁹F NMR (CDCl₃): 76.0 ppm. ³¹P NMR (CDCl₃): 29.0 (*W*/2 = 90) ppm.

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Registry No. 1, 64567-30-2; 2, 76136-84-0; 3, 64567-27-7; 4, 76136-85-1; 5, 76189-27-0; Pd(F₆acac)₂, 64916-48-9; RuH₂(CO)-(Ph₃P)₃, 25360-32-1; RuHCl(CO)(Ph₃P)₃, 16971-33-8; Rh(CO)H-(Ph₃P)₃, 17185-29-4.

Contribution from Union Carbide Corporation, Technical Center, Tarrytown, New York 10591

Migration and Localization of Thallium in Zeolites following Ozonation

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The redox behavior and localization of metal ions and metal-containing phases in ion-exchanged zeolites have been extensively studied¹⁻⁴ because of their potential impact on the performance and regenerability of metal-exchanged zeolite

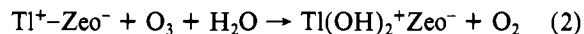
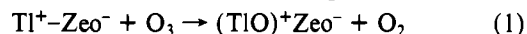
catalysts. For example, it was reported^{2,5,6} that treatment of Pd²⁺-Y, Cu²⁺-Y, and Ag⁺-Y zeolites with hydrogen at high temperatures caused formation of metal crystallites on the surface of the zeolites or of metal agglomerates in the pores. In some cases, high-temperature oxidation with oxygen re-oxidized the metal particles to ions (rather than metal oxides), which then migrated back into the zeolite matrix.^{7,8} However, oxide phases dispersed between zeolite crystals have also been identified.⁷⁻⁹ In a study of the regeneration and reuse of immobilized thallium reagents as organic oxidants, we have observed the room-temperature migration of thallium from internal sites to the surface when Tl⁺-exchanged zeolites were oxidized with moist ozone. On reduction, the ions returned to sites within the zeolite structure. However, the redox bulk ⇌ surface migration is only partially reversible.

This partial reversibility^{3,7} and the need for hydration¹⁰ have been reported by others studying redox migration of ions in zeolite. Otherwise, our results differ from most previously published studies on the subject. Notably, thallium migration occurred at 23-25 °C as opposed to the 100-400 °C range required to effect migration of Ag, Cu, Ni, Pt, and Pd. Additionally, the direction of thallium migration is the reverse of that usually observed with other metals.

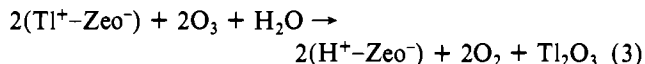
All the data reported herein were obtained on a Linde proprietary synthetic zeolite¹¹ (referred to here as Zeo) with SiO₂/Al₂O₃ = 49, which was ion exchanged with Tl⁺. However, qualitatively similar observations were also made with Tl⁺-Y and Tl⁺-mordenite. It is known that the Linde zeolite has a 6-Å pore size, but other details of the structure are yet to be determined.

Three successive treatments of H⁺-Zeo with aqueous TiNO₃ under reflux produced Tl⁺-Zeo (A) having an atom ratio of Tl/Al = 0.93 ± 0.14. NO₃⁻ analysis of A confirmed the absence of TiNO₃ contamination. Exposure of A to moist ozone (2 wt % in O₂) at 23-25 °C and 0.5 L min⁻¹ for 2-8 h caused the white solid to change to a dark brown material (B). The requirement for water as a coreactant was established by ozonation of A, which was previously dried at 108 °C in vacuo for 11 h, under rigorously anhydrous conditions. No color change occurred, and HF dissolution of the white powder followed by iodometric titration demonstrated the total absence of Ti(III).

