Selective Propane Dehydrogenation with Single Site Co^{II} on SiO₂ by a Non-redox Mechanism

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Abstract

We report the synthesis, characterization, and catalytic performance for gas phase propane dehydrogenation of single site Co^{2+} ions supported on silica. Spectroscopic characterization by resonance Raman, electron paramagnetic resonance, and X-ray near edge and extended absorption fine structure revealed that tetrahedrally coordinated Co^{2+} ions are chemisorbed into the trisiloxane rings on the surface of amorphous silica. *In situ* XAS shows that Co is not oxidized by air nor reduced by hydrogen even at 650°C. For catalytic propane dehydrogenation, single site $\text{Co}^{2+}/\text{SiO}_2$ exhibits selectivities > 95% at 550°C and > 90% at 650°C with stable activity over 24 h. Calculations with hybrid density functional theory support a non-redox mechanism for activation of C-H and H-H bonds by Co^{2+} similar to that previously reported for single site $\text{Zn}^{2+}/\text{SiO}_2$.

1. Introduction

C-H activation is a fundamental and key chemical step in hydrocarbon processing, which in turn underlies production of fuels and petrochemicals. Recently, there has been a growing interest in the use of ‘base metal’ catalysts for hydrocarbon functionalization.[1-4] Recent examples of low temperature hydrocarbon transformations mediated by homogeneous cobalt catalysts include hydrogenation[5, 6] (with enantioselective variants reported), C-C bond formation,[4, 7, 8] C-H functionalization,[3, 9-11] and cycloaddition reactions.[12] These reactions occur at quite mild temperatures and are the thermodynamically exergonic reactions.

In these systems cobalt has been found to activate C-H bonds and commonly it is postulated the mechanism proceeds through a Co^{1+} intermediate and an oxidative addition/reductive elimination pathway with Co^{3+} in C-C bond forming reactions.[7] The reaction has also been subjected to theoretical analysis by Yang et al. and a viable redox pathway was elucidated.[13] However, we and others have found that non-redox pathways are a viable route in high-temperature[14] Thus, it is an open question whether redox or non-redox pathways would be operative in a high-temperature, cobalt dehydrogenation catalyst.

There are a few recent examples of low-temperature, cobalt-catalyzed hydrogenation. The Chirik group has been studying bis(arylimidazol-2-ylidene)pyridine

cobalt complexes, e.g. (ⁱPrCNC)CoCH₃ [6] and other variants[5, 6] as highly active olefin hydrogenation catalysts under very mild conditions (50°C). Because hydrogenation of olefins is the microscopic reverse of alkane dehydrogenation, cobalt should also be catalytically active for dehydrogenation if the catalyst is stable at high temperatures. The cationic cobalt(II) alkyl complex [(PNHP^{Cy})Co(CH₂SiMe₃)]BAr₄ (PNHP^{Cy} = bis[(2-dicyclohexylphosphino)ethyl]amine) was reported as a pre-catalyst for alcohol dehydrogenation by Hanson et al.[15] That catalyst had been previously demonstrated to be active for olefin and ketone hydrogenation.[16] A intramolecular sp³ C-H activation of the three-coordinate cobalt complex [Co(IMes)₂Cl] (IMes = 1,3-dimesitylimidazol-2-ylidene) was reported by Deng et al.[17] Such C-H activation ability indicates the promising catalytic potential of cobalt for alkane dehydrogenation.

Alkane dehydrogenation at high temperatures (500°C) on cobalt-substituted zeolite ZSM-5 has been studied by Iglesia et al,[18, 19] who found that Co-ZSM-5 exhibits catalytic activity similar to that of Zn-ZSM-5 and Ga-ZSM-5.[20-23] However, the ion-exchange method used to incorporate cobalt into the zeolite results in formation of multiple cobalt species in the catalyst. In addition, the zeolite contains residual strong Brønsted acid sites, which also contribute significantly to catalyst reactivity. The presence of multiple active species in Co-ZSM-5 complicates elucidation of the role of cobalt in facilitating propane dehydrogenation. This complication motivates the development of a catalyst containing a single, well-defined Co species on a support containing no other active sites.

Well-defined, single site heterogeneous catalysts have received significant attention in the literature. The use of well-defined catalytic sites enables the development of structure-function relationships, which reveal the molecular level origins of catalytic activity and selectivity and thereby guide the development of new catalytic materials. In addition, single-site catalysts often exhibit desirable catalytic properties, including greater selectivities to desired products than those observed over non-single-site catalysts of similar composition. Preparation of single-site catalysts typically requires controlled synthetic techniques.[24] A seminal example is the thermolytic molecular precursor technique, extensively developed by Tilley and co-workers (see [25] and references therein). Basset and Coperet[26, 27][26, 28] have examined single site Zr and Ta

hydrides supported on silica for hydrogenolysis and metathesis of alkanes. The Marks group[29] has investigated isolated ionic species supported on sulfated alumina with high activities for olefin hydrogenation and polymerization. Several groups have demonstrated that single site oxovanadium catalysts provide greater selectivity than less well-dispersed oxovanadium catalysts for oxidation of alkanes[30, 31] and reduction of nitric oxide[32]. These examples and many other similar works[33-36] demonstrate the advantageous properties exhibited by well-defined single site catalysts prepared through controlled synthesis.

We have been interested in stabilizing single-site catalysts at high temperatures so that reactions that are thermodynamically disfavored at room temperature can be driven at temperatures where equilibrium favors the reverse reaction. For example, a challenging but industrially important example of C-H bond activation chemistry is the dehydrogenation of propane. Propane is the simplest molecule capable of undergoing both dehydrogenation and monomolecular cracking, allowing facile comparison between the relative rates of C-H and C-C bond activation, and while thermal cracking to form ethylene and methane becomes thermodynamically favorable below 250°C, propane dehydrogenation remains thermodynamically disfavored below about 550°C. The high temperatures required for high conversion in the dehydrogenation reaction therefore provide a stringent challenge for catalyst selectivity and stability.

We recently reported that a single site Zn^{2+} on silica catalyst is catalytically active for propane dehydrogenation, exhibiting 95% selectivity at 550°C.[37] A density functional theory study indicates the rate limiting step is beta hydride elimination, which is consistent with the known stability of zinc alkyls. The active site was a low coordinate Zn^{2+} ion that did not undergo a change in the oxidation state during the catalytic cycle. In contrast with zinc, transition metals with partially filled d orbitals normally undergo facile β -hydride elimination and might be superior catalysts if the C-H over C-C activation selectivity remains high. For example, β -hydride elimination from a cobalt alkyl has recently been observed by the Holland group.[38] Given the recent examples of low-temperature, homogeneous Co hydrocarbon chemistry, along with observation of C-H bond activation at higher temperatures in Co-exchanged zeolites, we chose to explore whether a similar type of single-site Co^{n+} species could be stabilized on SiO_2 . Moreover,

cobalt is a redox active metal which could possibly catalyze propane dehydrogenation in a different (redox) mechanism and reaction intermediates than that previously observed on the Zn^{2+} /silica catalyst. Thus, a well-defined cobalt-on-silica catalyst is of interest as a possible propane dehydrogenation catalyst.

We report here the synthesis and characterization of a single site Co on silica catalyst and its catalytic activity for propane dehydrogenation. Monomeric hexaminecobalt(III) ($\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$) was grafted onto silica surface through electrostatic absorption. The resulting material was characterized by Raman spectroscopy, electron paramagnetic resonance spectroscopy, and in-situ and ex-situ X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Four-coordinate, single site Co^{2+} was confirmed as the catalytic active species for propane dehydrogenation. Raman spectroscopy indicates that cobalt ions preferentially bond to a particular subset of sites on the silica surface. Single site $\text{Co}^{2+}/\text{SiO}_2$ is active for propane dehydrogenation, exhibiting high selectivity toward propene with little formation of ethylene and methane. The oxidation state of Co is unchanged under propane at reaction temperature and no reduction was observed for Co even at 650°C in hydrogen. Density functional theory calculations reveal a non-redox C-H activation mechanism similar to that reported previously for C-H activation on single site $\text{Zn}^{2+}/\text{SiO}_2$.

2. Experimental

2.1 Catalyst Preparation

Catalysts **3L** and **3H** (catalysts prepared from Co(III) ions at low and high cobalt loadings, respectively): 20 g of silica (Davisil 646, 35-60 mesh, 300 m²/g and 1.1 cm³/g, Aldrich) was suspended in approximately 200 mL of deionized water. The pH of the solution was adjusted to about 11 using concentrated ammonium hydroxide (NH_4OH , Aldrich). In a separate flask, 0.125 g (catalyst **3L**) or 5.00 g (catalyst **3H**) of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (Aldrich) was dissolved in 50 mL of deionized water, and the pH adjusted to 11 with NH_4OH . The basic Co(III) solution was rapidly added to the silica and stirred for 10 min at RT. The solid was allowed to settle for 5 min and the solution decanted. The resulting wet powder was vacuum filtered and rinsed several times with deionized water, dried overnight at room temperature followed by drying overnight in air at 125°C.

