

Effect of Calcination Conditions on the Dispersion of Cobalt Over Re, Ru and Rh Promoted Co/ γ -Al₂O₃ Catalysts

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Abstract

The effects of catalyst calcination conditions, such as calcination temperature and calcination atmosphere composition on the dispersion of cobalt particles over Co/ γ -Al₂O₃ catalysts for Fischer–Tropsch conversion of synthesis gas are studied. A number of catalysts were prepared by incipient wetness impregnation of 20-wt% of cobalt onto γ -Al₂O₃ and promoted with 0.5 wt% ruthenium, rhenium, and rhodium. Metal dispersions of active metals were studied by chemisorption of carbon monoxide. The highest dispersion for Co/ γ -Al₂O₃ catalyst was achieved by calcination at 400 °C in a flow of N₂. Co metal dispersion seem to be increased in the calcination steps if a flowing gas was used instead of static calcination conditions. The addition of promoter metals like Ru, Re or Rh enhances the dispersion of the active metal.

Keywords

Cobalt

Ruthenium

Rhodium
Rhenium
Calcination
Dispersion
Catalyst

1. Introduction

Preparation of active heterogeneous catalysts by impregnation includes at least the following steps: (i) impregnation of the active metal(s) and promoter metals onto a porous support, (ii) removal of excess solvent and drying of the catalyst, (iii) calcination of the dried catalyst in order to break down precursor salts and produce metallic oxides, and finally (iv) reduction of metallic oxides to obtain the active metal. All these preparation steps will affect the performance of the final catalyst. According to [1], calcination conditions are the most important in order to provide catalysts with high specific surface area and a well-defined, desired, morphology, the calcination conditions will subsequently influence the catalytic performance of the catalyst. In this study, the calcination step of the catalyst preparation is examined for three series of Al_2O_3 supported Co catalysts promoted by Ru, Re or Rh. Various calcination conditions such as calcination temperatures and gas atmosphere are investigated and the effects of calcination conditions on the catalytic properties are measured as changes in the dispersion of the active metal. Dispersion is defined as the ratio of the number of surface Co^0 sites to the total number of metallic Co after reduction of the catalyst [2, 3]. Typically the degree of dispersion for cobalt based catalysts is low, usually ranging from 2% up to a maximum of 10% [2].

Co catalysts are already widely used in the Fischer–Tropsch synthesis (FT) both for catalytic research and for the production of transportation fuels. The use of a FT reaction in the catalytic conversion of synthesis gas produced by biomass gasification might be an interesting opportunity to produce these transportation fuels as an alternative to the fossil fuels presently used [4, 5]. Highly active and selective cobalt catalysts are needed for the FTS independent of the source of the synthesis gas used, and therefore, the understanding of metal-support interactions and the role of promoting metals is extremely important [6].

The addition of promoter metals like ruthenium, rhodium or platinum can enhance the activity of the catalysts by different mechanisms: by enhancing the reduction of the active metal, by increasing the dispersion of the active metal and by easing the transfer of electrons between the support and the active metal. Some of the metals used as promoters; like platinum and ruthenium; can themselves act as FT catalysts but due to the high prices of these metals they are

more often used as promoters only [7, 8, 9]. Of the promoters used in this study ruthenium and rhenium are well known as promoters in the FTS. The third metal used, rhodium, is rarely used in the Fischer–Tropsch reaction and no references for the use of Rh have been found.

Activity of the FT catalyst depend on a number of properties of the catalyst, e.g. metals and supports used, the size of the supporting particles, dispersion of the active metal on the surface of the support [10, 11, 12]. The selectivity is related to the properties of the catalyst used but also to a high degree dependent of process parameters used like pressure, temperature, gas composition and gas flow. The FT reaction produces a mixture of hydrocarbons ranging from methane to long-chained hydrocarbons in the range C_{60+} . The selectivity of a catalyst is described by the probability of chain growth described by the α -value, ranging from 0 to a value close to 1. A α -value of 0 means that there is no chain growth and the reaction produces methane only; the other extreme is a α -value close to 1 when the reaction produces as main products a mixture of predominantly long chained hydrocarbons [11].

