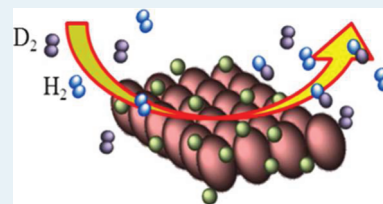


Fischer–Tropsch Synthesis: Investigation of the Partitioning of Dissociated H₂ and D₂ on Activated Cobalt Catalysts

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ABSTRACT: To define the mechanism of the Fischer–Tropsch synthesis, numerous experiments probed the rate-determining step by performing isotopic experiments during CO hydrogenation. The aim of this work was to determine if there is an isotopic effect for adsorption for either hydrogen or deuterium on the cobalt metal surface of a Fischer–Tropsch synthesis catalyst. If a partitioning effect is noticed, there is a possibility for this to interfere with measurements of the inverse kinetic isotopic effect during CO hydrogenation. In this investigation, the partitioning of hydrogen and deuterium on an activated cobalt catalyst was examined using temperature programmed desorption and gas chromatography. The results indicate that there may be hydrogen–deuterium exchange with the support, but there is no significant isotopic partitioning on the cobalt metal surface.



KEYWORDS: Fischer–Tropsch synthesis, H–D isotope effect, inverse kinetic isotope effect, cobalt catalyst

1. INTRODUCTION

Fischer–Tropsch (FT) synthesis is a complex catalytic process by which H₂ and CO are converted into hydrocarbons and oxygenates.¹ The mechanism occurring on the catalyst is still under scrutiny. Although some authors prefer a CH₂ insertion mechanism² and suggest that addition to the chain is the rate-determining step, others claim a CO insertion mechanism and argue that the rate-determining step is where CO insertion occurs.³ Controversy has also arisen where some researchers have argued that if CH₂ insertion was the favored mechanism, then no oxygenated material could be produced. From this controversy, Dry et al.⁴ argued for a mechanism that involves both CH₂ and CO as active surface intermediates. Since the rate-determining step still remains a point of contention, a number of H₂/D₂ studies have been performed, but, unfortunately, with no clear conclusion. Most of these studies have examined replacing H₂ with D₂ in the syngas over Ru,^{5,6} Co,^{7–9} and Fe^{7,9} catalysts during FT synthesis. Briefly, in switching from H₂ to D₂, the rate of CO conversion increased, suggesting an overall inverse kinetic isotope effect. This contribution examines whether preferential partitioning of either H or D on the cobalt metal surface occurs such that it may influence data when measuring the kinetic isotope effect. Moreover, by examining both unsupported cobalt and alumina or silica supported cobalt catalyst, the potential for hydrogen exchange with the support influencing the results was also examined.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. A 25% Co/Al₂O₃ catalyst was prepared by a slurry impregnation method using Catalox 150 (high purity γ -alumina, \sim 150 m²/g) as the support. Al₂O₃ was calcined for 4 h at 673 K before impregnation and then cooled to room temperature. Co(NO₃)₂·6H₂O (99.9% purity) was used as the precursor for Co. In this catalyst preparation method, which follows a Sasol patent,¹⁰ the ratio of the volume of solution used

to the weight of alumina was 1:1, such that \sim 2.5 times the pore volume of the loading solution was used. Two impregnation steps were carried out, each to load about 12.5% of Co by weight. Between steps, the catalyst was dried under vacuum using a rotary evaporator at 353 K, and the temperature was slowly increased to 368 K. After the second impregnation/drying step, the catalyst was calcined under air flow at 623 K for 4 h.

The 15% Co/SiO₂ catalyst was also prepared using the aqueous slurry phase impregnation method, with cobalt nitrate as the cobalt precursor. The support was PQ-SiO₂ CS-2133, surface area about 352 m²/g). The catalyst was calcined in flowing air or flowing 5% nitric oxide^{11–14} in nitrogen at a rate of 1 L/min for 4 h at 623 K. The NO-calcined catalyst was used for isotopic studies, since the Co particles were expected to be smaller and one of the aims of the paper is to explore the possibility of hydrogen exchange with the support.

2.2. BET Surface Area and Porosity Measurements. The surface area, pore volume, and average pore radius of the calcined catalyst were measured by BET using a Micromeritics Tri-Star 3000 gas adsorption analyzer system. Approximately 0.35 g of sample was weighed and loaded into a 3/8 in. o.d. sample tube. Nitrogen was used as the adsorption gas, and sample analysis was performed at the boiling temperature of liquid nitrogen. Prior to the measurement, the sample was slowly ramped to 433 K and evacuated overnight to approximately 6.7 Pa.