Subsequently the catalyst was calcined by ramping over 1 h to 300°C and holding for 3 h. Total cobalt loadings by elemental analysis (Galbraith Laboratories, Inc.) were 0.1 wt% (**3L**) and 2.1 wt% (**3H**).

Catalysts **2L** and **2H** (catalysts prepared from Co(II) ions at low and high cobalt loadings, respectively): 20 g of silica (Davisil 646) was suspended in approximately 200 mL of deionized water. The pH of the solution was adjusted to about 11 using concentrated ammonium hydroxide. In a separate flask, 0.125 g (catalyst **2L**) or 5.00 g (catalyst **2H**) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) was dissolved in 50 mL of deionized water, and the pH adjusted to 11 with NH_4OH . In the preparation of catalyst **2H**, addition of NH_4OH to the solution of Co(II) nitrate led to partial precipitation of an uncharacterized product; this precipitate was removed from the solution by filtration. The remaining cobalt solution was added to the silica solution, stirred for 10 min, allowed to settle, and decanted. The resulting wet powder was rinsed several times with deionized water, dried overnight in air at 125°C, and subsequently ramped over 1 h to 300°C and calcined for 3 h. Total cobalt loadings by elemental analysis were 0.1 wt% (**2L**) and 3.1 wt% (**2H**).

2.2 Catalyst Characterization

Co K-edge (7709.0 eV) X-ray absorption spectroscopy (XAS) measurements were conducted on the bending magnet beamline of the materials Research Collaborative Access Team (MRCAT, 10-BM) at the Advanced Photon Source (APS) at Argonne National Laboratory. Ionization chambers were optimized for the maximum current with linear response (ca. 10^{10} photons detected per second) using 20% He in N_2 (10% absorption) in the incident X-ray detector and 30% Ar in N_2 (70% absorption) in the transmission X-ray detector. A cobalt metal foil and third X-ray detector were placed in the beam path beyond the transmission detector to allow acquisition of a reference spectrum concurrent with each sample measurement. Use of a custom built reactor cell allowed samples to be pre-treated at 650°C under flowing air or 3.5% H_2 in He (Praxair), and maintained under a static pretreatment atmosphere while being cooled to RT and examined by XAS. To facilitate data analysis, XANES reference spectra were collected of $\text{Co}(\text{PPh}_3)_3\text{Cl}$, $\text{Co}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{acac})_2 \cdot \text{H}_2\text{O}$, CoCl_2 , CoF_2 , $\text{Co}(\text{acac})_3$, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, and LiCoO_2 (all obtained from Aldrich). Co(III) acetylacetonate (6 Co-O at 1.91 Å[39])

was used to prepare Co-O phase and amplitude functions for EXAFS fitting of the first shell coordination. Standard fit procedures within WINXAS 3.1 software were used to fit the XAS data. The cobalt coordination environments were obtained by a least squares fit to the first nearest neighbor shell in R-space obtained from a k^2 -weighted Fourier transform of the EXAFS data.

2.3 Electron Paramagnetic Resonance (EPR) spectroscopy was conducted at X-band frequencies (9 GHz) in continuous wave mode using a Bruker ELEXSYS E580 EPR spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a TE₁₀₂ rectangular EPR resonator (Bruker ER 4102st). A helium gas-flow cryostat (Air Products, Allentown, PA) and a Lakeshore temperature controller (Westerville, OH) were used for low temperature measurements. Spectra were recorded at 5 K. Data processing was done using Xepi (Bruker Biospin) and MatlabTM 7.11.1 (MathWorks, Natick, MA) software.

2.4 Raman spectroscopy: The excitation wavelength of 287 nm for in-situ UV Raman measurements are provided by third-harmonic generation output of a 4 kHz repetition rate, nanosecond pulsed, wavelength-tunable Ti:Sapphire laser (Coherent, Indigo-S).[40] The laser power delivered to the catalyst was 3 mW. UV Raman spectra were recorded with a triple-grating spectrometer (Princeton Instruments, Trivista 555) equipped with a liquid N₂-cooled, UV-enhanced CCD detector. Prior to the measurement, samples were calcined at 300°C for 4 h. *In situ* Raman spectra were collected at room temperature with flowing He in the fluidized bed reactor described previously.[40]

2.5 Infrared spectroscopy of adsorbed pyridine: For pyridine adsorption experiments, catalysts were preheated at 200°C under vacuum (< 5 mTorr) and cooled down to room temperature. Then, pyridine was injected through a septum by a syringe onto the catalysts under vacuum at room temperature. And then, the catalysts were heated at 200°C for 1 hr under vacuum to remove physisorbed pyridine. The adsorbed catalysts were cooled down to RT and mounted in an infrared cell having CaF₂ windows. Nitrogen gas was used to purge the sample chamber as well as the spectrometer. The FTIR spectra were recorded using a Nicolet Nexus 670 FTIR spectrometer coupled to an MCT detector with 2 cm⁻¹ resolution.

2.6 Catalytic Testing

Catalyst performance testing was conducted in a vertical, quartz tube reactor. Gas flow was controlled using mass flow controllers, and product distribution was determined via on-line gas chromatography (J&W Scientific) equipped with a 50 m GS-Alumina capillary column and a flame ionization detector to which H₂ (99.999%, Airgas USA) and air (<2 ppm H₂O, Airgas) were also supplied. Approximately 1 g of catalyst was supported on quartz wool with an internal thermocouple placed at the top of the catalyst bed. Initially, the catalyst was purged with He (99.999%, Airgas USA) that had been further purified with an oxygen trap at 300 mL/min at room temperature, then for 15 min at 100°C. The temperature was then raised to reaction temperature (550°C and 650°C for dehydrogenation; 200°C and 550°C for hydrogenation). Temperature was allowed to stabilize for 2-3 h before introduction of reactant gases. For propene hydrogenation, the reaction mixture comprised 88 mL/min of 4% H₂/Ar mixture (Airgas USA) and 16 mL/min 4% propene/Ar mixture (Airgas), yielding a weight hourly space velocity (WHSV) of 6.0 m³ h⁻¹ (kg catalyst)⁻¹ on a total gas flow basis. For propane dehydrogenation, the reaction mixture comprised 3% propane/Ar at 55 mL/min, or a WHSV of 3.3 m³ h⁻¹ (kg catalyst)⁻¹. These flow conditions generally resulted in less than 10% conversion; however, the flow rate and temperature were also varied to obtain higher conversions.

2.7 Density functional theory calculations

First-principles calculations based on the hybrid density functional theory (B3LYP)[41] have been performed to investigate the C-H activation mechanism in propane by Co/SiO₂ catalysts. The catalyst surface is represented using a cluster model consisting of different size siloxane rings (silsequioxane), which has been shown[42] to be a good approximation of the local structure of surface sites on amorphous silica. Since electronic effects on amorphous silica are mostly local, cluster models are reasonably accurate for studying chemical reactions. The structure optimizations and free energy calculations of different reaction intermediates and transition states were performed using Gaussian-09 quantum chemistry software.[43] The accuracy of transition state calculations was verified by performing intrinsic reaction coordinate scans[43, 44] and by

frequency analysis. Triple-zeta quality (TZVP) basis sets[45] were used to perform all calculations. Computed energies reported in this paper are Gibbs free energies.

3. Results

3.1 Catalyst Synthesis and Characterization

The method of strong electrostatic absorption was used to prepare a monolayer of chemisorbed Co^{3+} on SiO_2 . This method utilizes charge balance to bind a cation complex to a negatively charged silica surface in basic solution. The resulting orange powder is easily prepared on multigram scale and serves as a convenient entry point into surface-stabilized Co ions. Upon mild drying/calcination at 100-120°C, the color changes to a vivid ‘cobalt’ blue. This color is well-known to be a result of pseudo-tetrahedral Co^{2+} and persists in under a variety of conditions (He, air, and H_2), including during dehydrogenation catalysis up to 650°C. The coordination environment of the Co on the surface under these different conditions as well as the nature of these transformations was interrogated by a variety of techniques, including X-ray absorption spectroscopy (XAS), electron paramagnetic spectroscopy (EPR), resonance Raman spectroscopy, and infrared spectroscopy.

