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Atomic Layer Deposition for Preparing Isolated Co Sites on SiO2 for Ethane Dehydrogenation Catalysis

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Abstract: Unlike Co clusters, isolated Co atoms have been shown to be selective for catalytic dehydrogenation of ethane to ethylene; however, preparation of isolated Co sites requires special preparation procedures. Here, we demonstrate that Atomic Layer Deposition (ALD) of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III) (Co(TMHD)_3) on silica and other supports is effective in producing these isolated species. Silica-supported catalysts prepared with one ALD cycle showed ethylene selectivities greater than 96% at 923 K and were stable when CO_2 was co-fed with the ethane. Co catalysts prepared by impregnation formed clusters that were significantly less active, selective, and stable. Rates and selectivities also decreased for catalysts with multiple ALD cycles. Isolated Co catalysts prepared on Al_2O_3 and MgAl_2O_4 showed reasonable selectivity for ethane dehydrogenation but were not as effective as their silica counterpart.

Keywords: ethane dehydrogenation; cobalt; silica; atomic layer deposition (ALD); Co/SiO_2; oxidative dehydrogenation; single-site catalysts

1. Introduction

Ethylene is one of the most important building blocks for the chemical industry and is widely used as a feedstock for producing polymers, ethylene oxide, and other derivatives [1]. Most ethylene has been produced by steam cracking of light naphtha or as a by-product of fluidized catalytic cracking of crude oil. More recently, steam cracking of ethane has taken on increased importance due to the abundance of ethane from shale gas [2]; however, lower-temperature dehydrogenation of ethane would be desirable for energy efficiency and reduced NO_x emissions [3–5].

High temperatures are required in order to achieve high equilibrium conversions by direct catalytic dehydrogenation of ethane to H_2 and ethylene. Oxidative dehydrogenation (ODH) eliminates the equilibrium requirement by consuming the H_2 to form water, while simultaneously generating the heat required to raise the temperature of the reactants. The mostly extensively studied catalysts for ODH of ethane are chromium-based [6–8] and gallium-based [9,10] materials. In addition to other issues, the toxicity of CrOx and the severe coking behavior of GaOx-containing materials have prevented their wide-scale application. Other metal oxides, including those of V [11], Mo [11], and Co [12], have also been investigated and show some potential. Over-oxidation of the ethylene product is usually an issue in ODH with strong oxidants, and it would be particularly attractive if one could use a “soft” oxidant, such as readily available CO_2 [13].

There have been several recent reports that cobalt-based catalysts can be active and selective for ODH of ethane using CO_2 [12,14]. Of particular interest, Koirala et al. [12] demonstrated that
flame-synthesis of CoOₓ/SiO₂ produced a catalyst capable of selectivities above 85%. Their observation that selectivities increased with decreasing Co content suggested that the selective sites are associated with isolated Co. Spectroscopic data implied that the active species was Co²⁺ in a tetrahedral environment, strongly bound to the silica. Others have also shown that isolated Co can exhibit selective C–H activation of alkanes [15–17]. For example, Hu et al. used electrostatic adsorption of monomeric hexamminecobalt(III) with low metal loadings to produce silica-supported catalysts with isolated Co [15]. However, preparation of isolated Co species remains challenging; and conventional preparation by impregnation usually results in catalysts that have metal atoms in a variety of coordination environments [16].

In the present work, we will demonstrate that isolated Co sites on silica and other supports can be prepared easily by atomic layer deposition (ALD). The basic idea behind ALD is that a precursor reactant is first allowed to react with a surface in a self-terminating way. After the excess precursor has been purged, the adsorbed precursor is oxidized in a separate step. By choosing the correct conditions, conformal films can be deposited on either flat or porous surfaces, as described in several reviews [18,19]. For the present application, it is important to recognize that a single deposition cycle of Co precursors with large ligands results in spatially isolated Co atoms that retain that site isolation after removal of the ligands. For example, previous work has shown that the growth rate for ALD with tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III) (Co(TMHD)₃) is 5 × 10⁻¹⁷ Co/m² [20,21], a coverage that is roughly a factor of ten lower than that which would be expected for Co in a monolayer of CoOₓ. This low coverage per cycle, which is almost certainly due to steric crowding by the large TMHD ligands, causes the Co ions to be spatially isolated. The resulting catalysts exhibit exceptional activity, selectivity, and stability for dehydrogenation of ethane. A comparison of Co²⁺ on silica, alumina, and MgAl₂O₄ shows that the silica-supported catalysts are superior but reasonable performance could be achieved with isolated Co²⁺ on the other supports as well.