One could envision two simple reactions by which Ti(III) could be formed in the zeolite pores to balance the framework anionic charge (designated Zeo⁻), viz., eq 1 and 2. [Zeo is



used as a convenient abbreviation. It is not intended as a new nomenclature and it is not the Union Carbide name for the zeolite.] Instead, we found that the thallium ions migrate to form brown Tl₂O₃ on the surface of the zeolite particles (eq 3). The framework charge neutrality is presumably main-



tained by protons from water vapor, while the driving force for migration arises, at least in part, from the energy of crystallization of Tl₂O₃.

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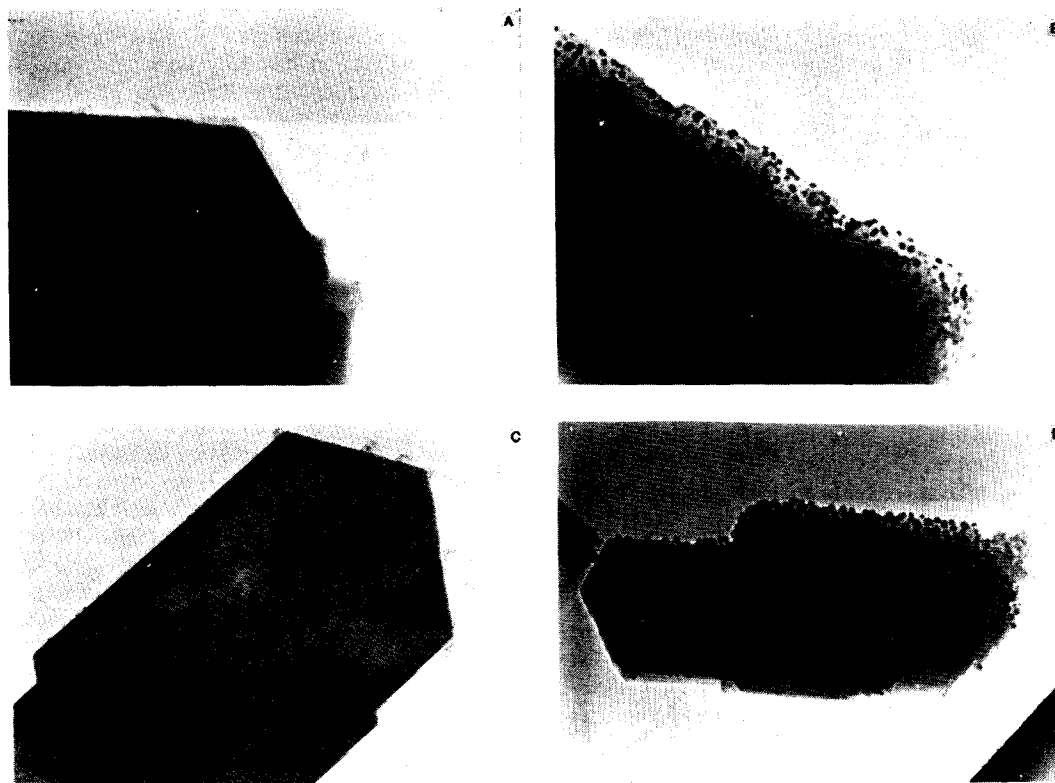


Figure 1. JEOL JEM-200 photomicrographs ($\times 70\,000$) of thallium-exchanged zeolite samples (1 mm = 660 Å): A, Tl^+ -Zeo; B, sample A after treatment with moist ozone (note Tl_2O_3 particles, ~ 76 -Å size, on surface); C, sample B after calcination in air at 600 °C for 16 h (Tl_2O_3 decomposed); D, sample C after treatment with moist ozone (Tl_2O_3 reappears).