In order to achieve high activity in the FT reaction used for conversion of synthesis gas into transportation fuels and chemicals in combination with a high selectivity for higher hydrocarbons (C_{5+}) the cobalt particles must exceed a certain size. In general, the smaller the metal particles are the higher is the catalytic activity, measured as turn-over frequency (TOF). The effect of particle size has been investigated by Borg et al. [10] and according to their findings the activity of the catalysts increases with increasing size of the Co particles in the region of 1–10 nm, having a maximal activity at a particle size of 7 nm. For Co particles 10–100 nm in diameter the activity, measured as TOF, is independent of the particle size.

In a study by de Jong et al. [13], small particles of cobalt and nickel were obtained using a flowing gas of 1% NO in helium to flush the reactor during the calcination process. The size of the Co_3O_4 particles was reported to be 8–60 nm after flushing with air and 4–5 nm when flushed with 1% NO in He. These results were obtained with Co catalysts supported on silica and therefore a direct comparison with other supports is difficult. In a study by Zare et al. [13] the effects of the calcination conditions on the properties of Al_2O_3 supported bimetallic Co–Ni catalysts were investigated. In this study, two different atmospheres, nitrogen, and air were tested.

A measure of the dispersion of the active metal alone is not a proof on how the catalyst will perform under real catalytic conditions for the Fischer–Tropsch reaction [pressure of 20 Bar (2 MPa) and a temperature of 210–220 °C]. The

next step after calcination in the catalyst preparation is the reduction of the active metal. Finally, catalysts have to be tested for activity and selectivity under real conditions in order to correlate the effects of calcination conditions and promoter additions with the performance of the catalysts.

In the present study, the effect of calcination conditions (temperature, gas atmosphere) on the degree of dispersion of cobalt was studied over Co/Al₂O₃ catalysts. The effect of calcination conditions on the degree of dispersion, metal particle size, and active metal surface are determined. Further, the possible effect of promoter metal (Re, Ru or Rh) is considered. The use of Re and Ru as promoters is known to lower the temperature for the reduction of cobalt as described by [14].

2. Experimental

2.1. Preparation of Catalysts

Four series of Al₂O₃ based catalysts were prepared, each containing 20 wt% cobalt as the active metal, one of these (zero sample) contained 20% Co only. This sample was calcined in static air conditions at 320 °C. Series one contained 0.5 wt% rhenium as promoter, while the corresponding series 2 and 3 contained rhodium and ruthenium as their promoters, 0.5 wt% each. All catalysts were prepared by a one-step incipient wet impregnation onto γ -Al₂O₃ (Sasol Puralox SSCa) with a specific surface area of 196 m²/g. The metal salts (Co(NO₃)₃·6H₂O, Rh(NO₃)₃, Ru(NO)(NO₃)₃ and perrhenic acid HReO₄) or solutions of these salts were dissolved in distilled water in volumes equal to the pore volume of the support. Impregnation of precursor salts was performed for 16 h with continuous mixing onto the support of alumina oxide dried at 80 °C for 1 h prior to impregnation. After impregnation the catalysts were dried, first at a sub-atmospheric pressure at 60 °C for 30 min followed by 2 h at 105 °C. The dried catalyst was sieved in order to obtain particles in the range of 50–100 μ m. The sieved catalyst samples were split into different subsamples prior to the calcination. All the catalysts contain 20 wt% of Co and 0.5 wt% of Re, Ru, and Rh, and are denoted in the text as Co/Al₂O₃, ReCo/Al₂O₃, RuCo/Al₂O₃ and RhCo/Al₂O₃ catalysts respectively.