2. Materials and Methods

2.1. Catalyst Preparation

SiO₂, Al₂O₃, and MgAl₂O₄ were used as the supports in this work. The SiO₂ (Fuji Silysia Chemical G-6, Nagoya, Japan, 10 μm) was calcined in air at 973 K for 1 h. The Al₂O₃ used in this study was obtained as γ-Al₂O₃ (Strem Chemicals, Newburyport, MA, USA) but was then stabilized by calcination in air at 1173 K for 24 h. The MgAl₂O₄ was prepared in our laboratory by co-precipitation and the synthesis has been described in previous publications [22]. It was also calcined in air at 1173 K for 12 h to stabilize its surface area. All support powders were pressed into thin wafers and then broken into small pieces before further use.

The cobalt was deposited onto different supports by ALD using a home-built, static system that has been described in detail previously [23,24]. The ALD precursor was Co(TMHD)₃ (Strem Chemicals). During the deposition process, approximately 0.7 g of support material were evacuated and exposed to 5 Torr of the precursor vapor at 523 K for 5 min, after which the samples were evacuated to remove excess precursors and then oxidized in a muffle furnace at 773 K for 7 min to fully remove the ligands. Samples with n ALD cycles on a particular support are referred to here as nCo-support.

A silica-supported sample was also prepared by conventional incipient wetness, using aqueous solutions of Cobalt(II) nitrate hexahydrate (98%, Sigma-Aldrich, St. Louis, MO, USA). To minimize CoOₓ cluster size, this sample was prepared with 1-wt% Co on SiO₂. After impregnation, it was calcined for 3 h at 873 K and is referred to as impCo-SiO₂.

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns were measured on a MiniFlex diffractometer (Rigaku, Tokyo, Japan) equipped with a Cu Kα source (λ = 154.05 pm). Co loadings were initially determined by weight changes following ALD but then confirmed by Inductively-Coupled Plasma, Optical Emission Spectrometry (ICP-OES, Spectro Genesis, Kleve, Germany). Specific surface areas were
obtained by the Brunauer–Emmett–Teller (BET; home-built device) method using N₂ at 78 K. UV–Vis, diffuse-reflectance spectra were recorded on a Cary 5000 UV–Vis–NIR spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory (Harrick Scientific Products, Pleasantville, NY, USA). The spectra were measured against a Spectralon background. A thermogravimetric analyzer (Q600, TA Instruments, New Castle, DE, USA) was used to quantify the amount of coke in the spent catalyst after 24 h on stream. For these measurements, the samples were first held at 373 K for 1 h in flowing, dry N₂ before ramping the temperature in flowing air to 1173 K at a rate of 10 K/min. Temperature programmed desorption (TPD) measurements were performed in a high-vacuum system (10⁻⁷ torr), using 50-mg samples and a quadrupole mass spectrometer (RGA100, Stanford Research Systems, Sunnyvale, CA, USA) for product detection [25]. The heating rate in these measurements was again 10 K/min.

2.3. Catalyst Testing

The dehydrogenation reactions were conducted in a 1/2-inch, quartz, tubular flow reactor. Gas flow was controlled using simple rotameters with metering valves (FL3600-3800, Omega Engineering, Norwalk, CT, USA). Products were detected by on-line gas chromatography (Model 310, Buck Scientific, city, country) with a Haysep Q column and a thermal conductivity detector using Helium (He, 99.999%, Airgas, Allentown, PA, USA) as the carrier gas. In a typical run, 0.5 g of catalyst was loaded in the center of the tube between two quartz-wool plugs. The catalysts were heated to the desired reaction temperature at 10 K/min in He flow before introducing the reaction mixtures. The reactant gases were ethane (C₂H₆, 99.99%, Airgas) and carbon dioxide (CO₂, 99.99%, Airgas). The total flow rate of the reactant gases and He was maintained at 30 mL/min throughout the study. To increase the residence time, we either increased the catalyst loading or reduced the total flow rate. In all cases, the carbon balances were greater than 98% for reactions when CO₂ and ethane were co-fed and 96% in the absence of CO₂.

3. Results

3.1. Sample Characterization

A list of all the samples used in this study is reported in Table 1, together with their metal loadings and BET surface areas. The specific Co coverages in the table were calculated from the Co weight loading and the BET surface area, assuming the Co was present as CoO. On the SiO₂ support, catalysts were prepared with between one and ten ALD cycles of Co(TMHD). As shown in Table 1, the Co loading increased linearly with the number of cycles, as expected; however, the growth rate, 2.5 × 10¹⁷ Co/m²-cycle, was about half that reported previously for deposition of Co with this precursor on Al₂O₃ and MgAl₂O₄ [20,21]. Since only one ALD cycle was deposited onto the Al₂O₃ and MgAl₂O₄ supports in the present study, there was significant uncertainty in the growth rates for these samples; but the values, 8 × 10¹⁷ Co/m²-cycle, were more similar to what has been reported previously [20,21]. We suggest that the lower growth rate on SiO₂ was due to the fact that this support had a much higher surface area than the supports used in earlier work and therefore had smaller pores. It is likely that the Co precursor with large TMHD ligands was unable to access smaller pores. However, we cannot rule out the possibility that the silica simply had a lower concentration of reactive sites [26].

