



# Effects of Lewis acidity of metal oxide promoters on the activity and selectivity of Co-based Fischer–Tropsch synthesis catalysts



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## ARTICLE INFO

### Article history:

Received 29 January 2016

Revised 18 March 2016

Accepted 19 March 2016

Available online 31 March 2016

### Keywords:

Fischer–Tropsch synthesis

Heterogeneous catalysis

Cobalt

Promotion

Lewis acidity

## ABSTRACT

Metal oxides of Ce, Gd, La, Mn, and Zr were investigated as promoters for improving the activity and selectivity of Co-based FTS catalysts. The extent to which these promoters decrease the selectivity toward CH<sub>4</sub> and increase the selectivity toward C<sub>5+</sub> hydrocarbons was found to depend on both the loading and the composition of the oxide promoter. Elemental mapping by STEM–EDS revealed that the propensity for a given metal oxide to associate with Co affects the sensitivity of the product distribution to changes in promoter loading. For all promoters, a sufficiently high loading resulted in the product distributions becoming insensitive to further increases in promoter loading, very likely due to the formation of a half monolayer of promoter oxide over the Co surface. Simulations suggest that the fraction of Co active sites that are adjacent to the promoter moieties approaches unity at this degree of coverage. The oxidation state of the promoter metal cation under reaction conditions, determined by in situ XANES measurements, was used to calculate relative Lewis acidity of the promoter metal cation. A strong positive correlation was found between the C<sub>5+</sub> product selectivity and the Lewis acidity of the promoter metal cations, suggesting that the promotional effects are a consequence of Lewis acid–base interactions between the reaction intermediates and the promoter metal cations. Rate data obtained at different pressures were used to estimate the apparent rate coefficient and the CO adsorption constant appearing in the Langmuir–Hinshelwood expression that describes the CO consumption kinetics for both unpromoted and the metal oxide-promoted catalysts. Both parameters exhibited positive correlations with the promoter Lewis acidity. These results are consistent with the hypothesis that the metal cations of the promoter act as Lewis acids that interact with the O atom of adsorbed CO to facilitate CO adsorption and dissociation.

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## 1. Introduction

Fischer–Tropsch synthesis (FTS) over Co-based catalysts offers a means for converting synthesis gas, a mixture of CO and H<sub>2</sub> produced from gasification of biomass, coal, and natural gas, to transportation fuels. Since the products of FTS over metallic Co contain a significant portion of CH<sub>4</sub> and light alkanes and alkenes, considerable effort has been devoted toward identifying and optimizing promoters that reduce the formation of light hydrocarbons and enhance the formation of C<sub>5+</sub> hydrocarbons, since the latter products can be used to produce transportation fuels [1]. It has been demonstrated that the desired goal can be met using metal oxide promoters [2,3]. For example, work by de Jong et al. [4,5] and Weckhuysen et al. [6–10] has reported that promotion with MnO

enhances the rate of CO consumption and C<sub>5+</sub> selectivity. Studies by these authors and others have shown that these effects are a consequence of good contact between metallic Co and MnO [11,12]. Similar findings have also been reported for ZrO<sub>2</sub> [13–16] and for oxides of Ce [17,18], Gd [19], La [20–23], Mo [24,25], and Ti [26–28]. However, despite the abundance work on metal oxide promotion, there have not been extensive efforts to compare promoter elements directly and rationalize any differences in terms of periodic trends.

It has been reported that the electronic and catalytic properties of metal sites located at the interface between metal nanoparticles and an oxide support may differ from those of sites located farther from the oxide support due to the local transfer of charge between metal atoms of the nanoparticle and the oxide in the region of the metal–metal oxide interface [29,30]. A similar effect has also been proposed for metal sites located at the interface between a metal oxide promoter and a metal nanoparticle. For example, the rate of CO methanation over Pd has been observed to be enhanced

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when the catalyst is promoted with  $\text{La}_2\text{O}_3$  moieties [31]. Similarly, the rate of CO hydrogenation over Rh has been found to increase when Rh nanoparticles are partially covered by metal oxides [32,33]. These findings have led to the hypothesis that sites located at the metal–metal oxide interface in Co-based FTS catalysts facilitate cleavage of the C–O bond, a necessary step in the hydrogenation of CO to hydrocarbons [34]. Specifically, it has been proposed that metal cations of the promoter located at the metal–metal oxide interface act as Lewis acids that interact with the O atom of CO bound through the C atom to the metal nanoparticle, thereby weakening the C–O bond and facilitating its dissociation either directly or following partial hydrogenation [35]. This reasoning suggests that the magnitude of metal oxide-based promotional effects should be related to the Lewis acidity of the promoter. Recently, we have reported the existence of correlations between the  $\text{C}_{5+}$  selectivity of Co-based FTS catalysts and the Lewis acidity of promoter metal cations [36,37]. This line of reasoning is also supported by the work of Prieto et al. who have reported a relationship between both the FTS turnover frequency and  $\text{C}_{13+}$  selectivity and the Lewis acidity of oxide supports [38]. These cited results identify the role of Lewis acidity in understanding promotional effects, but the importance of interface formation between the Co and the metal oxide promoter and the effects of Lewis acidity on the rate law parameters have not been clearly defined yet.

