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Influence of the activation atmosphere on the catalytic performance of cobalt oxides

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Influence of the activation atmosphere on the catalytic performance of cobalt oxides

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Abstract:

The concentration of carbon dioxide in the atmosphere has been increasing throughout the years, and it is continuously becoming a much bigger worldwide problem [1]. Carbon dioxide is one of the greenhouse gases causing global warming. Not only is temperature increasing due to global warming, but it also causes melting icebergs and rising sea levels. This study, however, offers a ray of hope by presenting a new perspective on nanostructured cobalt oxides. When used as catalysts for hydrogenating CO₂ under different activation atmospheres, these oxides show promising potential to mitigate the effects of increasing CO₂ levels. Pure helium, a mixture of helium and hydrogen, and a reaction atmosphere were selected as activation atmospheres. Total gas flow was 50 ml/min. In the case of a mixture of helium and hydrogen, the flow ratio was 28 ml/min of H₂ and 22 ml/min of He. The reaction atmosphere comprises hydrogen, carbon dioxide, and helium in the ratio of 28 ml/min of H₂, 7 ml/min of CO₂, and 15 ml/min of helium. Helium is used as an inert atmosphere in all of the experiments. Activation was performed for 4 hours at 250 °C, and the experiments were kept at 250 °C and 300 °C for 20 hours.

Graphical abstract:



Catalyst preparation

The catalyst preparation, cobalt (II, III) oxide (Co_3O_4), was a meticulous two-step synthesis process. It involved the precise precipitation of cobalt nitrate-hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) in a basic solution stabilized by polyacrylic acid (PAA) and thermal decomposition in a muffle furnace. This attention to detail in the preparation process instills confidence in the reliability of the research's methodology. First, 0,1 mmol $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 ml of deionized water and 3 ml of 1% PAA was added. Then, 0,1 M was slowly added to the solution under vigorous stirring. The 100 ml of 0,1 M NaOH was calculated for complete precipitation. The solution was heated to a boiling point. After 10 minutes of boiling, the solution was left at room temperature to cool down. The formed brown precipitates were separated on a 2-16KL centrifuge (*SIGMA*) for 10 minutes at 12,000 rotations per minute. Separated product – $Co(OH)_2$ was dried in the air overnight. Catalyst Co_3O_4 was prepared from pre-catalyst $Co(OH)_2$ by thermal decomposition in an air atmosphere at 300 °C for 1 hour. A centrifuge rotation speed of 12,000 min⁻¹ was used for the best separation results due to the poor separation of cobalt hydroxide (Fig. 1).



Figure 1: Graphical interpretation of the preparation of the catalyst

Catalytic testing

The catalytic activity was rigorously tested in the fix-bed reactor Microactivity Effi (PID Eng&Tech) [2]. The prepared Cobalt(II, III) oxide samples were tested under different activation atmospheres. Silica was used as a support for the catalyst to avoid sintering. The thoroughness of the testing process, which included using a steel capillary with a 5,1 mm diameter and activating the catalyst under different atmospheres at 250 °C before each test, ensures the validity of the research's findings. Total gas flow remained at 50 ml/min for all three atmospheres. Pure helium atmosphere gas flow was stabilized at 50 ml/min, and the gas flow of the mixture of hydrogen and helium was 28 ml/min of H₂ and 22 ml/min of He. The reaction atmosphere consists of 28 ml/min of H₂, 7 ml/min of CO₂, and 15 ml/min of helium. Helium is considered to be an inert atmosphere. After 4 hours of activation, the temperature rose to 300 °C (250_300) or remained at 250 °C (250_250), at which the whole reaction was held for 20 hours under the reaction atmosphere. The reaction temperature ramp is shown in (Fig. 2 and 3).

The flow rates were chosen concerning the determined maximum amount of inert gas (He) at 1/3 of the total flow rate and the non-stoichiometric ratio of hydrogen and carbon dioxide in favor of excess hydrogen with the assumption of the formation of higher hydrocarbons.