2.2. Calcination

Calcination was performed in a laboratory oven in a static air environment or in the cases of gas flow, in a quartz reactor inserted in a tubular oven; a gas supply was connected to the reactor tube. For calcination in the quartz reactor gas flows giving a GHSV value of 3000 ml/h/g_{cat} were used. Samples calcined in the

quartz reactor were flushed with nitrogen or pressurized air respectively during the calcination processes. For all samples, calcination temperatures of 350, 400 and, 450 °C with an initial temperature rise of 100 °C /h were used in all cases. All calcinations were performed for 16 h.

2.3. Determination of Metal Dispersions and Metal Particle Sizes

Metal dispersion and metal particle sizes were measured with a Micromeritics ASAP 2020 on calcined samples by chemisorption of carbon monoxide (CO) assuming a stoichiometric mean ratio of 2:1 between cobalt particles and adsorbent assuming an associative adsorption [15]. A portion of each sample (about 500 mg) was weighed into a U-shaped quartz tube, the sample was supported on both sides by quartz wool. The samples were first evacuated and then reduced in a flow of H₂, first at a temperature of 110 °C for 30 min followed by reduction at 350 °C for 2 h using an initial temperature ramp of 10 °C/min. After the reduction, the samples were evacuated for 2 h at 350 °C followed by 2 h at 40 °C. Before the measurements, the samples were tested for leaks of any remaining H₂ followed by a final evacuation for another 40 min at 40 °C. Known volumes of CO were added to the catalysts and the gas was adsorbed onto the Co surface. The quantity of gas adsorbed was plotted as a function of the pressures used. The metal dispersions were calculated using data from the isotherms obtained, the sizes of the Co metal particles (d_{Co^0}) were calculated according to the formula $d_{Co^0} = 96/Dispersion\%$ [16].

2.4. Determination of Specific Surface Areas

For some of the catalysts representing the highest and lowest metal dispersion for each promoter metal; surface areas and pore distributions were measured on a Micromeritics ASAP 2020 by adsorption of N₂. The results are compared with those obtained for un-impregnated Al₂O₃ support calcined in static air at 350 °C. For the physisorption of N₂ about 200 mg of each catalyst was weighed into a quartz tube. Prior to measurement the samples were evacuated at 10 μm Hg at an elevated temperature (140 °C) in order to remove any contaminating gases from the samples. Surface areas were measured under isothermal conditions obtained by immersing the sample container into liquid nitrogen by the addition of small portions of N₂. The final results were calculated according to the Brunauer–Emmett–Teller (BET) [17] model.

2.5. Determination of the Degree of Reduction

The degree of reduction for the Ru and Rh promoted catalysts were measured on a Micromeritics Autochem by reoxidation of reduced catalysts. Small portions,

about 25 mg, of each catalyst were weighed into a quartz tube. Prior to analysis, the samples were dried at 100 °C for 1 h and then reduced for 1 h at 350 °C in a flow of 10% H₂ in Ar according to reactions (1) and (2). Co surface was rinsed with He flow until the signal from the TCD detector returned to the baseline. Small pulses (1 ml each) of oxygen (5% in He) were added using a calibrated loop until signals with a constant area were obtained. Between the pulses, the signal was allowed to return to baseline before applying next pulse. The degree of reduction was calculated from the moles of oxygen consumed assuming that all Co⁰ was oxidized to Co₃O₄ according to reaction (3) compared to the amount of oxygen theoretically needed for a complete re-oxidation of Co⁰. Any oxidation of the promoter metals or other reductions/oxidations of other Co species were not considered in the calculations.



2.6. XRD Diffraction Patterns

Crystalline phases and structures of calcined, unreduced samples were analyzed by X-ray diffraction (XRD). The XRD patterns were recorded by a Siemens D5000 X-ray diffractometer using monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA at the Center of Microscopy and Nanotechnology at the University of Oulu.

3. Results

3.1. Effect of Calcination Conditions on the Dispersion of Cobalt

In cobalt catalysts supported on Al₂O₃, the dispersion of the active metal is generally rather low, most in the region of 6–8%, the results from the calcination tests are summarized in Table 1.