3.2 X-ray Absorption Spectroscopy

The oxidation state and coordination environment at cobalt in catalyst 3H was investigated at each step from pre-catalyst synthesis to *in-situ* investigation of the working catalyst using X-ray absorption spectroscopy (XAS). In this technique, incident X-rays are used to excite Co 1s electrons. Depending on the energy of the incident X-ray, a variety of phenomena may be observed. When the incident X-ray energy is similar to the Co 1s binding energy, core electrons are photo-excited into the valence states with the typical dipole selection rules. The 1s to 3d transition, which is formally forbidden since the states differ by more than one orbital angular momentum quantum number, is enabled by spin-orbit coupling between the 1s $j=1/2$ state and the 3d $j=3/2$ state. Spin-orbit coupling in Co, however, is relatively weak, resulting in small pre-edge peak at lower energy than the absorption edge. When the ligand environment around cobalt lacks a center of inversion, this feature is more evident. As a result, it is larger for tetrahedrally

coordinated than for octahedrally coordinated Co. The energy level of the 3d electrons is a strong function of the occupancy of the 3d states; thus, the energy difference between the 1s and 3d states is diagnostic of the oxidation state of the metal.

At higher X-ray energies, the Co 1s electrons are excited directly into unoccupied Co np orbitals ($n \geq 4$). This transition is allowed and leads to a strong adsorption up to the Co 1s ionization limit and gives rise to a prominent adsorption edge. Since the Co 4p orbitals participate in cobalt-ligand bonding, the energy of the adsorption edge is a function of the ligand environment around Co. Within a ligand family, the edge energy often correlates with the average formal oxidation state. For example, the edge energy increases systematically for the series Co, CoO, Co₃O₄ (i.e. from Co⁰ to Co²⁺ to Co^{2+/3+}). However, edge energies are typically not comparable across different ligand families; e.g. the edge energies of CoO and CoCl₂ differ even though both contain Co²⁺. For this reason, determination of the oxidation state at the metal using the pre-edge feature, which directly measures 1s → 3d excitation, is more reliable than determination of the oxidation state using the edge energy.[46] The validity of this method is demonstrated in Table 1, which shows that the pre-edge adsorption energy is a reliable indicator of the formal oxidation state regardless of the chemical composition of the compound. Collection and analysis of the edge and pre-edge features of the X-ray absorption spectrum is referred to as XANES, or X-ray absorption near edge spectroscopy.

When the energy of an incident X-ray exceeds the ionization energy of the Co 1s electron, the electron is ejected from the sample via the photoelectric effect. The kinetic energy of the outgoing photoelectron has a characteristic wave length and scatters off atoms neighboring the Co atom. The outgoing photoelectron wave interferes constructively or destructively with the incoming X-ray wave in a manner that depends upon the X-ray energy and the number, type and bond distance(s) of the neighboring atoms. The resulting X-ray absorption vs. energy data, referred to as the X-ray Absorption Fine Structure or EXAFS spectrum, provides information about the local coordination environment around the absorbing Co atom.

The cobalt oxidation state, as determined from XANES, and coordination environment, as determined from EXAFS, in catalyst **3H** at various stages of catalyst synthesis are shown in Table 2. The Co(NH₃)₆Cl₃ precursor exhibits a pre-edge

adsorption at 7710.1 eV, consistent with a +3 formal oxidation state. EXAFS reveals that the first coordination shell around Co consists of six ligands at an average distance of 1.97 Å, consistent with the octahedral coordination and average Co-N bond distance of 1.963 Å observed[47] in crystalline $\text{Co}(\text{NH}_3)_6\text{Cl}_3$. When the precursor is deposited on silica followed by drying at RT, the oxidation state by XANES remains +3, and the average coordination number and first-neighbor bond distance remain 5.8 and 1.96 Å, respectively. The essentially unchanged coordination number and bond length support the interpretation that the $\text{Co}(\text{NH}_3)_6^{3+}$ structure adsorbed unchanged onto the silica surface, with the +3 charge balanced by three outer sphere SiO^- anions.

Upon heating to 125°C, the position of the Co pre-edge feature decreases from 7710.1 eV to 7709.3 eV, consistent with a change in oxidation state from +3 to +2. The average first nearest neighbor coordination number decreases to 4.1, and the average distance to these neighbors increases to 2.03 Å. A similar 2.01 Å distance has been measured[48] by EXAFS for the Co-N distance in tetrahedral $\text{Co}(\text{pa})_4^{2+}$ where pa = propylamine. The *increase* in average nearest neighbor distance upon *loss* of coordination can be attributed to the greater Co-N distance for Co^{2+} as compared to Co^{3+} : the ionic radius of Co^{2+} is estimated[49] to be ~ 0.16 Å greater than that of Co^{3+} . For comparison, note that in octahedral $\text{Co}^{2+}(\text{NH}_3)_6\text{Cl}_2$, the Co-N bond distance is 2.164 Å, longer still than that observed in the catalyst after heating to 125°C.

Figure 1: a.) XANES spectra of catalyst **3H** after drying at RT (black), heating to 125°C (blue), and calcining at 300°C (red). b.) k^2 -weighted magnitude of the Fourier transform of the EXAFS from $k = 2.6 - 10.8 \text{ \AA}^{-1}$ of catalyst **3H** after drying at RT (black), heating to 125°C (blue), and calcining at 300°C (red). Spectra identical to that shown in red are obtained upon heating to 550°C in air, helium, or propane.

Upon heating in air to 300°C or 550°C, no further changes in cobalt oxidation state are observed. Thus, once formed, Co^{2+} ions do not reoxidize to Co^{3+} even in air at 550°C. The average coordination number suggests that the Co^{2+} coordination geometry remain four-coordinate, with average coordination numbers of 3.9 and 4.1 observed at 300°C and 550°C, respectively. There is, however, a slight decrease in the average distance to the first nearest neighbor shell, from 2.03 Å to 1.98 Å, upon heating from 125°C to 300°C. This change may reflect replacement of N with O in the first coordination sphere around Co. This interpretation is supported by IR spectroscopy (not

shown), which suggests that no N-H vibrations are observable in the catalyst after heating to 300°C. The Co-O distance for tetrahedral Co^{2+} in Co_3O_4 is 1.947 Å, while Co-O distances vary from 1.906 Å to 1.992 Å for tetrahedral Co^{2+} ions in mesoporous cobalt phosphate.[50]

Table 1: XANES pre-edge energies of cobalt reference compounds in various oxidation states.

Reference Sample	XANES Pre-edge Energy, eV	Oxidation State
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	7710.1	+3
LiCoO_2	7710.1	+3
$\text{Co}(\text{AcAc})_3$	7710.2	+3
$\text{Co}(\text{AcAc})_2$	7709.7	+2
$\text{Co}(\text{Acetate})_2$	7709.7	+2
CoCl_2	7709.6	+2
CoF_2	7709.6	+2
$\text{ClCo}(\text{PPh}_3)_3$	7708.8	+1
Co Foil	7709.0	(calibration)

In addition to the first nearest neighbor (Co-O) scattering shell observed at 1.5 Å in the (Figure 1b, phase-uncorrected) Fourier-transformed EXAFS data for sample **3H** heated above 300°C, a small scattering peak is also observable near 2.5 Å. This peak could arise from second-nearest-neighbor scattering off silicon atoms in Co-O-Si structures. A distribution of possible Co-O-Si distances and bond angles are expected to exist for Co grafted to an amorphous silica support. Only weak scattering from Si second-nearest neighbors is expected since the intensity of the scattering decreases rapidly with increasing distance. It is also possible that the peak near 2.5 Å indicates the presence of Co-Co scattering from Co-O-Co dimers or small oligomeric structures; the presence of such structures cannot be unequivocally ruled out by EXAFS analysis, and is addressed by other techniques detailed below. The presence of particles with the rocksalt CoO structure, however, can be definitively ruled out, since the Co-O coordination number and bond distance, 6 and 2.09 Å, respectively, do not match those of the catalyst. CoO is also ruled out via EPR experiments detailed below.

XAS was also used to analyze the oxidation state and coordination environment of catalyst **3H** under high-temperature inert and working catalytic conditions. Exposure to helium at 550°C, hydrogen at 550°C, and propane at 550°C each yielded XAS spectra

identical to that obtained during exposure to oxygen at 550°C (Table 2). Cobalt ions remain four-coordinate and in the +2 oxidation state regardless of gas phase environment under catalytic conditions. There is no evidence for oxidation to Co^{3+} in air, no evidence for reduction to Co^0 in hydrogen or propane, and no evidence for change in the structure or coordination environment at the Co^{2+} catalytic site. Similar recalcitrance to changes in oxidation state have been observed for Co^{2+} -exchanged zeolites.[19]

Table 2: Cobalt formal oxidation state and coordination environment from EXAFS.