The aim of the present study was to compare and contrast the effects of metal oxide promoters ( $\text{CeO}_x$ ,  $\text{GdO}_x$ ,  $\text{LaO}_x$ ,  $\text{MnO}_x$ , and  $\text{ZrO}_x$ ) on the catalytic properties of Co-based FTS catalysts. Of particular interest was the extent to which each of these oxides associates with Co and the dependence of promotion effects on promoter composition. Co/ $\text{SiO}_2$  promoted with increasing levels of the metal oxide promoter was prepared and their performance was investigated at various temperatures, pressures, and space velocities. The distribution of the oxide on the support and the degree of contact between the oxide and the dispersed Co nanoparticles were determined from STEM–EDS elemental maps. These measurements revealed that the degree of Co–promoter interaction is a strong function of the metal oxide composition and loading. Recognizing this, efforts were undertaken to determine the effects of promoter composition on the rate parameters governing the rate of CO consumption using catalysts with nearly equivalent levels of contact between the metallic Co and the promoter. This work strongly suggests that the formation of an interface between the Co and the promoter oxide is responsible for the promotional effects. The active sites in the promoted catalysts are presumed to occur at the metal–metal oxide interface, and evidence is found that such sites enhance CO adsorption and dissociation of the C–O bond. Moreover, the strength of these promotional effects is found to correlate with the Lewis acidity of the promoter, supporting the hypothesis that Lewis acid–base interactions are responsible for metal oxide promotion of FTS on Co.

## 2. Experimental section

### 2.1. Catalyst synthesis

Catalysts were prepared following the procedures described previously [39]. For the unpromoted catalyst, incipient wetness impregnation was used to deposit  $\text{Co}(\text{NO}_3)_2$  (Sigma–Aldrich, 99.999% purity) onto porous  $\text{SiO}_2$  (PQ Corporation, CS-2129). The promoted catalysts were prepared by co-impregnation with an aqueous solution of  $\text{Co}(\text{NO}_3)_2$  and the precursor for the promoter element. For this work, the promoted catalysts were prepared using either Mn acetate or nitrate salts of Ce, Gd, La, or Zr (Sigma–Aldrich, 99.999% purity).  $\text{Mn}(\text{CH}_3\text{CO}_2)_2$  was used because this precursor has previously been shown to yield the desired cat-

alyst structure [40]. When using precursors with limited solubility, multiple impregnation steps were used to achieve the desired metal loadings. The solvent from the previous impregnation step was allowed to evaporate at ambient conditions prior to conducting the next impregnation step. After the metal precursors were deposited onto the  $\text{SiO}_2$ , the sample was dried overnight at ambient temperature and then heated at 5 K/min to 723 K under flowing  $\text{H}_2$  (100 mL/min) and held at 723 K for 2 h. After this step, the reduced catalyst was cooled to ambient temperature under flowing He (100 mL/min). The catalyst was then exposed to 500 ppm  $\text{O}_2$  (100 mL/min) to passivate the Co.

### 2.2. Temperature-programmed reduction

The reduction profiles for the passivated catalysts were obtained by heating the samples from ambient temperature to 850 K at 5 K/min in a quartz tube reactor under flowing 1%  $\text{H}_2$ , 1% Ar, and 98% He (30 mL/min). The composition of the reactor effluent was monitored by an MKS Minilab quadrupole mass spectrometer. Corrections for variations in the reactor effluent flow rate were made using the Ar signal as an internal standard.

### 2.3. $\text{O}_2$ titration

$\text{O}_2$  titrations of the reduced catalysts were performed using a Micromeritics AutoChem II 2920 instrument. In a typical measurement, a sample of passivated catalyst was loaded into a quartz U-tube, which was then inserted into the instrument. The sample was reduced by heating it at 5 K/min to 723 K under flowing  $\text{H}_2$  (100 mL/min) and then holding it at 723 K for 2 h. The sample tube was subsequently flushed with He (100 mL/min) until the thermal conductivity detector (TCD) in the instrument achieved a stable baseline signal. Pulses of 20%  $\text{O}_2$  in He (3.1  $\mu\text{mol O}_2/\text{pulse}$ ) were then injected into the He carrier gas flow every 6 min in order to titrate the reduced catalyst. The final  $\text{O}_2$  uptake was determined by the number of pulses required to achieve TCD peaks of equal area.

### 2.4. $\text{H}_2$ chemisorption

Static  $\text{H}_2$  chemisorption was performed using a Micromeritics 3Flex surface characterization analyzer. Passivated catalyst samples were loaded into a quartz U-tube and then reduced by heating at 5 K/min to 723 K under flowing  $\text{H}_2$  and holding at 723 K for 2 h. The sample tube was then evacuated for 2 h at 723 K and cooled to 373 K. An  $\text{H}_2$  adsorption isotherm was then collected by dosing a fixed quantity of  $\text{H}_2$  into the sample tube and allowing the pressure to equilibrate. Based on work by Reuel and Bartholomew [41], it was assumed that the total  $\text{H}_2$  uptake from a single isotherm collected at 373 K corresponds most closely to a 1/1 H/Co adsorption stoichiometry, neglecting any  $\text{H}_2$  spillover onto the promoter oxide. As described in the Results section, severe  $\text{H}_2$  spillover occurred on the lanthanide-promoted catalysts, which prevented the  $\text{H}_2$  uptake data from being used to determine the quantity of surface Co metal for these catalysts.

### 2.5. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) measurements were conducted at beamlines 5-BM (DND-CAT) and 10-BM (MRCAT) [42] at the Advanced Photon Source synchrotron at Argonne National Laboratory. All spectra were acquired in transmission mode with the energy of the incident X-rays controlled by a Si(111) monochromator. The samples were placed between two gas ionization detectors to measure the absorption of X-rays, and a reference metal foil was placed between the second and a third detector

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