Table 1

A summary of the results from the calcination experiments performed under different calcination temperatures and atmospheres

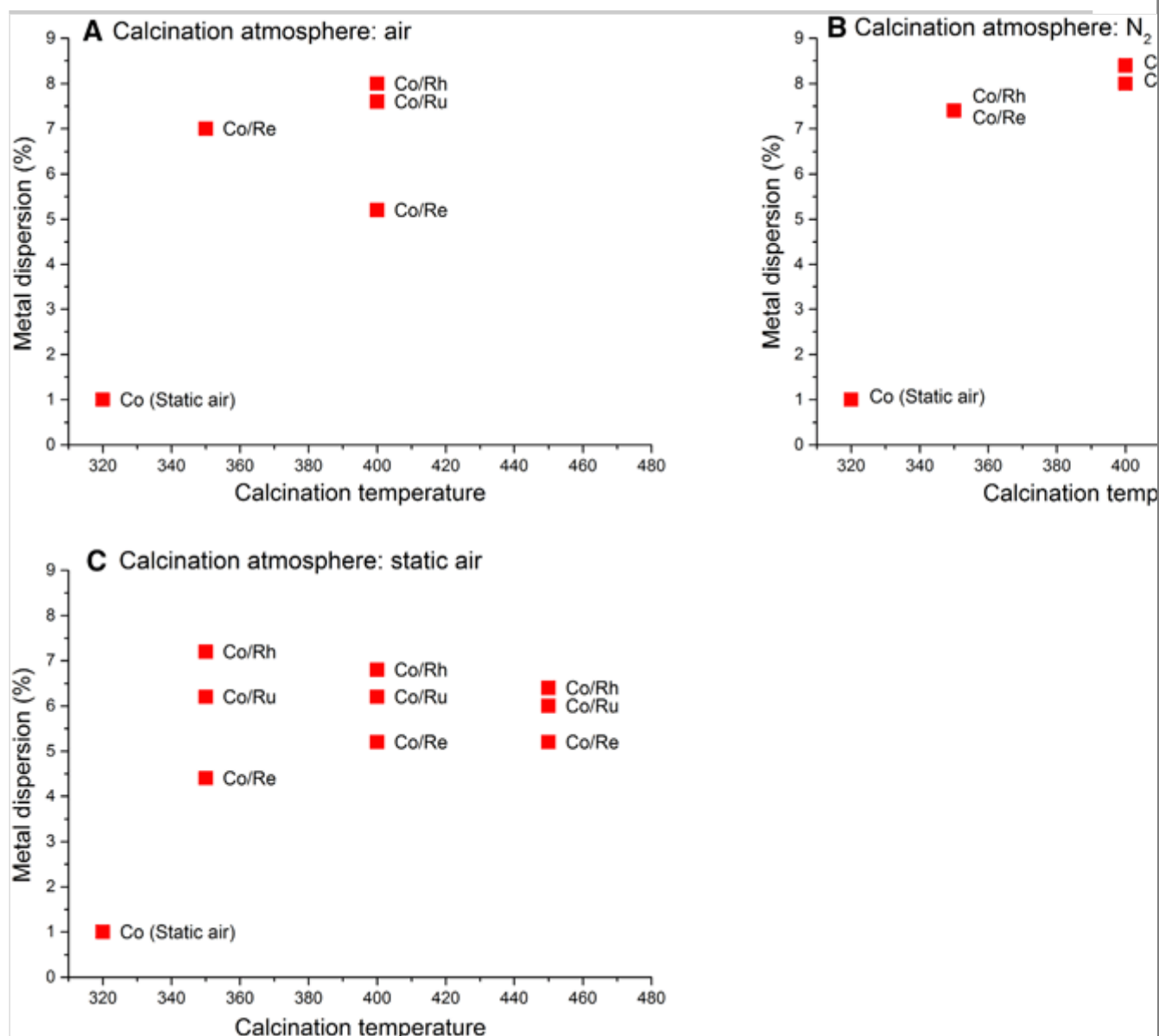
Metal/promoter	Calcination temperature (°C)	Calcination atmosphere	Metal dispersion (%)	Metallic surface area (m²/g sample)	Degree of reduction %
Co	320	Static air	1.0	1.4	
Co/Re	350	Air	7.0	10.0	
Co/Re	350	N ₂	7.4	10.0	
Co/Re	350	Static air	4.4	6.0	65
Co/Re	400	Air	5.2	7.0	
Co/Re	400	N ₂	8.0	11.0	33
Co/Re	400	Static air	5.2	7.0	62
Co/Re	450	N ₂	4.0	5.0	
Co/Re	450	Static air	5.2	7.0	82
Co/Rh	350	N ₂	7.4	10.0	37
Co/Rh	350	Static air	7.2	9.8	
Co/Rh	400	Air	8.0	10.8	
Co/Rh	400	N ₂	8.4	13.4	
Co/Rh	400	Static air	6.8	9.0	
Co/Rh	450	N ₂	7.6	10.2	
Co/Rh	450	Static air	6.4	8.6	55
Co/Ru	350	Static air	6.2	8.0	48
Co/Ru	400	Air	7.6	10.4	
Co/Ru	400	N ₂	8.0	11.0	
Co/Ru	400	Static air	6.2	8.0	42
Co/Ru	450	Air	8.0	11.0	
Co/Ru	450	N ₂	6.6	9.0	39
Co/Ru	450	Static air	6.0	8.2	39