Treatment	Pre-Edge Energy, eV	Formal Oxidation State	Coordination Number	Nearest Neighbor Distance, Å	Nearest Neighbor
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	7710.1	+3	6.0	1.97	Co-N
Dry RT	7710.1	+3	5.8	1.96	Co-N
Dry 125°C	7709.3	+2	4.1	2.03	Co-N
Calcine 300°C	7709.4	+2	3.9	1.98	Co-O
Air 550°C	7709.4	+2	4.1	1.98	Co-O
He 550°C	7709.4	+2	4.0	1.98	Co-O
He 550°C (at 550°C)	7709.4	+2	4.0	1.97	Co-O
Propane 550°C (cooled to RT)	7709.4	+2	4.0	1.97	Co-O
Propane 550°C (at 550°C)	7709.3	+2	4.0	1.96	Co-O

3.3 EPR Spectroscopy

While XAS confirms that catalyst **3H** contains only four-coordinate Co^{2+} and the absence of bulk CoO_x phases, the existence of dimeric or small oligomeric Co_xO_y clusters with non-bulk-like structures cannot be excluded from EXAFS analysis. As noted above, the presence of Co^{1+} and Co^{3+} in the sample have not been observed by EXAFS/XAS, nor could be generated upon exposure to oxygen or hydrogen, even at high temperatures. Since tetrahedrally coordinated Co^{2+} is an electron paramagnetic resonance (EPR) active ion, we investigated the nuclearity of cobalt in the catalyst by this technique. The EPR spectra of catalysts **3L** and **3H** are shown in Figure 2. The shape of the two spectra is nearly identical, with a single prominent peak evident around $g = 5.4$ appearing in both spectra. The greater intensity of this peak in sample **3H** is a result of the greater number

of magnetic centers present (2.1 wt% Co in **3H** vs. 0.1 wt% Co in **3L**). The narrow signal at the free electron value $g = 2.0$, frequently observed in EPR measurements on powdered samples, is most likely due to ppm levels of radicals or defects in the support material, and is not attributed to cobalt. The spectra in Figure 2 are essentially identical to those reported by Dzwigaj and Che for isolated tetrahedral Co^{2+} incorporated into beta zeolite,[51] by Weckhuysen and co-workers for Co^{2+} incorporated in microporous crystalline aluminophosphates,[52] and by Iton and co-workers for isolated tetrahedral Co^{2+} species substituted into an aluminophosphate molecular sieve framework.[53] Tetrahedral Co^{2+} in CoAl_2O_4 spinel and tetrahedral CoCl_4^{2-} ions in an AgCl matrix both also yield similarly shaped spectra.[54] Thus, the EPR results of **3L** and **3H** are consistent with the presence of magnetically isolated (no significant electron dipolar or exchange interaction with neighboring Co^{2+} sites), high spin, tetrahedrally coordinated d^7 Co^{2+} .

Figure 2: Continuous wave X-band EPR spectra of catalysts **3L** (blue; top) and **3H** (green; bottom) at 5 K.

3.4 Raman Spectroscopy

In order to obtain further information about the local structure surrounding supported Co^{2+} cations, *in situ* UV Raman spectra were collected on catalyst **3H** under flowing He after treatment at 300°C in flowing 5% O_2 , and compared to the Raman spectrum of the silica. The results are shown in Figures 3a and 3b. The Raman spectrum in Figure 3a of Co/SiO_2 shows no evidence for the presence of CoO (455 and 675 cm^{-1}), CoOOH (367, 482, 599, and 809 cm^{-1}), or Co_3O_4 (482, 519, 621, and 690 cm^{-1}) phases.[55] A notable band at 608 cm^{-1} present in the silica is absent in samples containing Co. The disappearance of this mode upon incorporation of Co onto the SiO_2 surface can be rationalized by the model shown in Figure 4. The vibrational mode at 608 cm^{-1} is attributable to the symmetric stretching mode of trisiloxane rings (Figure 4a) present in partially dehydroxylated silica.[56] Such rings are formed via condensation of neighboring silanol groups upon heating at or above 300°C. In the basic aqueous media used to impregnate cobalt onto the SiO_2 support, these trisiloxane rings are rehydrated

(Figure 4b). The resulting silanol groups are oriented such that they are well-suited to serving as anchoring sites for cobalt atoms, which assume roughly tetrahedral coordination environments upon attachment to the support (Figure 4c). Silanol groups linked to cobalt cannot condense to re-form trisiloxane rings; as a result, the Raman mode observed at 608 cm^{-1} in dehydrated silica does not re-appear when the catalyst is heated to 300°C . Although Raman spectroscopy is generally not quantitative, comparison of the peak intensity at 608 cm^{-1} between the silica and the Co-grafted samples obtained under identical conditions after the same treatment at 300°C suggests that most of the opened trisiloxane rings become anchoring points for grafted Co. These results are similar to those obtained for Zn grafting to SiO_2 in previous work.[37]

Figure 3: Raman spectra of sample **3H** (red) and silica (blue) after calcination in air at 300°C .

(a) (b) (c)
Figure 4: Dehydrated silica contains trisiloxane rings (a) which are opened to form silanol groups (b) upon exposure to aqueous base. These groups can then act as anchoring sites for cobalt (c).

Additional information on the structure of the Co grafting site is evident in Figure 3a in changes to the peak near 978 cm^{-1} upon grafting of Co. This peak, assigned to the Si–O stretching mode of terminal silanols,[56] develops a pronounced shoulder at $\sim 927\text{ cm}^{-1}$ after Co grafting. Likewise, the peak at 3740 cm^{-1} in Figure 3b assigned to the O–H stretching mode of terminal silanols develops a pronounced shoulder at $\sim 3705\text{ cm}^{-1}$ after Co grafting. In both spectra, the shoulder can be reasonably assigned to silanol groups perturbed by dative interactions with adjacent Co, as shown in Figure 4c. The isolated silanol O–H stretching mode in Figure 3b also exhibits an $\sim 3\text{ cm}^{-1}$ redshift on the Co-grafted sample as compared to the position observed in the bare silica, and a more prominent broad peak in the hydrogen bonded silanol O–H stretching region from $3300 - 3700\text{ cm}^{-1}$. These changes suggest that the silica surface undergoes structural modification during Co grafting.

3.5 Infrared Spectroscopy of Adsorbed Pyridine

The infrared spectrum of adsorbed pyridine is characteristic of the type of adsorption sites, e.g., Lewis or Brønsted acid sites. After exposure to pyridine vapor followed by evacuation under vacuum, catalyst **3H** shows IR adsorption bands at 1612

cm^{-1} , 1492 cm^{-1} , and 1451 cm^{-1} that are attributed to pyridine adsorbed on Lewis acid sites, while the bare silica support does not show these bands. Bands near 1630 cm^{-1} and 1545 cm^{-1} assignable to pyridine adsorbed on Brønsted acid sites are not observed. The IR results indicate the presence of significant Lewis acidity, but no Brønsted acidity, on catalyst **3H**. Thus, isolated, tetrahedral Co^{2+} cations supported on silica are Lewis acid sites.

3.6 Catalytic Activity of Isolated, Tetrahedral Co^{2+} on SiO_2

The activity of catalyst **3H** for propane dehydrogenation was investigated at 550°C . At this temperature, equilibrium conversion is $\sim 29\%$. We determined the overall turnover frequency (TOF; mol propene per mol Co per hour) under differential conditions with an initial conversion level is 4%, corresponding to a TOF of 0.44 h^{-1} (Figure 5a). The rate increased steadily with time on stream, approaching 10% conversion and a turnover frequency of 1.1 h^{-1} after 20 h. The selectivity also increased slightly with time on stream, from 91% approaching a limiting value of 95% selectivity to propene. Note that this selectivity (and conversion) value has been corrected for background contributions from thermal cracking of propane, as measured over cobalt-free silica under the same conditions. At 550°C , propane conversion due to cracking amounts to 0.6%, and is $\sim 52\%$ selective to propene.[57] The carbon balance for the reaction was 100% within error. Coke formation was negligible at 550°C , even after 24 h on stream. After a 24-hour run the physical appearance of the materials was white and cobalt blue, respectively. The spent catalyst and support was subjected to elemental analysis and the detected C on both materials was less than the detection limit of 0.5%. As a result, it can be inferred that propene does not undergo further dehydrogenation on Co/SiO_2 under the conditions studied.

