

The Effect of Different Iron Oxide Precursors on Catalytic Activity of $\text{FeO}_x/\text{CeO}_2$

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Abstract

Studies have been done on different metal oxide catalysts such as copper on CeO_2 support, however there are no current attempts for testing a cerium supported iron oxide catalyst using a nitrate and sulfate precursor. In this study, we will be testing the effects of using different precursors to synthesize iron oxide on cerium oxide support ($\text{FeO}_x/\text{CeO}_2$). Our goal is to prove that using different precursors yield a different catalytic activity and to determine whether the nitrate or sulfate precursor yields a more efficient $\text{FeO}_x/\text{CeO}_2$ catalyst. This can lead to further study of more cost and energy efficient precursors for other metal oxides. The results showed that the nitrate precursor had more catalytic activity than its sulfate counterpart in the 10 wt% loading of $\text{FeO}_x/\text{CeO}_2$.

Keywords: catalysts, precursors, catalytic activity, iron oxide, cerium oxide, Raman spectroscopy, NO reduction

1. Introduction

Supported transition metal or metal oxide materials are being used in several chemical reactions, due to low cost and high availability. Among the various transition metal oxides, iron oxide catalysts are being used in hydrocarbon oxidation, Fischer-Tropsch synthesis, methane dry reforming reaction, and water gas shift reaction, due to higher selectivity of target product(s), higher tolerance to impurities, and competitive cost [1, 2]. Due to the enactment of recent environmental protection laws, there has been a push for developing more efficient iron oxide catalysts. It was also found that synthesizing catalysts with supporting oxides lead to greater catalytic activity in comparison to unsupported (or bulk) catalysts [3, 4]. Cerium oxide in particular has been found to be a good support material and used in the catalytic converter, due to having high redox and oxygen storage capability [5, 6]. Nabil H. Amin et. al explored the importance of precursors used in synthesizing catalysts. In their paper, the nitrate precursor batch of $\text{CuO}/\text{Fe}_2\text{O}_3$ displayed higher catalytic activity than its sulfate counterpart when used in a H_2O_2 decomposition reaction [7]. In this experiment, the precursors were used to synthesize the support for the catalyst. In a similar manner, the goal of this research is to determine if synthesis with different precursors will affect the activity of the synthesized catalyst. The catalytic activity of a catalyst is related to its structure. It is important when synthesizing a catalyst to achieve monolayer coverage because this will maximize the number of active sites and increase catalytic activity [8]. Increasing the loading of the catalyst over monolayer coverage will lead to the development of a crystalline structure. This is not ideal because it will limit the active sites and therefore decrease the catalytic activity [3]. In this paper, the effects of different iron

oxide precursors (nitrate and sulfate) on the catalytic activity of an $\text{FeO}_x/\text{CeO}_2$ system will be investigated. The catalysts are synthesized at different weight percentages to compare the activities before monolayer formation, at monolayer formation, and at development of crystalline structure. The activity of the catalyst will be analyzed in an NO reduction reaction. This reaction is of interest because it occurs in the catalytic converter of many cars. Lowering automobile emissions using catalysts has been an important goal of the automobile industry [5, 9]. NO reduction is being used because previous studies have reported the ability for NO_x to adsorb onto molecular sieved surfaces [10].

2. Materials and Methods

2.1. Catalyst Synthesis

The supported iron oxide (FeO_x) was prepared by the incipient wetness impregnation of aqueous solution with varying concentrations of iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98+% metals basis (Alfa Aesar) and iron(II) sulfate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.999% trace metals basis (Sigma-Aldrich) onto CeO_2 (Rhodia, HSA 5). After impregnation, the samples were dried at room temperature for 12 hours. The initially dried samples were then transferred to a tube furnace (Lindberg/Blue Mini-Mite Tube Furnace, Model TF55030A-1) and further dried in air (dry grade, from Airgas) at 120°C ($2^\circ\text{C}/\text{min}$ ramping rate) for 12 hours and subsequently calcined at 400°C ($5^\circ\text{C}/\text{min}$ ramping rate) for 6 hours. After the calcination process, the samples were sieved through a 40-mesh sieve (Fisherbrand). The catalyst was then stored in a desiccator at room temperature in a vial as seen in Figure 1.



Figure 1: $\text{FeO}_x/\text{CeO}_2$ catalyst synthesized with iron (II) sulfate heptahydrate

2.2. Raman Spectroscopy

Ex-situ Raman spectroscopy is used in this experiment to analyze the different surface morphology, the molecular structure, and bonding vibration of the $\text{FeO}_x/\text{CeO}_2$ samples with sulfate or nitrate as precursors [11]. Previous studies on precursor effects on catalysts have tested copper on a $\text{CeO}_2/\text{FeO}_x$ support [12]. Raman spectra are recorded with visible (785 nm, HeNe laser) excitation (Renishaw, inVia Raman microscope) under the ambient atmosphere. The scattered photons are directed into a single monochromator and focused onto an air-cooled charge-coupled device. The Raman shift will be calibrated with a built-in silicon standard sample. The spectral acquisition times are 10-20 scans accumulated with 10-15 sec/scan.