3.1.1. The Effect of Calcination Temperature on the Dispersion of Cobalt

Calcination temperature and calcination atmosphere are the most important parameters that have an impact on the dispersion of the cobalt used as active metal. The highest levels of dispersion ($\geq 8.0\%$) were obtained at a calcination temperature of $400\text{ }^{\circ}\text{C}$ with the exception of one Ru promoted catalysts where a dispersion level of 8.0% was achieved for calcination at $450\text{ }^{\circ}\text{C}$ as presented in Table 1. In Fig. 1, a summary of the results from calcination performed at different temperatures and under different calcination atmospheres are presented.

Fig. 1 Should the caption be below the figure?

Effects of calcination on metal dispersions and crystallite sizes at different calcination temperatures in **a** air flow, **b** N_2 flow and **c** static air. Note: The unpromoted reference catalyst Co is calcined in an atmosphere of static air in figures (**a–c**)



3.1.2. Effect of Calcination Atmosphere on the Dispersion of Cobalt

The most important factor regarding the effect of calcination atmosphere seems, according to the results, to be if the atmosphere is static or is there a continuous gas flow. With some exceptions the catalysts having the lowest degree of dispersion are all calcined at static atmospheric conditions. The dispersion for most of the catalysts calcined at static condition were in the range of 7.0%. The highest dispersion, 8.4%, was achieved in an atmosphere of flowing N₂ for the Rh promoted catalyst. A summary of the results is presented in Fig. 1a–c and Table 1. Some results of the metal dispersion for the Co catalysts promoted with Re and calcined under different atmospheric conditions at different temperatures are presented in Fig. 1.

3.1.3. Effect of Promoter Addition on the Dispersion of Cobalt

The effect of promoters is difficult to evaluate based on the chemisorption experiments but according to the results presented in Fig. 1, there seems to be some differences between the catalysts promoted with different promoters (Re, Ru, and Rh) regarding the dispersion of the cobalt particles. The catalysts promoted with rhodium have the highest dispersion independent on the calcination temperature or calcination atmospheres used. The promoters might to at least some extent or even completely be covered by Co because much higher concentrations are present in the catalysts. The dispersion is much higher for all promoted catalysts compared to the unpromoted Co catalyst independent on calcination temperature, calcination atmosphere and promoter used. The rhodium promoted catalysts have under all conditions highest dispersions, followed by ruthenium and rhenium. The catalyst having the highest dispersion (8.4%) is also promoted with rhodium.