The dehydrogenation activity of the same catalyst was further tested at 650°C . As shown in Figure 5b, initial propane conversion was 60%, near to the 65% equilibrium limit at this temperature. The observed initial turnover frequency of 12 h^{-1} may, therefore, underestimate the true initial turnover frequency. However, activity decreased steadily with time on stream: after 20 h, conversion had fallen to 35%, and the turnover frequency decreased to 6.2 h^{-1} . Measured selectivity to propene also decreased with time on stream,

from 80% initially to 70% after 20 h. These selectivities have again been corrected for contributions from thermal cracking, which accounts for nearly 8% propane conversion at 650°C. Coke formation was also significant at 650°C. Although no attempt was made to quantify coke formation, the spent catalyst was visibly covered by carbon after 20 h on stream. Since non-catalytic cracking reactions contribute significantly to the overall rate at 650°C, it is not immediately obvious whether coke formation can be attributed to processes involving cobalt sites. Investigation of catalyst deactivation mechanisms, and strategies for catalyst regeneration, is beyond the scope of the present work. However, we note that the fresh catalyst is air stable at 650°C. If catalyst deactivation is the result of coke build-up on the catalyst surface, then it is likely that the Co/SiO₂ catalyst can be regenerated.

Since hydrogenation of propene is the microscopic reverse of dehydrogenation of propane, it was expected that catalyst 3H should also be active for propene hydrogenation at 550°C. This expectation is confirmed by the results in Figure 7. The catalyst is active for propene hydrogenation, and essentially stable rates are observed over the first 45 min on stream (the duration of the test).

Figure 5: Activity (a) and selectivity (b) of 2.1 wt% Co/SiO₂ for dehydrogenation of propane at 550°C.

Figure 6: Activity (a) and selectivity (b) of 2.1 wt% Co/SiO₂ for dehydrogenation of propane at 650°C.

Given that the related Zn/SiO₂ catalyst is active for propene hydrogenation at temperatures as low as 200°C, the Co/SiO₂ catalyst was also tested at this lower temperature. As also shown in Figure 7, initially, hydrogenation activity is observed over Co/SiO₂ at 200°C. However, the rate decreases rapidly upon continued exposure of the catalyst to propene. The activity can be recovered completely by H₂ treatment in the absence of propene; reintroduction of propene results in the same initial activity followed by rapid deactivation. A postulated mechanism for propene hydrogenation which explains these observations is presented below.

Figure 7: Propene hydrogenation activity over catalyst 3H at 550°C (green triangles) and 200°C (red squares).

3.7 Alternate Synthetic Approaches

While catalyst **3H** was prepared from a Co(III) precursor, under working catalytic conditions the oxidation state of Co is +2, unaltered by exposure to either hydrogen or oxygen at 550°C. It was, therefore, of interest to compare results from the catalyst directly from a Co(II) precursor. Substitution of $\text{Co}^{\text{II}}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (in excess NH_4OH) in place of $\text{Co}^{\text{III}}(\text{NH}_3)_6\text{Cl}_3$ as a cobalt source resulted in significant changes in the resulting pre-catalyst. The loading of Co as determined by elemental analysis was substantially higher with the Co(II) precursor, reaching 3.1 wt% in catalyst **2H** as opposed to 2.1 wt% from Co(III) in catalyst **3H**. Note that in both cases, sufficient cobalt precursor was used to enable a final weight loading of up to 5.0 wt%, so differences in final cobalt loading are indicative of differences in the grafting chemistry. The Co^{2+} derived catalyst **2H** was brown in color, rather than the cobalt-blue color expected for isolated tetrahedral Co^{2+} sites, immediately indicating the existence of Co in a different coordination environment.

Figure 8 compares the EXAFS spectra of sample **2H**, produced from Co(II), to that of sample **3H**, produced from Co(III). The samples in Figure 8 have been calcined at 300°C in air, and both contain Co^{2+} by XANES analysis. The first shell coordination peak for sample **2H** is significantly larger than that of **3H**, suggesting six-coordinate Co in **2H** as opposed to the four-coordinate Co present in **3H**. The peak positions are also different: after correcting for phase, the nearest neighbor distance in sample **2H** is 2.09 Å, significantly longer than the 1.98 Å nearest neighbor distance measured for sample **3H**. An average Co-O distance of 2.08 Å has been measured by EXAFS for the $\text{Co}^{\text{II}}(\text{H}_2\text{O})_6^{2+}$ ion in solution, while the Co-O distance in bulk CoO is a slightly longer 2.13 Å. The Co-OH bond distance[58] for octahedral Co in $\alpha\text{-Co}^{\text{II}}(\text{OH})_2$ is 2.12 Å.

Figure 8: Fourier-transformed k^2 -weighted EXAFS spectra of samples **3H** (red) and **2H**(blue).

Additional dramatic differences between the samples are visible in the second coordination shell. As discussed above, sample **3H** contains only a weak peak at ~ 2.5 Å that could be attributed either to Co-O-Si scattering or to small, non-bulk-like Co-O-Co

structures (and the presence of the latter is ruled out by EPR results). For sample **2H**, the second coordination shell is centered at a slightly greater distance of 2.6 Å, and has intensity nearly equal to that of the first coordination shell peak. These results are consistent with Co being present in an environment similar to that found in bulk CoO, in which 12 equidistant Co second-nearest-neighbors provide a strong signal for the second coordination shell. Some evidence can also be seen for a third coordination shell peak near 3.6 Å, also consistent with an ordered crystalline CoO phase.

Further evidence for different cobalt environments in catalysts **2H** and **3H** was obtained by EPR spectroscopy. Figure 9 presents the EPR spectra for catalysts **2L** and **2H** collected at 5 K after calcination at 300°C in air. The spectrum for catalyst **2L** is nearly identical to that for catalyst **3L** presented in Figure 3 above, indicating the presence of high spin, tetrahedrally coordinated Co²⁺ ions in catalyst **2L**. By contrast, the spectrum of catalyst **2H** differs significantly from those of **2L**, **3H**, and **3L**, particularly in the range below 100 mT. This result indicates the presence of additional Co²⁺ species present in catalyst **2H** with local environments that differ from those found in the other catalysts. Unlike the other three materials, catalyst **2H** also exhibits a well-resolved EPR spectrum at 295 K (not shown), further demonstrating the presence of additional populations of Co²⁺ ions in **2H** not found in **2L**, **3H**, or **3L**.

Figure 9: Continuous wave X-band EPR spectra of catalysts **2L** (blue) and **2H** (brown) at 5 K.

Sample **2H** was further examined under *in situ* conditions for propane dehydrogenation at 550°C. As seen in Figure 10, under catalytic reaction conditions, the EXAFS spectrum of catalyst **2H** evolves significantly, becoming quite similar to that of sample **3H**. The first coordination shell peak decreases to an intensity consistent with tetrahedral coordination, and the nearest neighbor distance decreases to 1.98 Å — identical to the distance recorded for sample **3H**. The second coordination shell also decreases significantly in intensity, falling almost to the level observed in sample **3H**. These results suggest that bulk-like CoO clusters formed from direct grafting of the Co(II) precursor onto silica are able to disperse and create significant populations of isolated, tetrahedral Co(II) sites upon heating to 550°C. Similar results have been

reported for dispersion of NiO on silica at high temperatures.[59] This observation is further supported by catalytic data, which yield similar rates of propane dehydrogenation on catalyst **3H** and **2H** on a per-cobalt-atom basis. The significant differences between the structure of the as-prepared **2H** catalyst after calcination in air at 300°C and the structure of the working catalyst observed *in situ* at 550°C underscore the crucial importance of characterizing catalysts under *in situ* conditions.

Figure 10: EXAFS spectra of sample **2H** after calcination in air at 300°C (blue) and under propane dehydrogenation conditions at 550°C (red).

4. Discussion

4.1 Catalyst Synthesis

Fully hydroxylated silica typically[60] has a surface silanol density of ~ 5 SiOH/nm². For silica with a surface area of 300 m²/g, this density equates to 2.4 mmol SiOH/g SiO₂. If 100% of these silanol groups participate in cobalt grafting, and each cobalt is attached to three surface silanol groups, with no silanol group anchoring more than one cobalt, then the maximum cobalt loading is 0.80 mmol Co/g SiO₂, or 4.3 wt% Co. The cobalt loading in sample **3H** was 2.1 wt%, allowing the possibility that up to 100% of the Co in this sample exists as isolated Co centers anchored to the silica support in tridentate fashion. The initial solution used to supply the Co during the synthesis of sample **3H** contained sufficient cobalt to allow for a final weight loading of 5.0 wt%. That a lower loading of 2.1 wt% was produced suggests (1) not all of the silanol groups on the silica surface have geometries conducive to participation in tridentate binding of cobalt, and (2) Co grafting is self-limiting, in that once all the tridentate anchoring sites are consumed, no further Co grafting takes place. Given the multitude of different silanol environments present on the surface of amorphous silica, result (1) is reasonable. Result (2) is also reasonable, as positively charged Co(NH₃)₆³⁺ ions anchored to the surface should repel other positively charged Co(NH₃)₆³⁺ ions in solution, preventing additional ions from grafting nearby.