2.3. Temperature Programmed Reduction. Temperature programmed reduction (TPR) profiles were recorded using a Zeton-Altamira AMI-200 unit, which makes use of a TCD detector. The sample was first ramped to 623 K in pure Ar to remove any residual H₂O from the sample prior to cooling to 323 K to begin the TPR. The test was performed using a 10% H₂/Ar

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mixture referenced to Ar at a flow rate of 30 mL/min. The sample was heated to 1373 K at a ramp rate of 10 K/min.

2.4. Hydrogen Chemisorption by TPD. Hydrogen chemisorption was conducted using a temperature-programmed desorption (TPD) technique with the Zeton-Altamira AML-200 instrument. Each catalyst sample was (~ 0.22 g) activated in a flow of 10 mL/min of H_2 mixed with 20 mL/min of argon at 553 K for 10 h and then cooled under flowing H_2 to 373 K. The sample was held at 373 K under flowing argon to remove and prevent adsorption of weakly bound species prior to increasing the temperature slowly to 623 K, the temperature at which activation of the catalyst was previously carried out. The TPD spectrum was integrated, and the number of moles of desorbed hydrogen determined by comparing its area to the areas of calibrated hydrogen pulses. The loop volume was first determined by establishing a calibration curve with syringe injections of hydrogen into a helium flow. Dispersion calculations were based on the assumption of a 1:1 H/Co stoichiometric ratio and a spherical cobalt cluster morphology. After TPD of hydrogen, the sample was reoxidized at 623 K using pulses of oxygen. The percentage of reduction was calculated by assuming that the metal reoxidized to Co_3O_4 .

2.5. Reactor System. A plug flow reactor with four mass flow controllers (MFC) was used at atmospheric pressure. The reduction gases H_2 , D_2 , or the H_2/D_2 mixture passed through a common MFC to obtain stable flow with little to no interference by switching gases. A digital soap meter was set after the plug flow reactor to periodically verify the flow rates.

2.6. Reduction and Desorption Using the H_2/D_2 Mixture. Thirty grams of the 25% Co/Al_2O_3 catalyst, 15 g of CoO , or 15 g of the 15% Co/SiO_2 catalyst was loaded into the plug flow reactor, then three separate experimental approaches were set up to run for each catalyst:

- (1) The cobalt catalyst was reduced under 15 sccm of the 1:1 H_2/D_2 mixture. The catalyst bed was heated at 1 K/min to 623 K and held for 48 h. The system was then cooled to 373 at 1 K/min, where neon was introduced, and the fixed-bed system was held at this condition for 1 h. The fixed-bed system was then cooled at 1 K/min to 373 K. The reactor was then heated to 673 K under 15 mL/min of neon so that the hydrogen/deuterium remaining on the catalyst desorbed and was collected into a hydrogen-specific gas bag using neon as the carrier gas.
- (2) The cobalt catalyst was heated to 623 K and held for 44 h under 15 sccm of H_2 flow. After 44 h of flow, an uninterrupted switch occurred to allow the 1:1 H_2/D_2 to flow for 4 h at the same temperature. The system was then cooled to 373 at 1 K/min, where neon was introduced, and the fixed-bed system was held at this condition for 1 h. The reactor was heated to 673 K under 15 mL/min of neon so that the hydrogen/deuterium remaining on the catalyst desorbed and was collected into a hydrogen-specific gas bag using neon as the carrier gas.
- (3) The cobalt catalyst was heated to 623 K and held for 44 h under 15 mL/min of D_2 flow. After the 44 h period, the D_2 flow was terminated, and the H_2/D_2 mixture was introduced at the same flow rate of 15 sccm. The system was then cooled to 373 at 1 K/min, where neon was introduced, and the fixed-bed system was held at this condition for 1 h. The reactor was heated to 623 K under 15 mL/min of neon to desorb the hydrogen/deuterium

remaining on the catalyst, which was collected in the hydrogen-specific gas bag using neon as the carrier gas.

Each experimental approach was repeated for each catalyst to ensure the repeatability of the experimental data.

2.7. Instrumentation. Each gas sample was manually injected into an Agilent 6890 cryogenic GC-TCD containing a 180 m mol sieve column. The temperature was held isothermal at 193 K, with a carrier gas flow of 4 mL/min. Neon was chosen as the carrier gas because of the inability to adequately separate the H_2/D_2 mixture with Ar or N_2 , and the poor thermal conductivity difference between H_2 and He.