It is useful to notice that the coverage of 2.7 × 10¹⁷ Co/m² would imply that each Co occupies an area of 4 nm², which would indicate that the metal atoms are separated by a distance of roughly 2 nm. Even after 10 ALD cycles, the average distance between Co atoms is expected to be greater than 0.6 nm. Finally, the decrease in BET surface area with the number of ALD cycles in the SiO₂-supported samples is mainly due to the increased mass of the samples, combined with a small change in pore size [27].
Table 1. Samples used in this study, together with their Brunauer–Emmett–Teller (BET) surface areas and Co loadings. nCo-MOx correspond to samples prepared by Atomic Layer Deposition (ALD), with n being the number of ALD cycles.

| Sample     | BET S.A (m²/g) | Metal Loading (wt%) | Cobalt Coverages (Co/m²) |
|------------|----------------|---------------------|--------------------------|
| SiO₂       | 472            | 0                   | 0                        |
| 1Co-SiO₂   | 457            | 1.2                 | 2.7 × 10¹⁷               |
| 2Co-SiO₂   | 445            | 2.3                 | 5.3 × 10¹⁷               |
| 3Co-SiO₂   | 438            | 3.5                 | 8.2 × 10¹⁷               |
| 5Co-SiO₂   | 419            | 5.5                 | 1.3 × 10¹⁸               |
| 10Co-SiO₂  | 343            | 12.1                | 3.6 × 10¹⁸               |
| impCo-SiO₂ | 453            | 1.0                 | 2.3 × 10¹⁷               |
| 1Co-Al₂O₃  | 102            | 0.9                 | 9.0 × 10¹⁷               |
| 1Co-MgAl₂O₄| 136            | 1.0                 | 7.5 × 10¹⁷               |

XRD patterns of the SiO₂, 1Co-SiO₂, 10Co-SiO₂, and impCo-SiO₂ samples, shown in Figure 1, demonstrate that the structure of the ALD-prepared samples differed significantly from that of the sample prepared by impregnation. Each of these samples was calcined above 773 K but only the impCo-SiO₂ sample exhibited features at 36, 44, 59, and 65 degrees 2θ. These peaks correspond to Co₃O₄ and demonstrate that, in the absence of very specialized procedures, such as the electrostatic adsorption procedure used by Hu et al. [15,28], impregnation leads to formation of metal clusters, even at relatively low Co loadings. From the XRD peak width and Scherrer’s equation, the Co₃O₄ crystallite size for impCo-SiO₂ was estimated to be 11 nm. By contrast, the samples prepared by ALD showed no observable XRD peaks for cobalt oxides, even at Co loadings ten times higher.

![Figure 1](image_url)

**Figure 1.** XRD patterns of SiO₂, impCo-SiO₂, 1Co-SiO₂, and 10Co-SiO₂. Characteristic peaks associated with Co₃O₄ are marked as (■).

The difference in the structure of the materials prepared by ALD and by impregnation was further shown by the UV–Vis spectra in Figure 2. Pure SiO₂ did not adsorb in the UV–Vis range that
is shown here and thus did not exhibit any features. The impCo-SiO₂ sample was visibly darker and exhibited broad absorption bands between 300 and 600 nm and between 650 and 800 nm. These bands were consistent with that expected for Co₃O₄ [29]. However, the 1Co-SiO₂ and 10Co-SiO₂ were both light blue in color and exhibited absorption bands centered at 530, 590, and 640 nm. These spectra imply that the Co is present as isolated Co²⁺ in a tetrahedral environment [17,28,30]. As expected, the intensity of the bands was stronger with 10Co-SiO₂ compared to 1Co-SiO₂ due to the increased metal loading but the features remained the same. It is also noteworthy that these spectra are the same as those reported for the flame-prepared samples in an earlier study [12,28].

