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1	Characterization of cobalt catalysts on biomass-derived carbon supports
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10	
11	Abstract
12	Cobalt catalysts are known to have a high activity and selectivity in the Fischer-Tropsch reaction converting
13	synthesis gas to higher hydrocarbons (C_{5+}). These catalysts have been supported by different porous
14	materials. Porous carbon materials like activated carbon (AC) have physical and chemical surface properties
15	that affect the preparation of supported metal catalysts and can easily be tailored.
16	In this study, AC was produced by carbonization and steam activation of lignin, a waste fraction from the
17	Kraft pulping process. A series of Co/AC-catalysts was produced and characterized by several techniques.
18	According to the results, tailored properties (high surface area, mesoporosity) were obtained for carbon
19	supports. Further, ash content could be reduced by acid treatment. Co/AC-catalysts prepared by ultrasonic
20	assisted impregnation have high metal dispersion (10.1%). It was also observed that small metal particles
21	were difficult to reduce, but acid (HNO ₃) treatment has a positive effect on reduction temperatures.
22	
23	Keywords: activated carbon, catalyst, characterization, cobalt, support
24	
25	
26	

27 **1. Introduction**

28 The sustainable catalytic conversion of renewable resources to chemicals and fuels is a rapidly growing field 29 in research. Practically all fuels and over 85% of the chemicals coming out of petrochemical refineries have 30 seen at least one catalytic conversion step in their production process. Conventional catalysts have been 31 supported by a number of supports, such as Al_2O_3 , SiO_2 and TiO_2 . Many recent reviews deal with the 32 advantages of carbon supports for the preparation of highly dispersed metal catalysts. Porous carbon 33 materials like activated carbon (AC) have physical and chemical surface properties that can easily be such as 34 a large surface area, the proper pore size distribution and acid-base characters on the surface that affect to 35 the preparation of metal supported catalysts.[1-3]

36 Cobalt-based catalysts are known to have a high activity in the Fischer-Tropsch reaction (FT) converting 37 synthesis gas into linear hydrocarbons and waxes and have low activity for the water gas shift reaction. Many 38 studies have been done with different preparation methods, cobalt loading, and supports.[4-9] It has been 39 found that the support materials have a significant role on the activity of the heterogeneous catalysts. 40 However, a strong metal-support interaction between cobalt and conventional oxide supports (Al₂O₃, SiO₂, 41 etc.) inhibits the formation of catalytically active high dispersed metal.[10,11] It is known that obtain optimal 42 catalytic FT performance both high surface area and a well-developed porosity are very important for 43 achieving a high dispersion of the active phase in the catalyst. Carbon materials, especially AC, has surface 44 areas significantly higher than another conventional oxide catalyst supports increasing surface area and 45 porosity of the carbon facilitates the loading of metal [12]. As a chemically inert material, carbon support can 46 reduce the interaction with the cobalt species and increase the cobalt reducibility [13]. Advantageously 47 carbon materials can be prepared from residual biomass and waste materials which is an attractive property 48 for decreasing the so-called "carbon footprint" of a biomass transformation process [2]. Beside the high 49 surface area carbon support also has many other advantages in the catalytic applications like tailored pore 50 size distribution that can be modified for specific reactions, resistance to acidic or basic media, amphoteric 51 character due to the presence of various oxygenated functional groups which enhances metal adsorption 52 and catalyst dispersion, the structure that is stable at high temperatures, even above 700 °C (except in the presence of oxygen >200 °C and for hydrogenation reactions >400 °C), less expensive compared to alumina and silica supports; porous carbons can be prepared in different physical forms (granules, extrudates, pellets, fibers, cloths, etc.), hydrophobic carbon can be modified to increase the hydrophilicity and active phase can be recovered by eliminating the support through burning away the carbon. [2]