Four-point calibration curves were created for H_2 , HD, and D_2 using a mixed standard bought from Cambridge Isotope Laboratories. Since a mixed standard was used, the relative ratios obtained were precise. Samples ranging from 5 to 100 μL were manually injected using a 100 μL syringe. Several injections were made for each to obtain a line with a correlation coefficient above 0.99 (Figure 1a–c). The gas bag obtained from the TPD mainly contained neon; therefore, a 1 mL syringe was used for multiple 500 μL injections of sample obtained from the CoO , 25% Co/Al_2O_3 , and the 15% Co/SiO_2 samples. Since neon was used during the TPD and also used as the carrier gas for the GC, there should be no contribution by neon in the TCD signal (Figure 2).

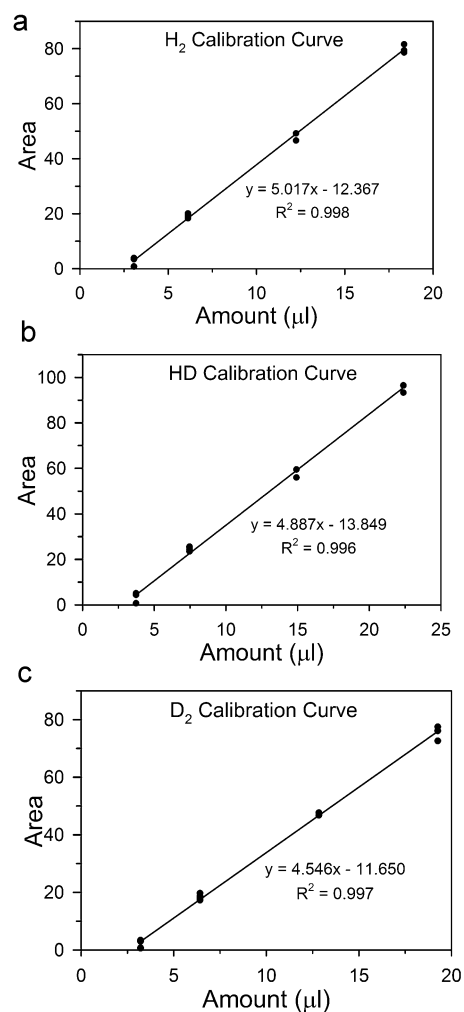


Figure 1. Calibration curves for (a) H_2 , (b) HD, and (c) D_2 built from injections of the $H_2/HD/D_2$ standard mixture.

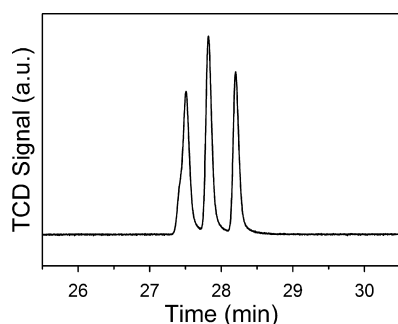


Figure 2. A standard TCD chromatogram of the standard mixture.

3. RESULTS AND DISCUSSION

3.1. Surface area Measurements. The catalyst was prepared by a slurry impregnation, as opposed to incipient wetness impregnation,¹⁵ to obtain a cluster size of ~ 10 nm and a narrow range of the catalyst particle size. The BET surface area, measured by adsorption of N_2 , for the 25% Co/ Al_2O_3 catalyst was $103 \text{ m}^2/\text{g}$. A 25% Co metal loading by weight percent is equivalent to 34% Co_3O_4 . If Al_2O_3 is the only contributor to the surface area, then the surface area should be close to $0.66 \times 150 = 99 \text{ m}^2/\text{g}$. The actual surface area measurement is approximately the calculated value, suggesting that pore blocking should not be a significant problem. The porosity results from the BJH adsorption tests (Table 1) of this catalyst were in agreement with the previous report.¹⁵

Table 1. Summary of BET Surface Area and Porosity Measurements

catalyst i.d.	BET SA (m^2/g)	av single-point pore volume (mL/g)	av pore radius (nm)
Catalox 150 $\gamma\text{-Al}_2\text{O}_3$	149	0.493	6.9
15% Co/PQ- SiO_2 , calcd in NO	298	1.06	7.1
15% Co/PQ- SiO_2 , calcd in air	263	1.04	7.7
25% Co/ Al_2O_3	103	0.258	5.0

For the case of the SiO_2 -supported cobalt catalysts, if SiO_2 is the sole contributor to the surface area, the value should be close to $0.80 \times 352 \text{ m}^2/\text{g} = 282 \text{ m}^2/\text{g}$. That the surface area of the air-calcined catalyst is less than this ($263 \text{ m}^2/\text{g}$) suggests some pore blocking by larger particles. As shown in Table 1, this was not observed for the case of the catalyst calcined in nitric oxide, where smaller particles, expected to alleviate pore blocking, were obtained.