The adsorption properties of the Co added by ALD were probed in TPD studies with 2-propanol, with results shown for SiO₂ and 1Co-SiO₂ in Figure 3. 2-Propanol adsorbs on silica via hydrogen bonding with surface silanols [31]. Some of the alcohol desorbed as 2-propanol below 550 K but a significant fraction desorbed as propene between 700 and 800 K. The propene was produced by the decomposition of the silyl/iso-propyl ether that formed when the alcohol reacted with silanols. The water formed in this reaction desorbed at lower temperatures, over a broad temperature range, so that the silyl/iso-propyl ether that remained at higher temperatures could not recombine back to the alcohol. While these same silica-related features were observed on the 1Co-SiO₂ sample, the Co-containing sample also exhibited acetone formation between 500 and 650 K. The formation of acetone is a clear indication of dehydrogenation activity.

![Figure 2. UV–Vis diffuse reflectance spectra of SiO₂, 1Co-SiO₂, 10Co-SiO₂, and impCo-SiO₂.](image)
3.2. Catalytic Performance

3.2.1. Comparison of 1Co-SiO₂ and impCo-SiO₂

To understand how the catalytic properties of isolated Co sites differ from that of CoOₙ clusters, we examined the reaction of ethane and CO₂ on the 1Co-SiO₂ and impCo-SiO₂ samples at 923 K, with data shown in Figure 4. These experiments were performed on the oxidized samples but prereduction of the 1Co-SiO₂ sample at 973 K in H₂ had no effect on either the conversion or the selectivity. As shown in Figure 4a, using the same amounts of catalyst and a CO₂:C₂H₆ ratio of one, the conversion on 1Co-SiO₂ was approximately three times higher than on impCo-SiO₂, 22% versus 7%. More importantly, the selectivity on 1Co-SiO₂ was 99% to ethylene, compared to a value of only 16% on impCo-SiO₂. The impCo-SiO₂ acted primarily as a reforming catalyst, producing CO and H₂. The 1Co-SiO₂ sample was also relatively stable for a period of at least 7 h, Figure 4b. Since the results on impCo-SiO₂ show that clusters were not selective for ethylene, the fact that the selectivity remained high on 1Co-SiO₂ implies that the isolated Co species did not sinter to form clusters under these conditions. Finally, it is interesting to note that the selectivities that we observed on 1Co-SiO₂ were actually somewhat higher than the dilute-Co catalysts that were flame-prepared by Koirala et al. [28]. While the conditions of our experiments were clearly different, this result suggests that preparation of the catalyst by ALD may be more effective in producing isolated Co compared to the flame-preparation method.
3.2.2. Influence of CO$_2$ Partial Pressure

In the reaction of ethane with CO$_2$, it has been proposed that the role of CO$_2$ can be either to push the equilibrium towards ethylene production by consuming H$_2$ via reverse water gas shift (RWGS) or to remove coke via reverse Boudouard reaction [1, 2, 32]. To determine which process was more important for the present system, we examined the conversion and stability of the 1Co-SiO$_2$ catalyst for different CO$_2$:C$_2$H$_6$ ratios, with results shown in Figure 5. Measurements were performed as a function of time at a fixed mole fraction of C$_2$H$_6$ of 0.167 and a fixed space time (30 mL/min total flow rate with 0.5-g catalyst). In all cases, the selectivity to ethylene was greater than 97%, demonstrating that the presence of CO$_2$ did not affect selectivity. In the absence of CO$_2$, the conversions were initially higher than what we measured in the presence of CO$_2$, implying that equilibrium considerations are not important. This conclusion is further supported by the fact that the equilibrium conversion of ethane to ethylene and H$_2$ at this temperature would be 69%. Furthermore, even with a CO$_2$:C$_2$H$_6$ ratio of 3, only about 5% of the H$_2$ produced in the reaction was consumed by RWGS. However, in the absence of CO$_2$, the conversion declined significantly with time. For CO$_2$:C$_2$H$_6$ ratios of both 1 and 3, the conversions were stable. The effect of changing the CO$_2$:C$_2$H$_6$ ratio was modest so long as some CO$_2$ was present in the reaction mixture. The conversions decreased, but only slightly, when the CO$_2$:C$_2$H$_6$ ratio increased from 1 to 3.
3.2.3. Stability and Regeneration of 1Co-SiO2

To gain further insights into the reasons for deactivation of 1Co-SiO2 in the absence of CO2, we performed additional, 24-h tests of the sample, with and without CO2. We also measured the carbon contents of the sample after running the reaction for this amount of time and attempted to regenerate the catalyst by oxidation. The results of these experiments are shown in Table 2. In agreement with Figure 5, the conversion of ethane in the absence of CO2 fell to 7.2% after 24 h while the conversion dropped only modestly, from 23.2% to 18.1%, when CO2 was added to the feed. The activity of the catalyst could be largely restored by oxidation at 923 K in flowing air, implying that deactivation was not due to some structural change in the catalyst. The carbon contents after 24 h of reaction were 3.7-wt% in the absence of CO2 and 1.0-wt% when the feed contained CO2. Since metallic Co nanoparticles can form large amounts of carbon due whisker formation [33,34], both of these values were relatively small, indicating that whisker formation did not occur; however, on an atomic basis, the C:Co ratio corresponding to 3.7-wt% C was greater than 20, so that this amount of carbon was sufficient to cover the active component.