2.3. NO reduction by CO

The catalyst was loaded into the CO reactor, and a leak test was performed with 50 mL/min of helium for 30 min. The system was then preheated to 200 °C before 20 mL/min of NO and 20 mL/min of CO was passed through the system. The temperature was increased by 50 °C every 30 minutes until the system reached 400 °C. This 200-400 °C range is ideal for the $\text{NO} + \text{O}_2$ reaction to determine which levels of NO are being reduced [10]. The levels of NO after the reduction are collected by gas chromatography (GC) with a thermal conductivity detector (TCD).

3. Results and Discussion

Ex-situ Raman spectroscopy is used to compare the different surface morphology, the molecular structure, and bonding vibration of samples [8]. This technique is used to identify monolayer and multilayer formation of bulk-like oxide micro-crystals by utilizing the surface density at which bulk formation occurs and signaling the point at which the monolayer was exceeded [3].

Figure 2 shows Raman spectrum of $\text{FeO}_x/\text{CeO}_2$ catalysts with nitrate precursor, using a 785 nm laser excitation. We found a strong peak around 460 cm^{-1} which is the CeO_2 peak [6]. However, from between 10.0 wt% to 30.0 wt%, two peaks emerge at around 218 and 285 cm^{-1} . This was attributed to the transition between monolayer coverage vs. multilayer coverage of FeO_x , which means, that between 8.0 wt% and 10.0 wt% the FeO_x turns from a monolayer coverage into a bulk phase iron oxide [13].

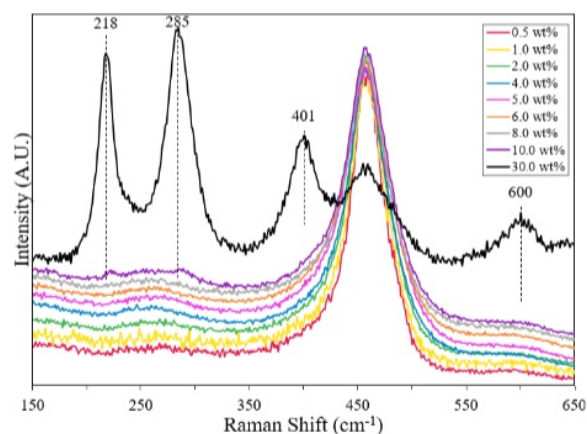


Figure 2: Raman spectra of $\text{FeO}_x/\text{CeO}_2$ catalysts with nitrate precursor using 785 nm laser excitation

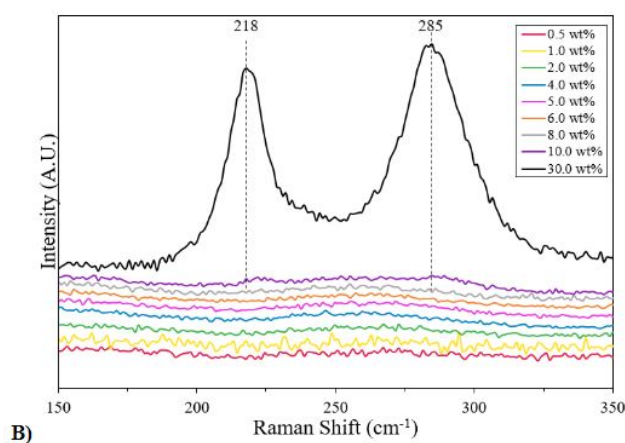


Figure 3: Raman spectra of $\text{FeO}_x/\text{CeO}_2$ catalysts with nitrate precursor using 785 nm laser excitation zoomed in on the 218 cm^{-1} and the 285 cm^{-1} peaks

In Figures 2 and 4, for the $\text{FeO}_x/\text{CeO}_2$ catalyst synthesized with nitrate, a small peak emerge at 220 and 287 cm^{-1} for the 10 wt% sample. This represents the initial formation of the crystalline layer. The monolayer peak fully splits into two peaks at around 218 cm^{-1} and two different peaks emerge at 410 and 600 cm^{-1} at 30 wt%. For the $\text{FeO}_x/\text{CeO}_2$ catalyst synthesized with