57 By modifying the carbon support, surface pore structure and functional groups (O, N, H) supported Co-58 catalysts with a high degree of reduction and high Co dispersion can be obtained. These functional groups 59 are considered anchoring sites for cobalt particles on the surface of AC, which can increase the cobalt metal-60 loading, dispersion, and stability.[13] It has been observed that the more acidic the groups are, the less 61 hydrophobic is the carbon surface, making the surface more accessible to the aqueous solution of the metal 62 precursor upon impregnation. The metallic dispersion is said to increase with the increased amount of oxygen 63 on the surface. Oxygen groups on the surface have been most studied since they are formed spontaneously 64 by exposure of the material to the atmosphere during the activation process. The concentration of these 65 groups can be increased with different oxygenation treatments such as nitric acid disposal. Fixation of the 66 acidic groups on the surface of the AC makes the surface more hydrophilic, decreases its pH, and increases 67 the negative surface charge density. These treatments can also affect the surface area and pore texture of 68 the activated carbons. [12, 14, 15]

69 Mesopore volume and mean mesopore size have been reported to be important parameters to control metal 70 particle size and dispersion on carbon materials. A support with modified mesoporous and macroporous 71 structure can have excellent advantages in FT reaction because larger pores benefits rapid molecular 72 transportation and enhances the production for longer hydrocarbon chain distribution. The microporous 73 structure of activated carbon is claimed to result in high methane and light hydrocarbon selectivity. [13,16] 74 A number of studies have been shown that addition of noble metals has a strong impact on the activity and 75 selectivity on cobalt catalysts. The addition of noble metal promoters can shift the temperature needed to 76 reduce cobalt oxide to metallic cobalt to lower temperatures, but its effect on the degree of reduction has 77 been reported to be rather minor. Instead, the improved activity of noble metal promoted cobalt catalysts 78 has been mainly attributed to higher cobalt dispersions. [17-19]

Many activated carbons have reported having high ash content. Ash content has a relatively small, but significant negative effect on the adsorption of the metal precursor. By selecting an appropriate precursor and modifying the carbon with different treatments, it is possible to prepare porous carbons with very low ash content. [2, 3]

Preparation of carbon supported metal catalyst can be done with impregnation methods, precipitation methods or by ion-exchange method. With impregnation methods, incipient wetness method is performed in which the metal precursor is dissolved in small amount of solvent just enough to fill the pores of the support. Cobalt-based catalysts are relatively seldom prepared with precipitation methods but few papers have been published. [20-24]

In this study, a series of unpromoted and promoted cobalt catalysts supported on AC used as such or modified by different acid treatments have been prepared and characterized. Effect of acid pretreatments (HCl and HNO₃) on AC and different preparation methods including impregnation methods and precipitation methods have been studied. Also, the effect of promoting the cobalt catalysts with noble metals ruthenium and rhenium have been tested in this study.

93

94 **2. Experimental**

95 **2.1 Preparation of activated carbon**

96 The lignin was dried and sieved to obtain particles of 0.8-1.2 mm in diameter. The sieved lignin was 97 carbonized and steam activated in a one-step process in a rotating guartz reactor (Nabertherm GmbH RSRB 98 80). The thermal profile during the whole process was divided into two parts: the first carbonization step, in 99 which the temperature was raised to 800 °C with a ramp of 6.7 °C /min, procured the total carbonization of 100 the lignin followed by the activation step. During the activation temperature was kept at 800 °C for 120 min 101 with a stream of water steam (120 g/h at 140 °C), created the proper surface activation. During the whole 102 process, the reactor was flushed with an inert gas, in ramping step only N₂ (flow 200 ml/min) and in activation 103 step carrier gas (N₂ flow 200 ml/min) and steam (120 g/h at 140 °C). The resulting AC was characterized for 104 ash content, carbon content (TC), specific surface area, and pore size distribution.