Table 2. The conversions and selectivities for ethane dehydrogenation over 1Co-SiO2, initially and after 24 h, with and without CO2 in the feed. Reaction conditions: T = 923 K; space time = 1 h·gcat·mL−1. Regeneration was performed in flowing air at 923 K for 1 h.

| Feed C2H6:CO2:He | Conversion (Selectivity) % | Amount of Coke |
|------------------|---------------------------|----------------|
| C2H6:CO2:He 1:0:5| 26.9 (98.8) 7.2 (98.8) 21.7 (98.8) | 3.7 wt% |
| C2H6:CO2:He 1:1:4| 23.2 (98.3) 18.1 (98.0) 17.0 (97.8) | 1.0 wt% |

3.2.4. Effects of Reaction Temperature and Space Velocity

The effect of reaction temperature on the 1Co-SiO2 sample was investigated between 923 and 1023 K, with results reported in Figure 6. While conversion increased with temperature, the selectivity decreased dramatically. At higher reaction temperatures, we observed evidence for both gas-phase, free-radical reactions from the presence of methane and higher-molecular weight products and dry reforming from the presence of CO in the products.
Figure 6. Effect of temperature on the conversion and selectivity for ethane dehydrogenation over 1Co-SiO2. Data were collected at a time-on-stream of 1 h. Reaction conditions: T = 923 K; CO2:C2H6:He = 1:1:4; space time = 1 h·gcat·mL⁻¹.

The effect of varying the space time on the 1Co-SiO2 sample is shown in Figure 7. As expected, the conversion increased with increasing space time. What is noteworthy is that the selectivity to ethylene remained high, greater than 96%, at conversions approaching 40%. Ethylene did not appear to be reactive on this catalyst under these conditions.

Figure 7. Effect of space time on catalytic performance for ethane dehydrogenation over 1Co-SiO2. Data were collected at a time-on-stream of 2 h. Reaction conditions: T = 923 K; CO2:C2H6:He = 1:1:4.

3.2.5. Effect of the Number of ALD Cycles on SiO2

It is expected that higher Co loadings should lead to higher rates if isolated Co sites can be maintained. Since the XRD and UV–Vis results in Figures 1 and 2 suggest that the Co still exists as isolated sites following multiple ALD cycles, we examined the conversion and selectivity of SiO2-supported samples as a function of the number of ALD cycles, with results shown in Figure 8. The conversion did increase slightly after the second ALD cycle but then declined monotonically. Selectivity remained high after as many as five ALD cycles but then decreased dramatically after 10 ALD cycles. We suggest that the most likely explanation for the decrease in rates with increasing ALD cycles is that only isolated Co sites are active. Additional ALD cycles create sites in which Co sites are paired, so that adding more Co lowers the rates. After 10 ALD cycles, some of the Co is present as clusters, which are active for non-selective reactions.
3.2.6. Isolated Co on Other Supports

Unlike the flame-synthesis [12] and electrostatic-adsorption [15] methods for preparing isolated Co sites, addition of Co by ALD is expected to provide isolated sites independent of the support. Therefore, to determine the effect of different supports on the reaction of ethane, samples were prepared with one ALD cycle of Co(TMHD)₃ onto Al₂O₃ and MgAl₂O₄. Although Co is expected to react with Al₂O₃ to form CoAl₂O₄ at higher temperatures [20], the presence of MgO should provide some stability [21]. Figure 9 compares the conversions and selectivities at a time-on-stream of 1 h for 1Co-SiO₂, impCo-SiO₂, 1Co-Al₂O₃, and 1Co-MgAl₂O₄. The 1Co-Al₂O₃ and 1Co-MgAl₂O₄ samples were less active and selective compared to 1Co-SiO₂ but both catalysts were significantly better than impCo-SiO₂. The lower activity of 1Co-Al₂O₃ and 1Co-MgAl₂O₄ compared to 1Co-SiO₂ could be explained by Co incorporation into the bulk of the Al₂O₃ and MgAl₂O₄ supports. While reaction of Co with the Al₂O₃ and MgAl₂O₄ supports cannot explain the higher selectivity of the 1Co-SiO₂ catalyst, these catalysts remained significantly better than the impCo-SiO₂, suggesting clusters were not formed.

