Atomic Layer Deposition (ALD) for Catalysis Applications

Preparing Isolated Co Sites on SiO_2 for Ethane Dehydrogenation Catalysis

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Abstract

Motivation

- Ethylene – building blocks for chemical industry, such as polymers, ethylene oxide
- Abundance of ethane from shale gas recently
- Lower-temperature dehydrogenation of ethane to ethylene is highly desired

Graphical abstract

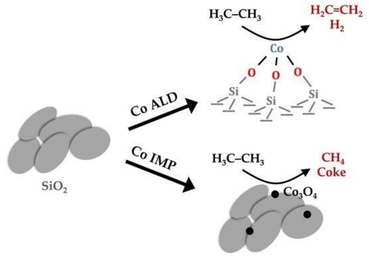


Fig. 1 Reaction scheme for the ethane dehydrogenation on ALD-prepared catalyst and conventional impregnation prepared catalyst.

- Single site cobalt on silica is prepared by ALD
- 1 cycle of ALD has conversion ~20% and selectivity ~99%
- Conventional method has conversion ~8% and selectivity ~17%
- Feeding CO_2 helps stability but does NOT facilitate dry reforming

Notations

Sample	BET S.A (m^2/g)	Metal Loading (wt%)	Cobalt Coverages (Co/m^2)
SiO_2	472	0	0
1Co-SiO_2	457	1.2	2.7×10^{17}
5Co-SiO_2	419	5.5	1.3×10^{18}
10Co-SiO_2	343	12.1	3.6×10^{18}
impCo-SiO_2	453	1	2.3×10^{17}
1Co-Al_2O_3	102	0.9	9.0×10^{17}
1Co-$MgAl_2O_4$	136	1	7.5×10^{17}

Tab. 1 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.**

ALD Setup

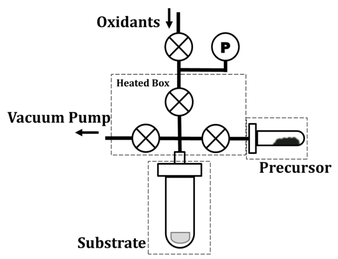
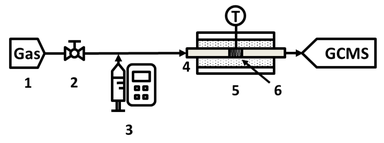


Fig. 2 Schematic diagram of the static ALD set up.

Reactor: Static ALD setup
Dosing Temp: 523K
Precursor Pressure: 5 Torr
Oxidizing Temp: 773K

Flow Reactor



1 Carrier gas feed
2 Pressure-reducing valve
3 Syringe pump unit
4 Continuous flow reactor
5 Furnace
6 Catalyst

Fig. 3 Schematic diagram of the continuous flow reactor.

Reactor: continuous flow reactor.
Condition: 923K and 1 bar
Space Time: 1 $h \cdot g_{cat} \cdot mL^{-1}$
Feeds: $CO_2 : C_2H_6 : He = 1 : 1 : 4$

Characterization

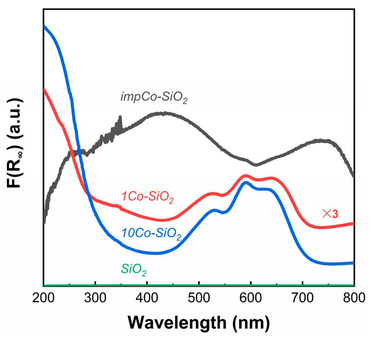


Fig. 4 UV–Vis diffuse reflectance spectra of *SiO_2*, *1Co-SiO_2*, *10Co-SiO_2*, and *impCo-SiO_2*.

- 530, 590, 640 nm → isolated Co^{2+}
- 430, 750 nm → Co_3O_4
- ALD method → isolate Co^{2+}

Reactivity Study

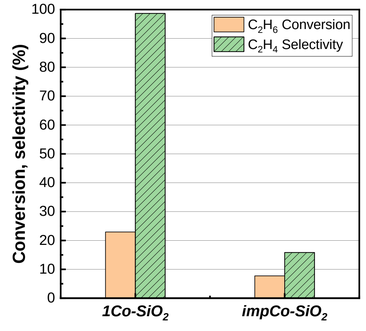


Fig. 5 Comparison of *1Co-SiO_2* and *impCo-SiO_2* for the reaction of CO_2 and C_2H_6 at 1 h. Reaction conditions were: T = 923 K; CO_2:C_2H_6:He = 1:1:4; space time = 1 $h \cdot g_{cat} \cdot mL^{-1}$.

- *1Co-SiO_2* shows **2x** higher conversion and **5x** higher selectivity than *impCo-SiO_2*.

Stability

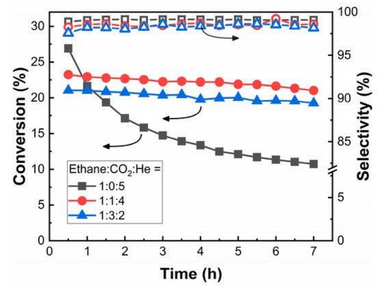


Fig. 6 Effect of CO_2 on ethane conversion and selectivity to ethylene over *1Co-SiO_2*: C_2H_6:CO_2:He = 1:0:5 (■, □); =1:1:4 (●, ○); and = 1:3:2 (▲, △).

Effect of ALD cycles

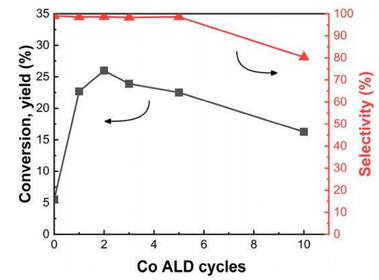


Fig. 7 Conversion (■) and selectivity (▲) on SiO_2-supported catalysts as a function of the number of Co ALD cycles.

Support effect

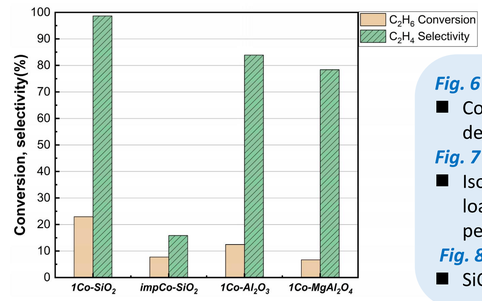


Fig. 8 Conversions and selectivities for *1Co-SiO_2*, *impCo-SiO_2*, *1Co-Al_2O_3*, and *1Co-$MgAl_2O_4$*.

Fig. 6
- Co-feed CO_2 suppresses deactivation

Fig. 7
- Isolated Co^{2+} is important, more loading results in worse performance

Fig. 8
- SiO_2 could be the best support

Conclusions

- We prepared isolated-site, Co catalysts on SiO_2, Al_2O_3, and $MgAl_2O_4$ supports by 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.

References

1. Huang, R.; Cheng, Y.; Ji, Y.; Gorte, R.J. Atomic Layer Deposition for Preparing Isolated Co Sites on SiO2 for Ethane Dehydrogenation Catalysis. *Nanomaterials* **2020**, *10*, 244,
2. Wang, Cong, "Selective Conversion of Biomass Model Compounds Using Promoted Metal Catalysts" (2019). *Dissertations available from ProQuest*. AAI13898839.

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