106 **2.2 Preparation of catalysts**

107 The formed AC was crushed and fractioned by sieving into particle size 50-100 µm. Some of the carbon was 108 used as such, other parts either acid-treated with hydrochloric acid (HCl) in order to demineralize the sample 109 or oxidized with nitric acid (HNO₃) in order to introduce functional groups into the carbon. Acid treatments 110 were performed with 30 wt. % HCl or with 10 wt. % HNO₃ refluxed 3h and washed with distilled H₂O until pH 111 was neutral. Finally, the AC was dried overnight at 105 °C. AC demineralized with HCl was used as a support 112 in the preparation of catalyst AC-HCI-Co-IW and AC oxidized with HNO₃ was used as a support in the 113 preparation of catalysts AC-HNO₃-Co-IW. AC-Co-IW was prepared by incipient wetness impregnation of 114 cobalt as such without any pretreatment of AC. Cobalt catalysts containing 10 wt. % of Co were prepared by 115 incipient wetness impregnation of the ACs using $Co(NO_3)_3$ *6 H₂O as a precursor. Promoter metals ruthenium 116 or rhenium were added in some catalysts using precursor metal salts Ru(NO)(NO₃)₃ (AC-CoRu-IW) or ReO₄H 117 (AC-CoRe-IW) in order to get 0.2 wt. % promoter metal on the catalyst. Promoter metal was added to 118 precursor solution and performed one-step incipient wetness impregnation. After impregnation, the 119 catalysts were dried overnight at 105 °C and calcined at 320 °C for 16 hours. The calcination step was 120 performed in a quartz reactor placed into a tubular oven and flushed with nitrogen (240 ml/h/ g_{cat}) during the 121 whole process. Beside incipient wetness impregnation method, precipitation method was used in the 122 preparation of AC-Co-PR catalyst. The cobalt precursor $Co(NO_3)_3$ *6 H₂O was dissolved in distilled H₂O together 123 with urea in a molar ratio of cobalt to urea of 1:2, and AC. The resulting solution was heated to 80 °C and 124 stirred overnight to precipitate the cobalt. Finally, the impregnated AC was dried overnight at 105 °C before 125 calcination. With catalyst AC-Co-US, ultrasonic assisted impregnation method was performed using an 126 ultrasonic bath (VWR USC 200 TH, 45 kHz) during the addition of precursor solution (Co(NO₃)₃*6 H₂O dissolved 127 in water) with a total US exposure time equal to 60 min at room temperature. After sonication, catalyst was 128 rotated overnight in a rotating mixer (Rotavapor) and then dried overnight at 105 °C. The calcination step 129 was performed in the same way for all catalysts as described above. A summary of the catalysts prepared 130 and the preparation methods of Co/AC-catalysts are presented in Table 1 and Figure 1.

132 2.3 Catalyst characterization

133 The resulting catalysts (see Table 1) were characterized by a number of methods including elemental analysis,

134 nitrogen physisorption, ICP-OES, SEM, TEM, DRIFT, XPS, XRD, and TPR analysis.

135

136 2.3.1 Total carbon and ash contents

137 The percentage of total carbon present in prepared ACs was measured using Skalar Primacs MCS instrument.

138 Dried samples were weighted in quartz crucibles, combusted at 1100 °C in a pure oxygen atmosphere and

the formed CO₂ was analyzed by an IR analyzer. The total mass of carbon in each sample was calculated as a

140 percent of the mass initially weighted.

141 All samples were analyzed for ash content. A known amount of AC was transferred to tared crucibles and

142 combusted in a muffle furnace for two hours at 815 °C with an initial temperature ramp of 9 °C /min. The ash

143 contents were calculated as a percent of the initial dried biomass.

144

145 2.3.2 Surface areas and pore distribution

Specific surface areas and pore size distributions were calculated from adsorption isotherms of N₂ at isothermal conditions in liquid nitrogen according to the BET (Brunauer–Emmett–Teller) theory. Pore distribution was calculated from the adsorption isotherms using the BJH (Barrett–Joyner–Halenda) method. Each sample (about 100mg) was weight in a quartz tube. Samples were evacuated and heated in order to remove any adsorbed components and moisture. Evacuated samples were measured under isothermal conditions by Micromeritics ASAP 2020.

152

153 **2.3.3 Metal content, dispersions and particle sizes**

154 Metal contents of samples were measured by inductively coupled optical emission spectrometry (ICP-OES) 155 using a Perkin Elmer Optima 5300 DV ICP–OES instrument. 0.10-0.12 g samples were added in 37 % 156 hydrochloric acid and 63 % nitric acid, then digesting in a microwave oven (MARS, CEM Corporation) at 200

157 °C for 10 min. After digestion, the solution was diluted to 50 ml and measured by ICP-OES.