The cobalt loading obtained upon preparation of the catalyst using a Co(II) precursor was 3.1 wt%, roughly 50% higher than that obtained using a Co(III) precursor. A simple interpretation consistent with the observed loadings is that 50% more Co²⁺ ions

than Co^{3+} ions are required to balance the number of negatively charged SiO^- groups generated on the silica surface at pH 11. However, spectroscopic characterization of the as-prepared catalysts suggests greater differences in the grafting chemistry of the Co(II) and Co(III) precursors than can be attributed to charge alone: the Co(III) precursor led to formation of exclusively isolated tetrahedral Co^{2+} centers upon calcination at 300°C , whereas the Co(II) precursor produced aggregated, bulk- CoO -like structures which only dispersed upon further heating to 550°C . Differences in the grafting chemistry of Co(II) and Co(III) can be understood by examining the aqueous chemistry of these ions, and the role of ligands and pH on the speciation of aqueous cobalt.

In order to synthesize well-defined surface transition metal species by strong electrostatic absorption, it is critical to control the formation of metal species in water. The aqueous coordination chemistry of Co^{2+} and Co^{3+} first studied by Werner provides a classic platform upon which to probe the influence of precursor chemistry on catalyst structure. Simple crystal field stabilization energy (CFSE) arguments explain the stability of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ as a d^6 octahedral, low spin, and stable cation as well as the labile nature of $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$. As discussed below, the inertness of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ to substitution, vs. the lability of $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$, is the primary cause of the differences in grafting chemistry between these two precursors.

The grafting procedure involves exposing the silica support to concentrated ammonium hydroxide, which deprotonates surface silanol groups to form SiO^- anions. Since the point of zero charge for silica occurs below pH 3.5, at pH 11 essentially all of the surface silanols are deprotonated. These negatively charged sites attract positively charged $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ($0 \leq x \leq 6$, $y = 2$ or 3) cations out of solution and bind them to the silica surface. Once anchored, positively charged $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ions at the silica surface repel additional positively charged $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ions in solution. Thus, as long as $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ions are stable in solution, the grafting reaction is self-limiting, and the surface will adhere only enough positively charged $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ions to balance the number of SiO^- groups at the surface of the silica. The success of the grafting procedure is, therefore, controlled by the stability of $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{y+}$ ions in solution.

The Co(III) precursor, $\text{Co}^{\text{III}}(\text{NH}_3)_6\text{Cl}_3$, contains the $\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$ ion ($x=6, y=3$). Substitution of H_2O for NH_3 is disfavored above pH 4.85, and ligand substitution is in any case kinetically hindered for this low spin, octahedral d^6 species. The redox potential E° for the $\text{Co}^{\text{II}}(\text{NH}_3)_6^{2+}/\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$ couple is +1.81 V, so the +3 oxidation state is strongly favored for the hexaammine ion. Cobalt hexaammine ions undergo neither protonation nor deprotonation in aqueous solution. Thus, the $\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$ ion is stable in basic aqueous media. Each $\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$ ion can titrate three SiO^- groups on the silica surface, leading to a theoretical maximum cobalt loading of $\sim 1.6 \text{ Co/nm}^2$. The experimentally observed 2.1 wt% loading produced upon exposure of silica to an excess of hexamminecobalt(III) solution corresponds to $\sim 0.65 \text{ Co/nm}^2$, well below the theoretical maximum surface coverage and indicating that either not all surface silanol groups are favorable for cobalt grafting, and/or repulsion between surface-bound $\text{Co}(\text{NH}_3)_6^{3+}$ ions is sufficiently strong to limit surface grafting to less than one monolayer coverage. Upon drying under vacuum at room temperature, the oxidation state of the cobalt remains +3. It is known that OH^- ions do not displace NH_3 ligands from hexaamminecobalt(III), so it is likely that the less basic surface SiO^- ions are also unable to displace NH_3 at room temperature. The surface of the precatalyst after drying at room temperature is therefore most likely populated by ion-paired structures of the type $\text{Co}(\text{NH}_3)_6^{3+} \cdot 3 \text{ SiO}^-$.

The Co(II) precursor, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, yields the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ion ($x=0, y=2$) in solution. This ion is not stable in basic conditions: at $\text{pH} > 7$, insoluble $\text{Co}(\text{OH})_2$ precipitates form, a process initiated by reaction (1). In sufficiently basic environments, some $\text{Co}(\text{OH})_2(\text{s})$ redissolves to produce $\text{Co}(\text{OH})_4^{2-}$ ions. However, the negative charge on these ions repels them from negatively charged surface SiO^- group, so such ions would remain in solution rather than charge balancing a silica surface.

In the presence of aqueous ammonia, ligand exchange to form mixed $\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x^{2+}$ ions is also possible (2), and in fact the hexaammine ($x=6$) species is thermodynamically favored above pH 9.8.[61] Thus, reactions (1) and (2) are in competition. As a result, precipitation of cobalt hydroxides was not observed in the

preparation of sample **2L**, and observed to only a limited extent in the preparation of sample **2H**. The low spin octahedral d^7 $\text{Co}(\text{NH}_3)_6^{2+}$ ion is substitutionally labile, and therefore able to form surface-bound species of the type $\text{Co}(\text{OSi})(\text{NH}_3)_5^+$ and $\text{Co}(\text{OSi})_2(\text{NH}_3)_4$ upon interaction with surface SiO^- groups. Interaction between surface-bound Co complexes and OH^- ions in solution can also produce species such as $\text{Co}(\text{OSi})(\text{OH})(\text{NH}_3)_4$ and $\text{Co}(\text{OSi})_2(\text{OH})(\text{NH}_3)_3^-$. As a result of the neutral or anionic charges of such species, the cobalt grafting reaction ceases to be self-limiting, and sites containing anchored cobalt can become favorable locations for further cobalt grafting. In sample **2H**, this leads to a higher cobalt weight loading than that observed using the self-limiting Co(III) precursor (3.1 wt% for **2H** vs 2.1 wt% for **3H**), and leads also to production of a rocksalt-structured CoO phase upon calcination at 300°C (as observed by EXAFS). Only in a solution containing a very low concentration of Co(II) precursor, such as that used to prepare sample **2L** (0.1 wt %), can isolated Co^{2+} ions be produced on silica. Production of a cubic CoO phase in this case is not prevented by a self-limiting grafting reaction, but by simple statistics: a Co loading of 0.1 wt% corresponds to a surface coverage of only 2.3% of one monolayer. Additionally, the stability of **3H** shows that once synthesized, isolated Co^{II} sites on SiO_2 are stable so at low loading it is possible to obtain isolated Co^{II} .

While the formation of isolated cobalt centers on silica from a Co(III) precursor can be explained in terms of the solution chemistry of hexaamminecobalt(III), it remains to explain how this Co^{3+} precursor results in production of a redox-inactive Co^{2+} site in the final catalyst. This too can be explained from the known properties of the hexaamminecobalt(III) ion. Upon heating above 80°C, the color of precatalyst **3H** changes from orange to blue, and signals attributable to Co^{2+} appear in the XANES. It is notable that 80°C is also the temperature at which aqueous solutions of cobalt hexaamine(III) undergo reduction. Newton and Swaddle[62] have studied the thermal decomposition of aqueous hexaaminecobalt(III), and proposed the following decomposition pathway:

The first step is rate-limiting, and does not depend on pH. Some reduction is also observed from the diaqua complex, but there is no evidence for formation of $Co^{II}(NH_3)_6^{2+}$ or $Co^{II}(H_2O)(NH_3)_5^{2+}$ complexes during thermal decomposition of hexaaminecobalt(III). The absence of these species is explained by Ji et al.[61], who showed that the standard reduction potentials for $Co(H_2O)_{6-x}(NH_3)_x^{2+/3+}$ couples decrease monotonically with x , from +1.81 V for the hexaamine to only +0.02 V for the hexaaqua complex. As a result, reduction of Co(III) is not thermodynamically favorable until at least two amine ligands have been displaced. Ligand substitution at octahedral Co^{3+} proceeds by a dissociative mechanism, the rate of which is governed only by the activation barrier for the process $Co^{III}(NH_3)_6^{3+} \rightarrow Co^{III}(NH_3)_5^{3+} + NH_3$. This dissociative process is identical whether it occurs in aqueous solution or on the surface of silica, and the rate of this process is what ultimately determines the rate of reduction of hexaaminecobalt(III) to cobalt(II). It is therefore entirely expected that reduction of $Co^{III}(NH_3)_6^{3+}$ occurs at the same temperature whether in solution or on the surface of silica.