3.2. Specific Surface Areas, Pore Sizes and Pore Volumes

Minor changes in the BET surface area for the metal impregnated and calcined catalysts were observed compared with the unimpregnated support. BET surface areas for the impregnated catalysts were smaller than for the un-impregnated γ -Al₂O₃ support as presented in Table 2, the same trend was also observed for pore volumes and pore diameters. The main reason for the lower surface areas measured for the impregnated catalysts compared to the support is most likely an indication of some degree of pore blocking due to the introduction of cobalt and precursors into the pores.

Table 2

BET surface analysis of some selected catalysts compared to calcined support

Catalyst	Calcination temperature (°C)	Calcination atmosphere	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
Al ₂ O ₃ (support)	400	Static air	196	0.51	10.6
CoRh/Al ₂ O ₃	400	N ₂	143	0.31	8.6
CoRh/Al ₂ O ₃	400	Static air	142	0.31	8.8
CoRu/Al ₂ O ₃	450	Static air	138	0.31	9.1
CoRu/Al ₂ O ₃	400	N ₂	140	0.31	9.0
CoRe/Al ₂ O ₃	400	N ₂	150	0.33	9.1
CoRe/Al ₂ O ₃	350	Static air	147	0.33	9.1

Pore volume is given at $p/p^\circ = 0.994$, Co content for each catalyst was 20 wt% and Re, Ru or Rh content was 0.5 wt%

3.3. Degree of Reduction

The degree of reduction was measured for the catalysts and the results are presented in Table 3. The highest value for DOR is obtained for a catalyst calcined at 450 °C also the catalysts calcined at 400 and 350 °C proved to have rather high level of DOR. The calcination atmosphere used seems to have a stronger impact on the DOR, all catalysts calcined in an atmosphere of static air seems to have the highest values for DOR. The difference in DOR between the catalysts calcined in static air and N₂ might be explained by the presence of CoO and Co⁰ in the catalyst calcined in N₂.

Table 3

Degree of reduction for the catalysts at different calcination temperatures and atmospheres

Metal/promoter	Calcination temperature	Calcination atmosphere	Degree of reduction %
Co/Re	350	Static air	65
Co/Re	400	N ₂	33
Co/Re	400	Static air	62
Co/Re	450	Static air	82

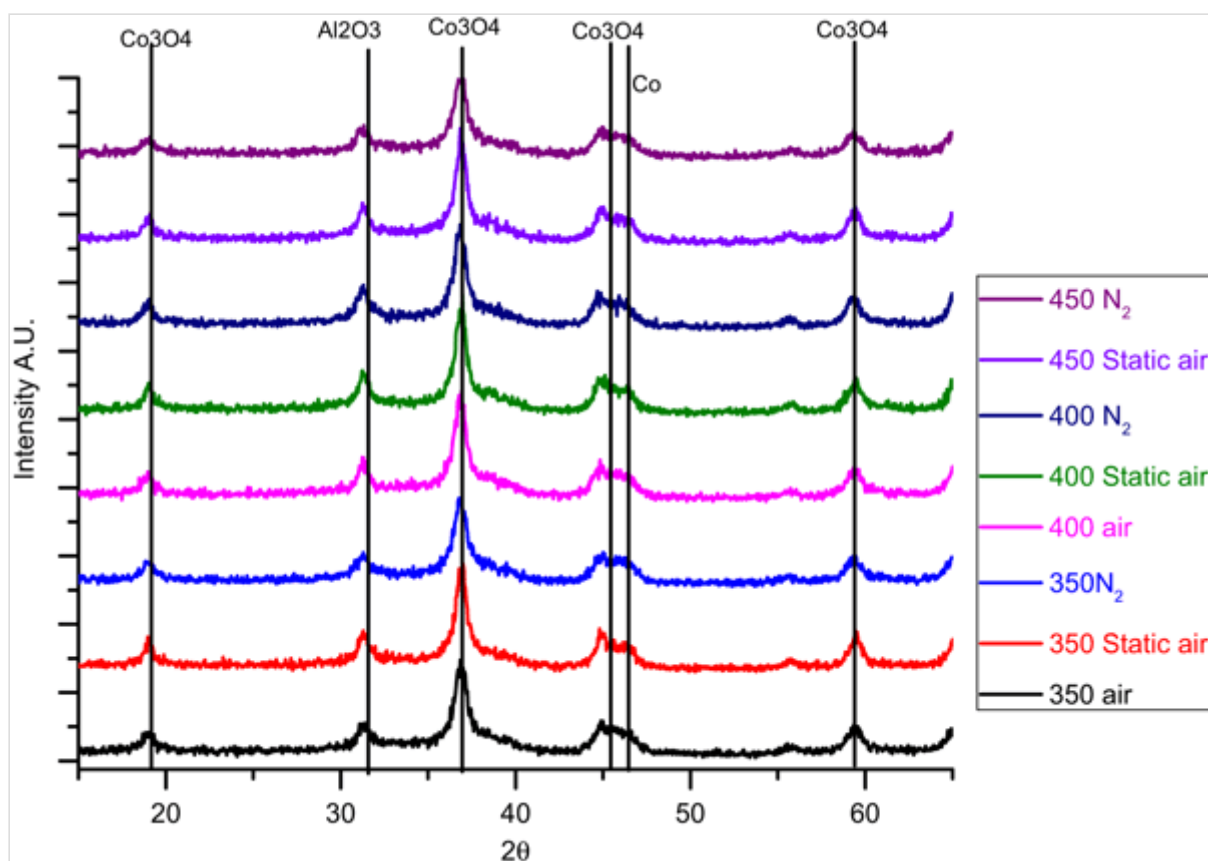
Metal/promoter	Calcination temperature	Calcination atmosphere	Degree of reduction %
Co/Rh	350	N ₂	37
Co/Rh	450	Static air	55
Co/Ru	350	Static air	48
Co/Ru	400	Static air	42
Co/Ru	450	N ₂	39
Co/Ru	450	Static air	39