Figure 2: Reaction temperature ramp for 250_250 experiment



Figure 3: Reaction temperature ramp for 250_300 experiment

Characterization

The catalyst (Co $_3O_4$) was characterized by multiple techniques. SEM, TEM, XRD, TGA/DSC and BET.

SEM images characterized surface morphology [3]. The catalyst consists of deformed hexagonal platelets wider than 100 nm. The height is only about a few nanometers. It can be described as a 1D material. Platelets are combined into aggregates. TEM images showed particles aggregated together, forming bigger particles; we can assume that there are many layers as particles are combined. The hexagons' size is about 12 nm, as shown in (Fig. 4). Some non-deformed hexagons are also shown in TEM images (Fig. 5).



Figure 4: SEM images of Co₃O₄ showing hexagonal platelets



Figure 5: TEM images of Co_3O_4 showing hexagonal platelets

XRD spectra were measured at *Aeris* in a range of 5-105° (2 Theta) for 64 minutes. XRD spectra claim the sample is pure Co_3O_4 and crystallizes in a cubic structure because peaks precisely fit the library measurement (Fig. 5). Lattice parameters are 0,8084 nm, and MCL shows 11 nm. [4]



Figure 6: XRD spectra showing Co peaks precisely fitting Co₃O₄

TGA/DSC measurement was performed for the sample prepared as referred to in chapter *Catalyst preparation* for dried and thermally decomposed sample and only dried sample in the air atmosphere. The sample and balance flow was 100 ml/min. The temperature range was 25 – 1000 °C. Figure 7 shows that there are two significant weight drops. The first one, about 250 °C, is transforming cobalt hydroxide(II) to cobalt oxide (II, III). In contrast, the second one refers to the decomposition of cobalt oxide (II, III) to cobalt oxide(II) that is stable at higher temperatures over 900 °C. We believe that differences in the TGA curves can be caused by the thermal decomposition of the sample and by the excess water contained in the dried sample without thermal decomposition than for the sample thermally decomposed.



Figure 7: TGA curve for Co₃O₄ dried and after thermal decomposition

The catalyst was also characterized by gas sorption using a nitrogen atmosphere. The BET isotherm is shown in (Fig. 8). The surface area is $86,306 \text{ m}^2/\text{g}$, and the pore volume is $0,161 \text{ cm}^3/\text{g}$. We can assume from the curvature of the BET isotherm that the sample has slotted pores. The sample was prepared by degassing at 200 °C for 180 mins. After that, the sample was measured at 130 °C for 720 mins.



Figure 8: BET isotherm for Co_3O_4 catalyst, (Mesoporous, type II (b); Surface: 86,306 m²/g)

Catalytic activity

Three activation atmospheres were tested at two different temperature ranges of reaction. The first temperature range was 250 °C for activation and remained at this temperature for another 20 hours for reaction (Fig. 2). The second temperature range was 250 °C, then the reaction temperature rose to 300 °C, where it remained for 20 hours (Fig. 3). Both temperature ranges showed significantly different results.

250_250 testing

Except for the first hours of the reaction, the conversion is rising over time in all cases of activation atmospheres. A sudden drop in the conversion at the beginning of the reaction can be caused by switching gases from the activation atmosphere to the reaction one. Conversion of CO_2 is for both activation atmospheres; H_2 + He (Fig. 9) and pure He (Fig. 10) atmospheres are nearly similar, and the highest conversion reaches a peak of 11 % at the end of the reaction time [5]. On the other hand, the reaction atmosphere (Fig. 11) provides shallow conversion of CO_2 , which peaks at the end of the reaction at 9 % (Fig. 12).