We propose that formation of tetrahedral Co^{2+} from hexaaminecobalt(III) on silica occurs according to:

Steps (7)-(9), in which the silica surface evolves from outer sphere anion to mono-, bi-, and tri-dentate ligand for Co^{3+} , are analogous to steps (3)-(5) in the aqueous decomposition mechanism above; likewise, step (10) is analogous to aqueous decomposition step (6). No attempt has been made to elucidate the details of the reduction mechanism as it occurs on silica. However, the absence of N-H stretches in the IR spectrum of the final catalyst (not shown) suggests that all six amine ligands are eventually lost either to desorption or to oxidation.

4.2 The Structure of the Catalyst

The 0.1 wt% loading of Co in catalyst **3L** corresponds to a surface coverage of less than 2.5% of one monolayer. Since this catalyst is synthesized using a monomeric precursor (the $\text{Co}^{\text{III}}(\text{NH}_3)_6^{3+}$ ion) and substantial aggregation of Co on the surface is statistically unlikely at such small loadings, it can be reasonably postulated that sample **3L** contains only monomeric Co. This hypothesis is supported by the X-band EPR spectrum for **3L**, which is essentially identical to those collected by other researchers for systems containing isolated, high spin Co^{2+} centers in tetrahedral environments.

All spectroscopic evidence suggests that catalyst **2L** is structurally identical to catalyst **3L**. Although self-condensation of Co(II) precursor species is possible both in solution and on the silica surface during the grafting process, the low concentration of these species again made substantial aggregation statistically unlikely.

The 2.1 wt% loading of Co in catalyst **3H** corresponds to enough Co to produce a surface coverage of 49% of one monolayer, so it is possible for all of the cobalt in this catalyst to be present as isolated monomers. The close similarity of the X-band EPR spectra of catalysts **3L** and **3H** supports this conclusion. In addition, the EXAFS spectra of sample **3H** shows only weak higher shell scattering near 2.5 Å, consistent with the expectation that Co-O-Si structures should show weak scattering, but inconsistent with the presence of a large population of Co-O-Co structures. By comparison, sample **2H** shows a strong Co-O-Co second-shell scattering at 2.6 Å and even some third-shell scattering at 3.6 Å. Sample **2H** also exhibits a different EPR spectrum, lower catalytic activity per Co, and most simply, is brown rather than cobalt blue.

In addition to providing evidence *for* the presence of isolated Co(II), the EPR spectra also provide evidence *against* the presence of dimeric species in samples **3L**, **2L**, and **3H**. For Co^{2+} dimers, the similar magnitudes of antiferromagnetic exchange, Zeeman splitting, and ion zero-field interaction give rise to rich, complex spectra very different from those observed here.[63] The presence of small clusters of Co_3O_4 can also be ruled out, as the tetrahedral Co^{2+} ions in this material give rise to an EPR signal near $g = 2.25$ not observed in Figure 3. Consideration of the evidence strongly supports the conclusion that samples **3L**, **2L**, and **3H** contain only tetrahedral, monomeric Co^{2+} .

4.3 Catalytic Mechanism

From the XANES and EXAFS data in Table 2, it is clear that single site Co^{2+} on silica catalysts cannot be oxidized to Co^{3+} at 550°C in air, and cannot be reduced to Co^0 at 550°C in helium or hydrogen. Similar resistance to both oxidation and reduction has been observed for tetrahedral Co^{2+} isomorphically substituted into zeolite beta, though debate exists about the reducibility of cobalt in zeolite structures.[64, 65] However, resistance to reduction has also been observed for Co-exchanged H-ZSM5.[19] Given the difference in ligand properties of zeolite *versus* SiO_2 , i.e. much more basic cobalt-oxygen bonds, we propose that hydrogenation of propene and dehydrogenation of propane over single site $\text{Co}^{2+}/\text{SiO}_2$ catalysts proceeds via a non-redox mechanism. Non-redox mechanisms for (de-)hydrogenation have been proposed for Co-exchanged ZSM5 catalysts,[18] as well as for related Zn^{2+} and Ga^{3+} catalysts.[20-23]

From pyridine adsorption studies, it is evident that the $\text{Co}^{2+}/\text{SiO}_2$ catalyst contains Lewis acid sites. Unlike Co-exchanged zeolites, however, the $\text{Co}^{2+}/\text{SiO}_2$ catalysts reported here do not contain any Brønsted acid sites. Thus, the mechanism for catalytic (de-)hydrogenation must involve Co^{2+} as a Lewis acid. By analogy with related Zn, Ga, and Cr catalysts, we postulate that (de-)hydrogenation involves *heterolytic* H-H and C-H activation across Co-O bonds.

(a) $\Delta E_a = 37.6 \text{ kcal/mol}$ (b) $\Delta E_a = 100.0 \text{ kcal/mol}$

Figure 11. Transition state structures representing (a) heterolytic and (b) homolytic activation of C–H bond in propane on Co/SiO_2 catalyst active site. Color: Co(blue), O(red), Si(teal), C(gray), and H(white).

In a previous study on $\text{Zn}^{2+}/\text{SiO}_2$ catalysts, we have shown that heterolytic C–H bond activation in propane on a $[\text{Zn}-\text{O}]$ active site is the energetically most favorable pathway. Heterolytic C-H bond activation at a d^{10} metal center is well-precedented, and can be understood in Lewis acid-base terms, with Zn^{2+} acting as a Lewis acid. In contrast, Co^{2+} with a d^7 electronic configuration has partially vacant d orbitals which may stabilize an alkyl radical and enable C–H activation via a homolytic route. Examples of homolytic C–H bond activation by homogeneous Co^{2+} catalysts can be readily found in the literature.[17] To understand the mechanism of C–H activation and dehydrogenation of propane on $\text{Co}^{2+}/\text{SiO}_2$ catalysts, density functional theory (DFT) calculations on

representative cluster models have been performed. The complete mechanism of propane dehydrogenation to propene on the $\text{Co}^{2+}/\text{SiO}_2$ catalyst is proposed to involve heterolytic cleavage of a C-H bond Co-O to form a Co alkyl and surface hydroxyl -OH, followed by β -hydride elimination to evolve propene. The resulting cobalt hydride then reacts with the neighboring hydroxyl proton to generate hydrogen, which desorbs to regenerate the initial Co-O resting state. , This mechanism is analogous to that previously reported on $\text{Zn}^{2+}/\text{SiO}_2$ and postulated in a number of other non-redox dehydrogenation mechanisms. A more detailed mechanistic analysis within density functional theory will be communicated in a subsequent publication.

The amorphous silica support is represented by using silsesquioxane type cluster models which have been used before by us and numerous other groups.[37, 42, 66] The XANES measurements suggest that cobalt in Co/SiO_2 is in +2 oxidation state. The EXAFS data indicate the presence of four neighboring atoms surrounding the metal center in a tetrahedral arrangement. This structure remains unchanged upon exposure to both oxidizing and reducing gases and at elevated temperatures. Therefore, the catalyst active site has been modeled as four-coordinate Co^{2+} center in which the metal atom interacts with four surface oxygen atoms. Two of the metal-oxygen bonds are covalent (Co-O-Si) and remaining two are dative bonds (Co-OH-Si). The Co-O covalent bond distance is 1.85 Å while the Co-O(H) dative bond distance is 2.11 Å. The average bond distance of 1.98 Å computed at the DFT level is in an excellent agreement with the estimated bond length (1.98 Å) from the EXAFS data.

The transition state (TS) for the heterolytic C-H cleavage in propane leading to a metal-alkyl intermediate and a surface silanol group is shown in Fig. 11a. The alternative heterolytic mechanism, in which a metal hydride and an alkyl silyl ether are formed, not only has a higher activation barrier for C-H dissociation, but also, the overall process is more endothermic. To estimate the electronic charge and spin on the metal center in the free catalyst as well as in the activated complex, natural bond orbital (NBO) analysis was performed. The charge on cobalt in the free catalyst is +1.2e, consistent with the +2 oxidation state of the metal. The electron spin value of 2.8 corresponds to the three unpaired electrons in high spin cobalt with the d^7 configuration. The formation of the four-membered activated complex does not change the charge or spin density on the

cobalt atom significantly, consistent with heterolytic C–H bond cleavage. The Co–C and O–H distances in the transition state structure are 2.15 Å and 1.25 Å, respectively, which are reduced to 1.98 Å and 0.98 Å, respectively in the resulting product (not shown here). The computed barrier for the heterolytic C–H bond activation is 37.6 kcal/mol. This is equal to within the accuracy of DFT to the heterolytic C–H bond activation energy (38.2 kcal/mol) determined previously for a silica supported Zn^{2+} catalyst.