3.4. XRD Diffraction Patterns

Some of the calcined but unreduced samples were analyzed for crystalline structures and phases from the XRD patterns obtained. According to the diffraction patterns, the crystalline structures for cobalt are almost the same in all samples independent of the different calcination conditions used. The most abundant phase in all samples is, besides the alumina oxide in the support, apparently cobalt oxide, the most abundant oxide observed is Co₃O₄. Regarding the samples calcined in flowing air, Co₃O₄ is the only phase of Co observed independent of the calcination temperature used. Co₃O₄ is the main phase observed in the samples calcined at static conditions but in this case also minor amounts of CoO was found. In the samples calcined in a stream of N₂ minor amounts of CoO and metallic Co (Co⁰) are observed but the diffraction peaks of CoO and Co⁰ are rather small and based on this conclusions cannot be made regarding this forms of cobalt. The diffraction patterns obtained from the different samples are presented in Fig. 2.

Fig. 2 Should caption text be moved below figure

Diffraction patterns for the catalysts calcined under different calcination conditions (gas atmosphere and temperature). Main compounds identified marked with *vertical bars*



4. Conclusions

In the present study, the effects of calcination temperature and atmosphere on cobalt catalysts supported on alumina oxide were studied. Some of the catalysts were promoted with rhenium, ruthenium or rhodium at concentrations of 0.5 wt%. Co metal dispersions were low for all the calcined catalysts, which is also consistent with earlier results reported for FT catalysts [1, 9]. Based on the results, calcination of the catalysts in a gas flow improved the dispersion of Co compared to the dispersion of an unpromoted catalyst calcined under static condition. Apparently the type of gas used, nitrogen or air, is less important than the gas conditions (flowing or static).

Regarding the effects of different promoter metals used on the dispersion of cobalt there is a significant difference between the unpromoted cobalt catalyst calcined under static conditions at 320 °C and the promoted ones. The role of promoter metals added can be seen as an increase in the dispersion of Co. Differences in the dispersion of Co were observed between Ru, Re and Rh promoted catalysts. The effect of promoter metals on the dispersion of Co particles decreases in the order Rh > Ru > Re.

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