Metal dispersions and particle sizes were measured from calcined samples by chemisorption of carbon monoxide (CO) assuming that stoichiometric ratio of was 1:1 between the adsorbent and cobalt (CO: Co) [25-26]. Each sample (about 500 mg) was weight in a U-shaped quartz tube and the sample was supported with glass wool. Prior to measurements, the sample was evacuated followed by a reduction in a stream of hydrogen (H₂) at 350 °C. Measurements were done using a Micromeritics ASAP 2020.

163

164 2.3.4 Catalyst morphology

A field emission scanning electron microscope (FESEM) Zeiss Ultra Plus equipped with and energy-dispersive X-ray spectroscopy (EDS) analysis system at the Center of Microscopy and Nanotechnology, University of Oulu was used to study the microstructure of the catalysts and for elemental analyses.

The morphology of the catalyst particles dispersed in the microemulsion was studied using an energy filtered transmission electron microscope EFTEM (LEO 912 OMEGA EFTEM). The catalysts samples were dispersed in acetone and pretreated in an ultrasonic bath for several minutes. A small drop of the microemulsion was deposited on a copper grid pre-coated with carbon and then evaporated in air at room temperature. The particle size of the samples was measured from TEM images of each sample and given in a reasonable range. The accelerating voltage and emission current in the measurements were 120 kV and 8-15 μA, respectively, while the resolution of the instrument was 0.37 nm.

175X-ray diffraction (XRD) patterns were recorded by a PANalytical X'Pert Pro X-ray diffraction equipment using176monochromatic CuKα1 radiation (λ =1.5406 Å) at 45 kV and 40 mA. Diffractograms were collected in the 20177range 5-80° at 0.017° intervals and with scan step time of 110 s. The crystalline phases and structures were178analyzed by HighScore Plus.

179

180 **2.3.5** Temperature programmed reduction and oxidation

The conventional temperature programmed reduction experiments (TPR) were performed using a Thermoquest Mod. TPR/D/O 1100 (TCD detector) by feeding 30 ml/min of a 5.1% v/v H₂ in Ar gas mixture while heating by 8 °C/min from 50 °C up to 900 °C. The samples have been initially pre-treated in a flow of argon at T= 200 °C for 0.5 h. The TPR profiles of the catalysts exhibit hydrogen consumption peaks attributed to two-step reduction of Co₃O₄ to metallic cobalt with intermediate phase consisting mainly of CoO but most likely other hard-reduced cobalt oxides are present in the second peak.

187 (1)
$$Co_3O_4 + H_2 \rightarrow 3 CoO + H_2O$$

188 (2)
$$3 \text{ CoO} + 3 \text{ H}_2 \rightarrow 3 \text{ Co}^0 + 3 \text{ H}_2\text{O}$$

189 The degree of reduction for the catalysts was measured on a Micromeritics Autochem by reoxidation of 190 reduced catalysts. Small portions, about 25 mg, of each catalyst were weighed into a quartz tube. Prior to 191 analysis, the samples were dried at 100 °C for 1 hour and then reduced for 1 hour at 350 °C in a flow of 10 % 192 H_2 in Ar according to reactions (1) and (2). Co surface was rinsed with He flow until the signal from the TCD 193 detector returned to the baseline. Small pulses of oxygen (5 % in He) were added using a calibrated loop until 194 signals with a constant area were obtained. Between the pulses, the signal was allowed to return to baseline 195 before applying next pulse. The degree of reduction was calculated from the moles of oxygen consumed 196 assuming that all Co^0 was oxidized to Co_3O_4 according to reaction (3) compared to the amount of oxygen 197 theoretically needed for a complete re-oxidation of Co⁰. Any oxidation of the promoter metals or other 198 reductions/ oxidations of other Co-species were not considered in the calculations.

199 (3) $3 \operatorname{Co}^0 + 2 \operatorname{O}_2 \rightarrow \operatorname{Co}_3 \operatorname{O}_4$

200

201 2.3.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Fisher Scientific ESCALAB
 250Xi XPS System at the Center of Microscopy and Nanotechnology, University of Oulu (Finland). The catalyst
 samples were placed on an Indium film. With pass energy of 20 eV, the spot size of 900 μm, the accuracy of
 the reported binding energy was ±0.2 eV. The Al, O, Co, Re or Ru, C, In and N were measured for all samples.