The transition state for the homolytic C–H bond activation is shown in Fig. 11b. Attempts to locate an alternative TS structure in which a Co(III)–H intermediate and propyl radical are formed have failed at the DFT level. Instead, we have found that homolytic C–H cleavage involves the support oxygen covalently attached to the metal atom. The C–H and Co–O distances in the homolytic TS structure are 1.21 Å and 2.01 Å, respectively, which suggest that these two bonds are significantly activated. The Co–C distance of 3.72 Å virtually rules out any interaction between the metal center and the alkyl radical.

In the homolytic C–H bond activation pathway, the electronic charge and spin on the Co atom change significantly from the free catalyst to the activated complex. The number of unpaired electrons on Co in the TS is close to 4, as opposed to 2.8 in the free catalyst, which suggests that the electron transferred to the catalyst during C–H bond homolysis locates on the cobalt atom. This also makes the metal atom less positively charged, as confirmed via NBO analysis ($+0.7e$). The spin and charge analysis indicate that the Co atom in the transition state structure is essentially in the +1 oxidation state (d^8). The remaining unpaired electron resulting from the homolytic C–H bond cleavage is located over the carbon and two oxygen atoms.

The activation barrier for the homolytic C–H bond activation in propane is 100 kcal/mol, significantly higher than the barrier calculated for the heterolytic pathway (37.6 kcal/mol), and comparable to the gas phase homolytic bond dissociation energies for C–H bonds in propane ($\text{CH}_3\text{CH}_2\text{CH}_3$, 100.9 kcal/mol; $\text{CH}_3\text{CH}_2\text{CH}_3$, 98.1 kcal/mol).[67] The rate of C–H bond activation via radical mechanisms on the catalyst surface is therefore not likely to differ significantly from the rate of non-catalytic gas phase cracking. A similar result was observed in calculations on Zn/SiO₂. An additional difference between the two pathways is observed for the selectivity in C–H bond activation in propane: for

the heterolytic mechanism, the primary C-H bond (carbon 1) is lower in energy, whereas activation of a secondary C-H (carbon 2) bond is preferred in the homolytic mechanism. This difference is consistent with the observation that carbanion stability increases with decreasing substitution at carbon, whereas radical stability increases with increasing substitution. In summary, the catalytic selectivity and calculated reaction pathways are both consistent with heterolytic C-H activation rather than a one electron, homolytic pathway.

At 550°C, the propane dehydrogenation turnover frequencies observed on Co/SiO₂ catalysts are 2-3x greater than those observed on the previously investigated Zn/SiO₂ catalysts. In comparing these rates, we note that in air- and moisture-free environments, zinc alkyls are stable species, as the lack of vacant *d* orbitals on the *d*¹⁰ Zn²⁺ ion leads to high barriers for β-hydride elimination. Previous theoretical analysis confirmed that for Zn/SiO₂, this β-hydride elimination step is rate-determining. The greater rate of reaction for Co/SiO₂ can thus be attributed to the fact that the β-hydride elimination reaction is far more facile on Co. Late transition metal alkyls,[68, 69] such as those of Co,[70] are known to be labile for β-hydride elimination. Although high spin tetrahedral Co²⁺ lacks vacant *d* orbitals to enable β-hydride elimination, a recent theoretical study by Holland et al[71] demonstrated that beta-hydride elimination of high spin Fe(II) and Co(II) alkyls is accessible via a spin-crossover mechanism to generate a low spin intermediate. A similar spin-crossover mechanism is postulated in the present system.

The microscopic reverse reaction, propene hydrogenation, necessarily proceeds by the same mechanism as propane dehydrogenation, but in the reverse order. At 200°C, Zn/SiO₂ catalyst exhibits stable activity for propene hydrogenation. By contrast, while Co/SiO₂ treated with H₂ at 200°C is active initially for propene hydrogenation, activity decreases rapidly with extended exposure to propene. When propene is removed and Co/SiO₂ treated with H₂, the same initial activity and same deactivation trend is observed. By hypothesis, the Co-H(HO-Si) species generated by treatment with H₂ is rapidly consumed by propene, and regeneration of this species is slow at 200°C. At 550°C, the barrier to heterolytic cleavage of H₂ can be overcome and Co/SiO₂ shows long-lived hydrogenation activity over several hours of testing. Computational results are also

consistent with the formation of Co-H and SiOH species by heterolytic cleavage of H₂ being endothermic, thus requiring the high temperatures to generate sufficient surface Co-H concentration for effective catalysis. In conclusion, the endothermicity of heterolytic cleavage step on Co/SiO₂ results in it being an extremely poor hydrogenation catalyst at low temperatures, despite the exothermicity of the overall hydrogenation reaction. At the high temperatures required by thermodynamics for effective propane dehydrogenation, the barrier to heterolytic C-H bond cleavage is easily overcome, and thus the Co/SiO₂ shows good performance in propane dehydrogenation.

Of note, Co/SiO₂ used for catalytic hydrogenation at high temperatures does not maintain its activity when cooled and tested at lower temperatures (e.g. 200°C or room temperature). This is consistent with the proposed mechanism, but inconsistent with hydrogenation activity arising from the presence of reduced Co metal nanoparticles. The presence of such nanoparticles is also not supported by spectroscopic data (XANES and EPR), and is further inconsistent with the high selectivity observed for propene dehydrogenation at 650°C, as Co metal nanoparticles would be expected to readily cleave C-C bonds.

5. Conclusion

Single site, high spin, tetrahedral Co²⁺ supported on silica can be conveniently prepared at any scale by grafting Co^{III}(NH₃)₆Cl₃ from ammonium hydroxide solution. The resulting catalyst is active for dehydrogenation of propane above 550°C, and exhibits selectivity for dehydrogenation vs. C-C bond cracking reactions in excess of 95% even at 650°C. The structure of the catalyst has been confirmed under reaction conditions by XANES and EXAFS, and *ex situ* by EPR and Raman spectroscopies. Isolated Co²⁺ on silica undergoes neither oxidation in air nor reduction in hydrogen or propane at 650°C, but does exhibit Lewis basicity toward pyridine. Density functional theory calculations support the interpretation that propane dehydrogenation proceeds through a mechanism involving heterolytic C-H bond cleavage across a Co-O_{support} bond, with no consequent change in the cobalt oxidation state. The microscopic reverse reaction, propene hydrogenation, can also be carried out on Co/SiO₂ at high temperatures, but is inhibited at low temperatures by the endothermicity of heterolytically cleaving H₂. There are

relatively few other examples in literature of heterolytic C-H bond activation by heterogeneous cobalt catalysts, though a number of recent studies[14, 72-74] have concluded that it is a viable mechanism for metal ions which are in non-zero valent states. For example, it has been proposed for chromium catalyzed dehydrogenation by the Weckhuysen and coworkers.[75] Recent work by the Coperét group studying the industrially important Phillips polymerization catalyst also concluded[74, 76, 77] that heterolytic cleavage was the key step in generating Cr alkyl that is the active polymerization catalyst. Low-coordinate main-group Lewis acids such as Al can stoichiometrically activate methane.[72] Finally, we found that heterolytic cleavage occurs readily with our single-site Zn/SiO₂ catalyst for propane dehydrogenation.[37] For the single site cobalt catalyst disclosed here, heterolytic cleavage of the propane C-H bond is the key step, which had also been demonstrated in other similar catalytic systems.[14] However, it is an open question whether redox-active metal catalysts will activate C-H bonds by oxidative addition and reductive elimination or heterolytic cleavage. This is especially in question for second and third-row transition metals more inclined to participate in two-electron redox chemistry and are well-accepted to perform olefin hydrogenation via oxidative addition/insertion/reductive elimination mechanisms. Developing a greater understanding of the site requirements for heterolytic C-H bond activation opens new opportunities for catalyst design. In particular, the results presented here suggest that superior catalysts for selective C-H bond activation could be developed using non-redox single site catalysts with lower barriers for both heterolytic cleavage and β -hydride elimination than C-C bond cleavage. Attempts to develop such catalysts in our lab are ongoing.

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