Figure 9. Conversions and selectivities for 1Co-SiO₂, impCo-SiO₂, 1Co-Al₂O₃, and 1Co-MgAl₂O₄. Data were collected at a time-on-stream of 1 h. Reaction conditions: T = 923 K; CO₂:C₂H₆:He = 1:1:4; space time = 1 h g⁻¹ cat mL⁻¹.
4. Discussion

In this work, we have demonstrated that isolated-site, Co catalysts can be synthesized readily using ALD with large precursor molecules. While other methods for preparing single-site catalysts have been demonstrated [12,15], the utility of ALD is that the conditions required to make the materials appear to be independent of support. One ALD cycle also appears to provide a nearly optimal metal loading, so that the effect of loading does not need to be explored. We should also note that preparation of materials using one ALD cycle can be accomplished in a simple, high-temperature adsorption system and does not require the expensive equipment that is more commonly used when rapid cycling is required [23]. Furthermore, since the oxidation step can be carried out at higher temperatures, possibly in a separate system, the precursor does not need to be a specialized compound designed to be easily oxidized at the deposition temperature. Any compound that remains stable to temperatures at which it has a vapor pressure can be used.

Isolated-site catalysts based on Zn have been successfully prepared by ALD in earlier studies [35], but the approach does not appear to have been successful in preparing single-atom, precious-metal catalysts [21,36,37]. A key factor in being able to achieve single-site catalysts is the requirement that the metal atoms be immobilized on the surface. Success in the case of Zn and Co is likely due to the fact that these atomic species remain in an oxidized form, bonded in some way to the support. This is likely the case also for Co. While bulk Co would be reduced to its zero-valence state at the low O$_2$ fugacities associated with ethane dehydrogenation, isolated Co atoms are likely much harder to reduce [38]. Furthermore, it has recently been demonstrated that interactions with the support can shift equilibrium constants to make the metals even more difficult to reduce [38]. By contrast, precious metals are always much easier to reduce. In the case of single-atom, precious-metal catalysts, the support almost always plays a key role [39,40].

Isolated-site Co catalysts are especially intriguing, given their high selectivity for dehydrogenation of ethane and remarkable tolerance against coking. The fact that we were able to achieve relatively high conversions (>25%) with almost 100% selectivity (99%) is very encouraging. Whether silica is playing a role as “ligand” for the supported Co is uncertain. While rates for isolated Co appear to be lower for Co on Al$_2$O$_3$ and MgAl$_2$O$_4$, this could be associated with formation of CoAl$_2$O$_4$. The Co/Al$_2$O$_3$ and Co/MgAl$_2$O$_4$ catalysts were still reasonably selective. It will be interesting to investigate the effects of other supports that may be less reactive.

Obviously, there is still much to learn about the nature and properties of the catalytic sites in single-site cobalt on silica. We believe the controlled synthesis of ALD could open the possibility for understanding and producing highly active and selective Co-based catalyst for various applications.

5. Conclusions

We have successfully prepared isolated-site, Co catalysts on SiO$_2$, Al$_2$O$_3$, and MgAl$_2$O$_4$ supports using ALD. The SiO$_2$-supported Co catalyst exhibited dramatically improved conversion and selectivity for ethane dehydrogenation compared to a catalyst prepared by the conventional impregnation. ALD provides a simple method for preparing these isolated-site catalysts.

Author Contributions: R.J.G. and R.H. were responsible for the initial concept behind the project and most of the writing. Experiments were performed and analyzed by R.H., Y.C., and Y.J. All authors have read and agreed to the published version of the manuscript.