Figure 9: Selectivity for selected products in the helium and hydrogen as an activation atmosphere



Figure 10: Selectivity for selected products in pure hydrogen as an activation atmosphere



Figure 11: Selectivity for selected products in the reaction atmosphere as an activation atmosphere



Figure 12: Comparison of the conversion of CO₂ based on different activation atmospheres

The most effective activation atmosphere at the temperature of 250 °C appears to be hydrogen with helium. The selectivity of carbon monoxide is up to 20 %. The remaining percentage is for C_1 – C_3 hydrocarbons. The highest selectivity provides methane with about 70 %. The selectivity for ethane is about 10 %, and for propane, 5 % (Fig. 13). Activation in the reaction atmosphere provides half to half methane and carbon monoxide and a few selectivity percentages of hydrocarbons. We can state that the helium atmosphere could be the least suitable activation atmosphere for this experiment because it provides over 80 % selectivity of CO, which is considered not the best transformation product.



Figure 13: Comparison of the selectivity of CH4 based on different activation atmospheres

250_300

Conversion of CO_2 in all cases of activation atmospheres fluctuates about one specific value. The highest conversion of CO_2 provides the reaction atmosphere at 37 %, then the helium atmosphere at 30 %, and hydrogen with helium at 28 % (Fig. 14). In this case, the two main products are CO and CH₄. Methane has a selectivity of over 90 % in all cases of activation atmosphere (Fig. 15). When we look closely at selectivities, they differ in percentages. The reaction atmosphere is the most suitable for methane, with a selectivity of about 95 %. Pure helium and helium with a hydrogen atmosphere have a selectivity of about 91-92 %. We observed that for this reaction, the reaction atmosphere for the activation is the most suitable of the three atmospheres we tested.



Figure 14: Comparison of the conversion of CO2 based on different activation atmospheres



Figure 15: Comparison of the selectivity of CH4 based on different activation atmospheres

Comparison of both experiments

Conversion of CO₂ was rising throughout the time for reaction 250_250, while conversion of CO₂ for reaction labeled as 250_300 fluctuated about one specific value. The highest conversion was provided by the reaction 250_300 for the reaction atmosphere as an activation atmosphere up to 36 %. Then, conversion was about 30 % for the helium atmosphere, and for a mixture of hydrogen and helium, it was up to 26 %. The reaction 250_250 showed a very low conversion of CO₂, but the conversion was rising over time. Both the helium and reaction atmosphere as activation atmosphere as activation atmosphere showed a conversion of CO₂ of up to 11 %.

While selectivity for methane remained at 15 % for the helium atmosphere in the 250_250 reaction, selectivity slowly dropped to 30 % for the reaction atmosphere over time. Experiment 250_300 showed high selectivity values for methane. The highest values are in the same order as those introduced in the conversion of CO_2 . The best results are for an activation atmosphere with a selectivity of up to 96 %. All selectivities of CH_4 for reaction 250_300 are in a range of 90-96 %.

The percentage yield was calculated for the main product of all reactions, methane. Yield is selectivity and conversion dependent, so the curves are very similar to the conversion of CO_2 curves due to the methane selectivity over 90 %.

Results and discussion

In this study, we observed differences in the selectivity and even conversion of CO_2 during the hydrogenation of carbon dioxide reaction using cobalt-based oxide [6]. The main difference between the two reactions was the reaction temperature. Reaction temperature was at 250 °C and 300 °C, while activation temperature was at 250 °C in both cases. Every case was also divided into three parts depending on the activation atmosphere.

We can observe significant differences in the conversion of CO_2 in both 250_250 and 250_300. We can describe the differences in conversion for every reaction atmosphere, but overall, reaction 250_300 has more than 20 % higher selectivity than 250_250 in all cases of the activation atmosphere.

Products also differ. In 250_250, products are CO and C_1 - C_3 saturated hydrocarbons, while 250_300 produces only CO and CH₄.

Better results are obtained, considering the conversion of CO_2 by 250_300 reaction, mainly reaction atmosphere. On the other hand, the 250_250 reaction is better for higher hydrocarbon production than 250_300. To conclude, the activation atmosphere strongly influences the course of the reaction. Depending on the reaction temperature, it would be better to consider testing different reaction atmospheres and use the right one for better results.

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