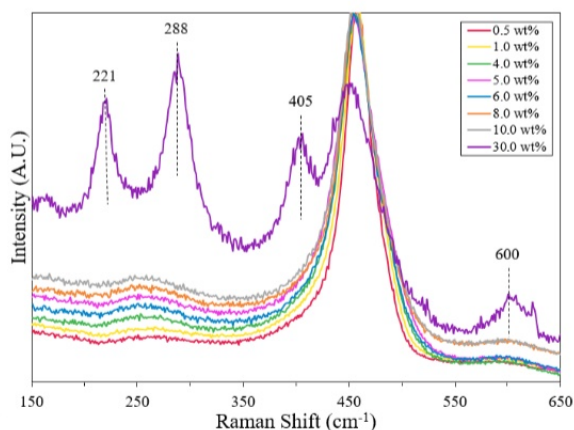


Figure 4: Raman spectra of $\text{FeO}_x/\text{CeO}_2$ catalysts with sulfate precursor using 785 nm laser excitation

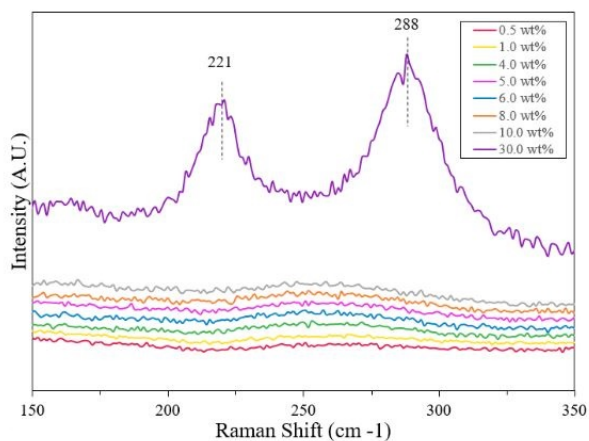


Figure 5: Raman spectra of $\text{FeO}_x/\text{CeO}_2$ catalysts with sulfate precursor using 785 nm laser excitation zoomed in on the 221 cm^{-1} and the 288 cm^{-1} peaks

sulfate precursor, four different peaks emerge at 221, 288, 405, and 600 cm^{-1} at 30 wt%. These four peaks confirm the complete formation of an iron oxide crystal phase.

Figure 4 shows that in general the $\text{FeO}_x/\text{CeO}_2$ catalyst synthesized with nitrate displays higher catalytic activity than the one synthesized with sulfate. This is due to the monolayer developing on lower weight percents for the catalyst synthesized with nitrate when compared to the one synthesized with sulfate. Due to the quicker formation of the FeO_x monolayer, the (nitrate) FeO_x also starts forming its crystalline layer at its 10 wt% whereas the (sulfate) FeO_x starts forming it somewhere inbetween 10 wt% and 30 wt% as evident in Figure 2 and 4. The precursors affected the wt% at which monolayers start forming on the catalyst. This increases catalytic activity in catalysts that form the initial monolayer at a lower wt%. The reason why the nitrate 10 wt% has a higher conversion rate of NO reduction than the nitrate 5 wt% is because the 10 wt% has more monolayer coverage.

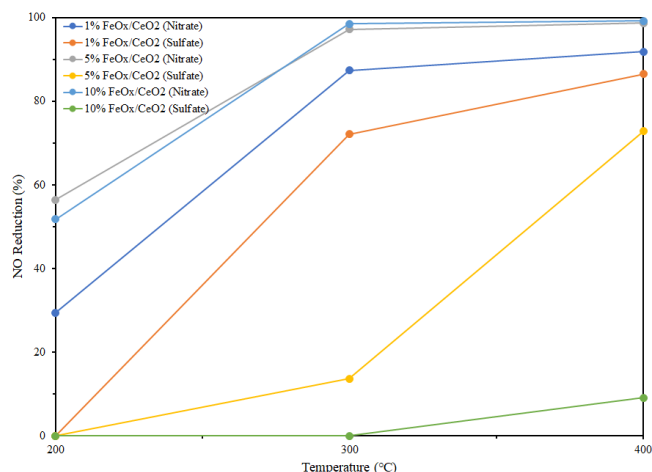


Figure 6: NO reduction by CO test of $\text{FeO}_x/\text{CeO}_2$ catalysts

4. Conclusion

In this paper, we examined how precursors affect the catalytic activity of $\text{FeO}_x/\text{CeO}_2$ for the NO reduction by CO Reaction. The Raman spectra showed that the nitrate precursor is better than sulfate since it shows an earlier formation of a Fe_2O_3 crystal phase, and CO conversions supported these findings by showing that the 10 wt% of the $\text{FeO}_x/\text{CeO}_2$ nitrate precursor is the most active since it facilitated higher conversions at lower temperatures.

For future research, we recommend using both 514 nm and 785 nm wavelengths when performing Raman spectroscopy on the catalyst samples. A 514 nm wavelength provides the same information as the 785 nm, but induces less stress on the catalyst sample. Moving forward, testing different precursors for other metal oxide catalysts may lead to a discovery of a cheap catalyst that can compete with the expensive platinum group catalysts that are currently being used in the industry.

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