Evidence to support the migration of thallium and formation of Tl_2O_3 is provided by the following data. The X-ray powder pattern of B showed, along with the expected peaks of Zeo, three intense peaks in the region $2\theta = 8$ – 56° , with intensity ratios and 2θ values consistent with those of authentic Tl_2O_3 .¹² By X-ray line-broadening measurements,^{7,13} it was determined that the average crystallite size of Tl_2O_3 was ~ 76 Å—too large for location within the 6-Å pores of the zeolite. These crystallites are visible in Figure 1B, which is a transmission electron micrograph (TEM) of B. Note their absence prior to ozonation (Figure 1A). ESCA measurements (Figure 2A,B) indicate that, upon ozonation, $\text{Tl}(4f_{7/2})$ electron binding energies shift from 120.3 eV in A to 118.3 eV in B. Although most elements show an increase of binding energy with an increase in oxidation state, the reverse trend for thallium and the 2-eV shift are well established in the literature.^{14,15} Also notable is the ~ 6 -fold increase in the intensity of the thallium peaks relative to the Si (2p) peak. This increase reflects the higher surface concentration of thallium following ozonation of the zeolite.

All the $\text{Tl}(\text{III})$ present was in the form of Tl_2O_3 . No TlO^+ and/or $\text{Tl}(\text{OH})_2^+$ ions were present in the zeolite in ion-exchangeable form, because the extract of B with aqueous NaNO_3 gave a negative starch iodide test. Also, rapid dissolution of B in $\text{HF}/\text{H}_2\text{SO}_4$ followed by iodometric titration showed that $68 \pm 5\%$ of the total thallium in B was in the +3 state. Similarly, quantitative analysis by X-ray peak area measurements revealed that $60 \pm 3\%$ of the thallium in B was

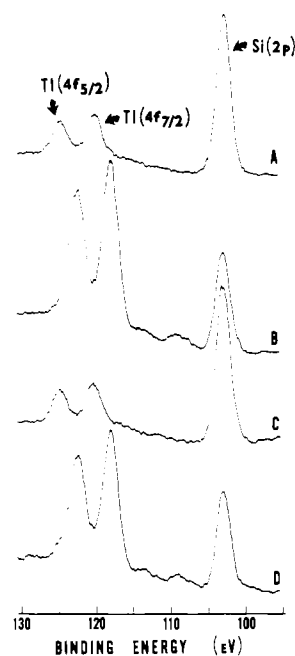
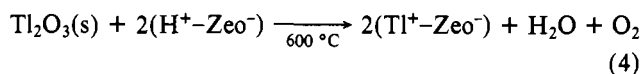


Figure 2. ESCA spectra of thallium-exchanged zeolite samples obtained with PEI Model SAM/ESCA surface analyzer: A, Tl^+ -Zeo; B, sample A after treatment with moist ozone; C, sample B after calcination in air at 600 °C for 16 h; D, sample C after treatment with moist ozone. The Si (2p) binding energy is at 103.0 eV in all samples.

in the form of diffracting Tl_2O_3 particles.

Calcination of the brown solid, B, at 600 °C for 16 h in air yielded C, a white powder of similar Tl/Al atom ratio (0.95 ± 0.14) to its precursor (eq 4). C was indistinguishable from A according to TEM, ESCA (Figure 2C), and X-ray powder diffraction data. No additional crystalline phase was detected

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in C. Moreover, its dissolution by HF followed by a starch iodide test for Tl(III) gave a negative result and confirmed the complete reduction of Tl(III) to Tl(I) upon calcination of B. Note that this thermal decomposition is inconsistent with published observations¹⁶ on anhydrous Ti_2O_3 . The facile thermal decomposition of hydrated Ti_2O_3 at $<100^\circ\text{C}$ has been reported by Hüttig et al.¹⁷

Exposure of C to moist ozone for 8 h regenerated the brown Ti_2O_3 surface. The particles were again $\sim 76 \text{ \AA}$, and the TEM (Figure 1D) X-ray powder diffraction pattern and ESCA (Figure 2D) of the product, D, are qualitatively similar to the original ozonation product, B. However, iodometric titration of the HF/ H_2SO_4 solution of D showed that only 82% of the total Ti_2O_3 present in B underwent reoxidation on the calcination/ozonation cycle. This number agrees well with the 86% reoxidation value obtained by both quantitative ESCA and area measurements of the Ti_2O_3 X-ray powder pattern peaks. Thus, although the observed thallium oxidation and migration can be reversed thermally or chemically (vide infra), the extent of Ti_2O_3 formation decreased with each subsequent redox cycle. The source of this degradation is not obvious. Careful quantitative comparison of X-ray peak areas and intensities of A and C revealed no experimentally significant changes, so gross zeolite structural collapse had apparently not occurred. Limited or partial collapse and trapping of Ti^+ inside pores or at sites with different charge densities cannot, however, be ruled out, because the powder diffraction pattern may be insensitive to these changes.