3.2. Reduction/TPD. The TPR from Jacobs et al.¹⁶ for the 25% Co/ Al_2O_3 displays a two-step reduction of Co_3O_4 particles (Figure 3a), a sharp peak around 600 K (Co_3O_4 to CoO), and a broader peak ranging from 700 to 1050 K (CoO to Co^0). By conducting two separate TPR experiments, one directly after calcination, the other following a 10 h reduction at 623 K, it was evident that a small fraction of the Co surface species interacting with the support remains unreduced following the standard 10 h H_2 activation. The reduction of Co_3O_4 was completed at this temperature; therefore, the focus was on the reduction of CoO species interacting with the support to Co^0 . For this specific catalyst, 42% was found to be reduced after standard 10 h activation, as measured by pulsed reoxidation.¹⁶ Considering 30 g of catalyst was loaded into the reactor, we used a 48 h activation at 623 K to ensure that a significant fraction (e.g., >42%) was

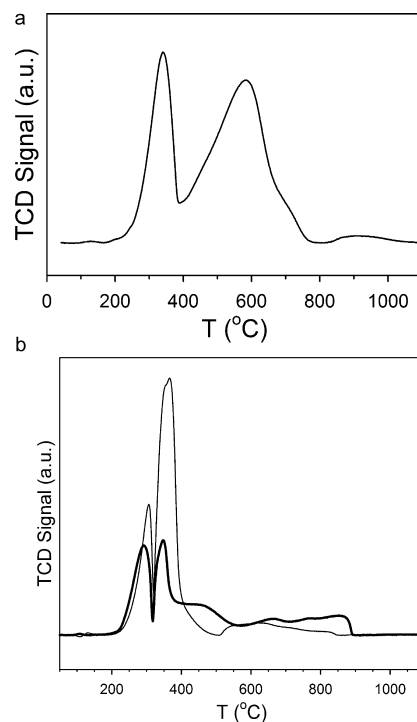


Figure 3. (a) TPR profile of 25%Co/ Al_2O_3 . (b) TPR profiles of 15% Co/ SiO_2 catalysts, including catalysts calcined in air (light line) or nitric (bold line) oxide.

reduced. The reduction temperature was kept below 700 K to prevent sintering of cobalt. On the basis of the calculations given from reference 16, Table 2 summarizes the chemisorption results

Table 2. Hydrogen Chemisorption by TPD with Pulse Reoxidation after Reduction for 10 h at 623 K

catalyst ID	H_2 evolved ($\mu\text{mol}/\text{g}_{\text{cat}}$)		uncorr diam (nm)	O_2 uptake ($\mu\text{mol}/\text{g}_{\text{cat}}$)		corr % disp	corr diam (nm)
	uncorr % disp	% reduced					
25% Co/ Al_2O_3	89.2	4.2	24.5	1058	37	11.2	9.2
15% Co/PQ- SiO_2 , calcd in NO	39.8	3.1	33.0	791	56	5.3	19.2
15% Co/PQ- SiO_2 , calcd in air	38.0	3.0	34.5	1436	85	2.7	38.5

and shows that a satisfactory active site density was obtained for carrying out the isotopic studies. The TPD shape was asymmetric, with the first and main desorption peak maxima occurring between 483 and 493 K; therefore, the hydrogen is deemed to exhibit suitable chemisorption strength as to be relevant to FT catalysis. The hydrogen desorbed above this temperature is also chemisorbed with sufficient strength as to be pertinent to what is on the surface at FT temperatures.