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References

1. Gärtner, C.A.; van Veen, A.C.; Lercher, J.A. Oxidative Dehydrogenation of Ethane: Common Principles and Mechanistic Aspects. Chem. Cat. Chem. 2013, 5, 3196–3217.
2. Sattler, J.J.H.B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. Chem. Rev. 2014, 114, 10613–10653.
3. Ren, T.; Patel, M.; Blok, K. Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. Energy 2006, 31, 425–451.
4. Bhasin, M.M.; McCain, J.H.; Vora, B.V.; Imai, T.; Pujadó, P.R. Dehydrogenation and oxydehydrogenation of paraffins to olefins. Appl. Catal. A Gen. 2001, 221, 397–419.
5. Zhang, J.; Shan, H.; Chen, X.; Liu, W.; Yang, C. Fluid Catalytic Cracking Study of Coker Gas Oil: Effects of Processing Parameters on Sulfur and Nitrogen Distributions. Energy Fuels 2014, 28, 1362–1371.
6. Olsbye, U.; Virmovskaia, A.; Prytz, O.; Timmermans, S.J.; Weckhuysen, B.M. Mechanistic insight in the ethane dehydrogenation reaction over Cr/Al2O3 catalysts. Catal. Lett. 2005, 103, 143–148.
7. Shi, X.; Ji, S.; Wang, K. Oxidative dehydrogenation of ethane to ethylene with carbon dioxide over Cr-Ce/SBA-15 catalysts. Catal. Lett. 2008, 125, 331–339.
8. Cheng, Y.; Miao, C.; Hua, W.; Yue, Y.; Gao, Z. Cr/ZSM-5 for ethane dehydrogenation: Enhanced catalytic activity through surface silanol. Appl. Catal. A Gen. 2017, 532, 111–119.
9. Nakagawa, K.; Okamura, M.; Ikenaga, N.; Suzuki, T.; Nakagawa, K.; Okamura, M.; Suzuki, T.; Kobayashi, T.; Kobayashi, T. Dehydrogenation of ethane over gallium oxide in the presence of carbon dioxide. Chem. Commun. 1998, 1025–1026.
10. Lei, T.Q; Cheng, Y.H; Miao, C.X; Hua, W.M; Yue, Y.H; Gao, Z. Silica-doped TiO2 as support of gallium oxide for dehydrogenation of ethane with CO2. Fuel Process. Technol. 2018, 177, 246–254.
11. Annamalai, L.; Liu, Y.; Ezenwa, S.; Dang, Y.; Suib, S.L.; Deshlahra, P. Influence of Tight Confinement on Selective Oxidative Dehydrogenation of Ethane on MoVTeNb Mixed Oxides. ACS Catal. 2018, 8, 7051–7067.
12. Koirala, R.; Buechel, R.; Pratsinis, S.E.; Baiker, A. Silica is preferred over various single and mixed oxides as support for CO2-assisted cobalt-catalyzed oxidative dehydrogenation of ethane. Appl. Catal. A Gen. 2016, 527, 96–108.
13. Gomez, E.; Yan, B.; Kattel, S.; Chen, J.G. Carbon dioxide reduction in tandem with light-alkane dehydrogenation. Nat. Rev. Chem. 2019, 3, 638–649.
14. Zhang, X.; Ye, Q.; Xu, B.; He, D. Oxidative dehydrogenation of ethane over Co-BaCO3 catalysts using CO2 as oxidant: effects of Co promoter. Catal. Lett. 2007, 117, 140–145.
15. Hu, B.; “Bean” Getsoian, A.; Schweitzer, N.M.; Das, U.; Kim, H.; Niklas, J.; Poluektov, O.; Curtiss, L.A.; Stair, P.C.; Miller, J.T.; Hock, A.S. Selective propane dehydrogenation with single-site CoII on SiO2 by a non-redox mechanism. J. Catal. 2015, 322, 24–37.
16. Xie, J.; Kammert, J.D.; Kaylor, N.; Zheng, J.W.; Choi, E.; Pham, H.N.; Sang, X.; Stavitski, E.; Attenkofer, K.; Unocic, R.R.; et al. Atomically Dispersed Co and Cu on N-Doped Carbon for Reactions Involving C–H Activation. ACS Catal. 2018, 8, 3875–3884.
17. Zhao, Y.; Sohn, H.; Hu, B.; Niklas, J.; Poluektov, O.G.; Tian, J.; Delferro, M.; Hock, A.S. Zirconium Modification Promotes Catalytic Activity of a Single-Site Cobalt Heterogeneous Catalyst for Propane Dehydrogenation. ACS Omega 2018, 3, 11117–11127.
18. Puurunen, R.L. Growth per cycle in Atomic Layer Deposition: Real Application Examples of a Theoretical Model. Chem. Vap. Depos. 2003, 9, 327–332.
19. Cremers, V.; Puurunen, R.L.; Dendooven, J. Conformality in atomic layer deposition: Current status overview of analysis and modelling. Appl. Phys. Rev. 2019, 6, 021302.
20. Mao, X.; Foucher, A.; Stach, E.A.; Gorte, R.J. A Study of Support Effects for CH4 and CO Oxidation over Pd Catalysts on ALD-Modified Al2O3. Catal. Lett. 2019, 149, 905–915.
21. Mao, X.; Foucher, A.C.; Stach, E.A.; Gorte, R.J. “Intelligent” Pt Catalysts Based on Thin LaCoO3 Films Prepared by Atomic Layer Deposition. Inorganics 2019, 7, 113.
22. Ohn, T.M.; Monai, M.; Dai, S.; Fonda, E.; Montini, T.; Pan, X.; Graham, G.W.; Fornasiero, P.; Gorte, R.J. Smart Pd Catalyst with Improved Thermal Stability Supported on High-Surface-Area LaFeO3 Prepared by Atomic Layer Deposition. J. Am. Chem. Soc. 2018, 140, 4841–4848.
23. Onn, T.M.; Küngas, R.; Fornasiero, P.; Huang, K.; Gorte, R.J. Atomic Layer Deposition on Porous Materials: Problems with Conventional Approaches to Catalyst and Fuel Cell Electrode Preparation. *Inorganics* 2018, 6, 34.