The brown Ti_2O_3 -coated solids B and D reacted with organic reagents to form oxidized products and Tl(I). ESCA and X-ray powder patterns confirmed the reduction of Ti_2O_3 and the location of Tl(I) within the zeolite framework. When B was slurried with a CH_2Cl_2 solution of phenol at room temperature and at dry ice/acetone temperature, brown oxidation products (quinones and oxidatively coupled phenols)^{18,19} were formed. The reduced zeolite, E, was reozonized to give brown Ti_2O_3 -coated F. After pumping in vacuo to remove excess ozone, F was used in both a flow-through and closed system to oxidize moist propylene at 25°C .²⁰ Acetone²⁰⁻²² was the only organic product detected by GC/MS. The white zeolite product had ESCA binding energies and an X-ray powder pattern identical with E and A. Iodometric titration also confirmed the total absence of Tl(III). However, the total thallium present was unchanged.

Laboratory oxidations of organic compounds with Tl(III) have been studied by McKillop and Taylor²³ and their co-workers. The potential commercial use of these reactions for the manufacture of epoxides, carbonyl compounds, and aromatic derivatives is evidenced by a large number of pertinent patents^{20,24-26} and articles. Patents claiming the use of immobilized Tl(III) reagents²⁷ or of Ti_2O_3 ^{22,28} for selective ox-

idations have also been granted. Despite this interest, however, commercialization has only been minimal, if at all. The principal technical drawback has been the absence of a cost-effective method of reoxidizing the stoichiometric amounts of Tl(I) formed back to Tl(III). Regeneration with hydroperoxide,²⁹ peracids,²⁴ and Ce(IV)³⁰ has been proposed. Oxygen or air effects the change only at high temperatures and pressures.^{31,32}

The standard reduction potential for the half-cell $\text{Ti}^{3+} + 2e^- \rightarrow \text{Ti}^+$ is 1.25 V. This value is 0.02 V greater than the standard electrode potential for the oxygen half-cell. That the electrode potential for ozone reduction is 0.82 V above that for thallium indicates that regeneration of Tl(III) by ozonation is thermodynamically favorable at 25°C . Prior to our work on the ozonation of Tl-zeolites, we established the kinetic feasibility of thallium oxidation by ozone by effecting $>95\%$ conversion of TlNO_3 to Ti_2O_3 in 45 min at 25°C with 2% O_3 in O_2 . Heretofore, only limited use³³ has been made of this thermodynamic and kinetic advantage. Our results show that regeneration with ozone yields an easily accessible surface oxidant, but the partial reversibility of the redox-migration phenomenon limits the utility of ozonation as a method of regeneration for thallium reagents immobilized in zeolites. Ozone can conceivably still function as a regenerant if the immobilization is done as described by Taylor et al.²⁷ Treatment with trimethoxymethane or other dehydrating agent will be necessary in order to avoid thermal decomposition of Ti_2O_3 under realistic reaction conditions.²²

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Investigation of Axial Anionic Ligand and Porphyrin Substituent Effects on the Oxidation of Iron(III) Porphyrins: Porphyrin-Centered vs. Metal-Centered Oxidation

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The electrochemical behavior of iron porphyrins is of current interest due to their diverse biological functions as redox catalysts. Iron porphyrins may exhibit formal oxidation states of +4, +3, +2, and +1,¹ with iron(II) and iron(III) porphyrins being characterized in high-, low-, and intermediate-spin states.²⁻⁵ In nonaqueous solvents many metalloporphyrins

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