The reduction profiles of the 15% Co/ SiO_2 catalyst are shown in Figure 3b, with the light line being that of a standard air calcined catalyst and the bold line corresponding to the catalyst calcined in nitric oxide. For standard air-calcined catalysts, SiO_2 is known to exhibit weak interactions with cobalt oxides, leading to larger particles than those observed on strongly interacting Al_2O_3 .¹⁶ In agreement with this, the profile of the air-calcined catalyst displays primarily two rather sharp peaks, with the first

one corresponding to the reduction of Co_3O_4 to CoO and the second being larger particles of CoO to Co^0 , very much like the reduction of bulk Co_3O_4 .^{15,16} On the other hand, the nitric oxide calcination lends itself to producing smaller particles,^{11–14} which interact more significantly with the support, such that the profile displays a decrease in the sharp, low temperature peak (i.e., larger particles) and a significant increase in peaks corresponding to smaller, more strongly interacting particles. The H_2 chemisorption/pulse reoxidation results confirm that smaller, less reducible particles are formed after activating the nitric oxide calcined catalyst. Since one goal of the paper is to examine the possibility of hydrogen exchange with the support, it is of interest to use a catalyst with smaller particles with greater interaction with the support. Thus, the catalyst calcined in nitric oxide was selected for the present study.

3.3. Competitive Desorption. After reduction, the plug flow reactor was cooled to 373 K while under the H_2/D_2 mixture to allow for the H/D atoms to be chemisorbed to the cobalt surface before starting the TPD. The reactor was then held at 373 K with a neon flow to prevent the retention of physisorbed or weakly bound hydrogen or deuterium. The temperature was then increased to desorb the chemisorbed H/D and sweep the evolved H_2 , D_2 , and HD into the sampling bag. The neon flow was decreased during this time to keep hydrogen isotopes in the bag concentrated enough to allow for sampling, especially in the case of the desorbed gas obtained from the reduced CoO . Reduced CoO serves as a reference, since the cobalt particles are not supported by a carrier.

Table 3. The Isotope Effect for the Reduced CoO Catalyst

CoO			
injection	approach 1	approach 3	
1	1.04	0.98	
2	1.04	0.99	
3	1.02	0.98	
4	1.02	0.99	

Table 4. The Isotope Effect for the Reduced 25% $\text{Co}/\text{Al}_2\text{O}_3$ Catalyst

25% $\text{Co}/\text{Al}_2\text{O}_3$			
injection	approach 1	approach 2	approach 3
1	1.03	1.16	0.93
2	1.04	1.16	0.93
3	1.05	1.13	0.90
4	1.01	1.12	0.87

Table 5. The Isotope Effect for the Reduced 15% Co/Si Catalyst

15% $\text{Co}/\text{Al}_2\text{O}_3$			
injection	approach 1	approach 2	approach 3
1	0.98	1.05	0.94
2	0.99	1.05	0.96
3	1.00	1.06	0.96
4	1.00	1.05	0.96

The H/D ratios presented in Tables 3–5 were calculated from the amounts determined for each injection on the basis of the calibration curves:

$$\text{H}_2 = y = 5.02x - 12.37$$

$$\text{HD} = y = 4.88x - 13.85$$

$$\text{D}_2 = y = 4.55x - 11.65$$

where y is the peak area and x is the calculated amount in microliters. Once the amounts are obtained, the H/D ratio is calculated by

$$\text{h/d ratio} = \frac{2(3.4 \mu\text{L of H}_2) + 4.1 \mu\text{L of HD}}{2(3.2 \mu\text{L of D}_2) + 4.1 \mu\text{L of HD}}$$

Therefore, if an inverse isotopic effect is obtained, the ratio would be less than 1 and vice versa.

The total amount of neon collected in the bag was 225 mL, on the basis of a flow of 5 mL/min and a time-on-stream of 45 min during the desorption process. Taking Table 3, injection 1, as an example, subtracting the amounts of H_2 (3.4 μL), HD (4.1 μL), and D_2 (3.2 μL) obtained from each calibration curve from the total injection volume (0.5 mL) and the ratio of H–D/Ne (3.0×10^{-2}) from the 0.5 mL injection, if the total amount of gas in the bag was 225 mL, then

$$\text{Ne total} = 225 \text{ mL} - (225 \times 3.0 \times 10^{-2}) = 218.6 \text{ mL}$$

The H_2 , HD, and D_2 amounts can be found from their percentages in Table 3 injection 1 from the remaining volume in the bag.

$$\text{H}_2 = (225 \text{ mL} - 218.6 \text{ mL}) \times 0.3 = 1.9 \text{ mL}$$

$$\text{HD} = (225 \text{ mL} - 218.6 \text{ mL}) \times 0.4 = 2.6 \text{ mL}$$

$$\text{D}_2 = (225 \text{ mL} - 218.6 \text{ mL}) \times 0.3 = 1.8 \text{ mL}$$

From here, given the following equation based on ref 16, the H–D uptake can be calculated.