24. Lin, C.; Mao, X.; Onn, T.M.; Jang, J.; Gorte, R.J. Stabilization of ZrO$_2$ Powders via ALD of CeO$_2$ and ZrO$_2$. *Inorganics* 2017, 5, 65.

25. Yeh, Y.-H.; Yu, J.; Luo, J.; Gorte, R.J. Endothermic Reforming of n-Hexane on Metal (Pt, Ga) Containing H-ZSM-5 at High Pressures. *Ind. Eng. Chem. Res.* 2015, 54, 10675–10683.

26. Zhang, B.; Qin, Y. Interface Tailoring of Heterogeneous Catalysts by Atomic Layer Deposition. *ACS Catal.* 2018, 8, 10064–10081.

27. Wang, C.; Mao, X.; Lee, J.D.; Onn, T.M.; Yeh, Y.-H.; Murray, C.B.; Gorte, R.J. A Characterization Study of Reactive Sites in ALD-Synthesized WO$_x$/ZrO$_2$ Catalysts. *Catalysts* 2018, 8, 292.

28. Koirala, R.; Safonova, O.V.; Pratsinis, S.E.; Baiker, A. Effect of cobalt loading on structure and catalytic behavior of CoO$_x$/SiO$_2$ in CO$_2$-assisted dehydrogenation of ethane. *Appl. Catal. A Gen.* 2018, 552, 77–85.

29. Bhargava, R.; Khan, S.; Ahmad, N.; Ansari, M.M.N. Investigation of structural, optical and electrical properties of CoO$_x$ nanoparticles. In Proceedings of the AIP Conference Proceedings; Bikaner, India, 2018; Volume 1953, p. 030034.

30. Okamoto, Y.; Nagata, K.; Adachi, T.; Imanaka, T.; Inamura, K.; Takyu, T. Preparation and characterization of highly dispersed cobalt oxide and sulfide catalysts supported on SiO$_2$. *J. Phys. Chem.* 1991, 95, 310–319.

31. Aronson, M.T.; Gorte, R.J.; Farneth, W.E. The influence of oxonium ion and carbenium ion stabilities on the Alcohol/H-ZSM-5 interaction. *J. Catal.* 1986, 98, 434–443.

32. Baker, R.T.K. Catalytic growth of carbon filaments. *Carbon* 1989, 27, 315–323.

33. Baker, R.T.K.; Harris, P.S.; Thomas, R.B.; Waite, R.J. Formation of filamentous carbon from iron, cobalt and chromium catalyzed decomposition of acetylene. *J. Catal.* 1973, 30, 86–95.

34. Camacho-Bunquin, J.; Aich, P.; Ferrandon, M.; “Bean” Getsoian, A.; Das, U.; Dogan, F.; Curtiss, L.A.; Miller, J.T.; Marshall, C.L.; Hock, A.S.; Stair, P.C. Single-site zinc on silica catalysts for propylene hydrogenation and propane dehydrogenation: Synthesis and reactivity evaluation using an integrated atomic layer deposition-catalysis instrument. *J. Catal.* 2017, 345, 170–182.

35. Lin, C.; Foucher, A.C.; Ji, Y.; Curran, C.D.; Stach, E.A.; McIntosh, S.; Gorte, R.J. “Intelligent” Pt Catalysts Studied on High-Surface-Area CaTiO$_3$ Films. *ACS Catal.* 2019, 9, 7318–7327.

36. Wang, C.; Hu, L.; Lin, Y.; Poeppelmeier, K.; Stair, P.; Marks, L. Controllable ALD synthesis of platinum nanoparticles by tuning different synthesis parameters. *J. Phys. D. Appl. Phys.* 2017, 50, 415301.

37. Bakhmutsky, K.; Wieder, N.L.; Baldassare, T.; Smith, M.A.; Gorte, R.J. A thermodynamic study of the redox properties of supported Co particles. *Appl. Catal. A Gen.* 2011, 397, 266–271.

38. Lou, Y.; Liu, J. CO Oxidation on Metal Oxide Supported Single Pt atoms: The Role of the Support. *Ind. Eng. Chem. Res.* 2017, 56, 6916–6925.

39. van Deelen, T.W.; Hernández Mejia, C.; de Jong, K.P. Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity. *Nat. Catal.* 2019, 2, 955–970.