$$\begin{aligned} &\text{H–D uptake (moles/g}_{\text{cat}}) \\ &= \text{calibration value (sample bag volume)} \\ &\quad / (\text{catalyst weight} \times 24.5 \text{ L/mole}) \end{aligned}$$

The H_2 is 3.1 $\mu\text{mol/g}_{\text{cat}}$, HD is 4.2 $\mu\text{mol/g}_{\text{cat}}$, D_2 is 2.9 $\mu\text{mol/g}_{\text{cat}}$, and the total H–D adsorbed is 10.2 $\mu\text{mol/g}_{\text{cat}}$. The H–D uptake value was expected to be low because of the low surface area for CoO before reduction. CoO was set as a control for the different experimental approaches to obtain, if any, isotopic preferences on the reduced metal surface. The first approach, a 48 h equal molar competitive reduction, led to no isotopic preference on the metal surface. The bag, containing the H–D atoms stripped from the reduced cobalt metal, was then taken from the system after the TPD. Several injections were made to ensure adequate reproducibility. As shown in Table 3, approach 1, the standard deviation was low for all the injections. This approach was repeated three times for the CoO to ensure the results were consistent, as shown in Table 3, approach 1. Duplicating this approach confirmed the initial results, where no isotopic preference was noted, and ensured the fixed-bed system and analytical setup were sound.

The reason for the different experimental approaches was to mimic the studies presented earlier,^{5–9} in an attempt to better understand the NKIE observed during CO hydrogenation. The first approach mentioned displayed results for a competitive reduction only; however, many of the references mentioned did not reduce the catalyst in a competitive manner. Two more

approaches were then designed to parallel the change over from H₂ to D₂ and vice versa. Again, reduced CoO was used as a control in an attempt to learn if preferential partitioning occurred for the metal surface only. Once the cobalt surface was completely covered with H or D atoms following a 44 h reduction at 623 K, the 4 h competitive reduction occurred. The 4 h competitive reduction at 623K with a 15 sccm flow allowed for at least 24 reactor turnovers. Reduced CoO displayed no isotopic preference for H or D, as displayed in Table 3, approach 3.

The next step was to include actual FT cobalt supported catalysts, in which two common supports for cobalt catalysts are SiO₂ and Al₂O₃. The approach was to run all three experimental procedures for each of the supported catalysts, and if a preference were observed, it would be due to exchange with the support. Since the reduced CoO displayed no partitioning preference for any of the approaches, the difference would be caused by hydrogen exchange with the surface of the support. The first approach did not show any partitioning preference for any of the catalysts. The second and third approach, however, displayed a small preference. The bias for both of the supported catalysts tended toward the gas used during the 44 h reduction period. The second experimental approach was to reduce the supported catalysts under H₂ for 44 h, and both catalysts resulted in an H/D ratio >1 (Tables 4 and 5, approach 2), whereas when the same catalysts were reduced under D₂ for 44 h, the H/D was <1 (Tables 4 and 5, approach 3).

4. CONCLUSIONS

From the initial 48 h competitive reduction in a H₂/D₂ mixture, no isotopic preference was observed after carrying out TPD on the activated CoO, 25%Co/Al₂O₃, and the 15% Co/SiO₂ catalysts. Understanding that no preferential partitioning of H or D occurs for adsorption of a 50%/50% H₂/D₂ mixture onto the surface of cobalt, the inverse kinetic isotope effect found during CO hydrogenation will not be affected by preferential isotopic partitioning on the metal surface. However, a slight isotopic preference for the 25% Co/Al₂O₃ and 15% Co/SiO₂ catalysts was identified, depending on which gas was used during the 44 h reduction, H₂ or D₂, prior to the 4 h treatment in H₂/D₂. Given that the control experiment of Co revealed no isotopic preference, and that the number of reactor turnovers was sufficient, this slight isotopic preference must be caused by retention of H or D on the Al₂O₃ and SiO₂ supports. This effect, whereby a slight positive isotopic effect was observed when the first treatment occurred using H₂ and a slight negative effect observed with D₂, could be caused by a minor H/D exchange with the hydroxyl groups on the support.¹⁷ Since the isotopic preference is small and seen only on the supported cobalt catalysts, it seems that neither preferential partitioning of H or D on the surface of cobalt nor hydrogen exchange with the alumina support contributes significantly to measurements of the negative kinetic isotopic effect during CO hydrogenation. On the latter point, further experiments are needed to verify this.

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Notes

The authors declare no competing financial interest.

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