The measurement data were analyzed by Avantage V5. The monochromatic AlKα radiation (1486.7 eV) operated at 20 mA and 15 kV. Charge compensation was used to determine the presented spectra and the calibration of the binding energies (BE) were performed by applying the C1s line at 284.8 eV as a reference.

205

210 2.3.7 The Diffuse Reflectance Infrared Fourier Transform

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) analyses were performed by Brüker PMA 50 Vertex 80v equipment. In the DRIFT measurements the sample was maintained in a nitrogen flow at 105 °C for 60 min for the removal of water, then the chamber was cooled down to 25 °C in a nitrogen atmosphere, Analyses resolution was 4 cm⁻¹ and 100 scans/min. Activated carbon samples were mixed with KBr (1:300) in a mortar to obtain a homogenous powder.

216

217 3. Results and discussion

218 3.1 Characterization results

219 Characterization results of untreated and treated samples are presented in Table 2. The table presents 220 surface areas, pore sizes, pore volumes, and distributions. Also, total carbon content and ash contents are 221 presented in Table 2. According to these analyses, carbonization and steam activation increased the carbon 222 content of the Kraft lignin remarkable. Surface area (see Table 2) increased from 4.6 to 810 m²/g and carbon 223 content from 65 to 96 %. According to ash content, treatment with acid removed ash/minerals from the AC. 224 Treatment with HCl seemed to remove some ash (from 6.1 to 4.8 %) and treatment with HNO₃ removed all 225 remaining (from 6.1 to 0.0 %) ash from the AC. HNO₃ treatment seemed to collapse some of the carbon 226 structure observed from decreasing surface area, pore volume, and total carbon content. Instead, HCI 227 treatment seemed to open some of the carbon pore structure that could be seen from the slight increase in 228 BET surface area.

The surface area of AC produced from Kraft lignin was rather high, 810 m²/g, (see Table 2) compared to conventionally used supports which surface area is approximately 200 m²/g or less [27-29]. Pore distribution according to BJH model of AC (see Table 2) was 32 % of micropores (diameter smaller than 2 nm), 62 % of
 mesopores (diameter from 2 nm to 50 nm) and 6 % of macropores (diameter larger than 50 nm).

Elemental analysis (C, H, O, N) was performed for activated carbon samples before Co addition and a summary of these results is presented in Table 3. Results from the elemental analysis showed that treatments with acid HNO₃ and HCl increased the amount of hydrogen in the carbon support. Treatment with HNO₃ increased nitrogen content in the AC support but the amount of oxygen decreased to zero. According to the literature, treatment with HNO₃ will increase oxygen at the carbon surface. In the results obtained from the elementary analyses, no such increase could be measured.

239 Surface area, pore volume, pore size, cobalt metal dispersion, metal particle size and metal surface area of 240 prepared and calcined Co/AC-catalysts are presented in Table 4. Impregnation with metal precursor 241 decreased the BET surface area about 10-26 % within range AC-HNO₃-Co-IW< AC-Co-IW< AC-Co-PR< AC-242 CoRe-IW< AC-CoRu-IW< AC-HCI-Co-IW< AC-Co-US. Pore volumes decreased about 10-32 % within range AC-243 HNO3-CO-IW< AC-CO-IW< AC-Co-PR< AC-CoRu-IW <AC-CoRe-IW< AC-HCI-Co-IW< AC-Co-US. With catalyst AC-244 Co-US and AC-HCI-Co-IW, the BET surface areas and pore volumes decreased most (BET surface areas 26 % 245 and pore volumes 32-27 %). Since the decrease of the surface areas and pore volumes were in some cases 246 quite high it seems an indication to that there might be some other compounds involved for example nitrates 247 from the precursor. Also, there is a possibility that some treatments e.g. US might collapse some of the AC 248 surface structure.

According to CO-chemisorption results dispersion of cobalt ranged from 0.7-10.1 % (see Table 4) within range AC-HCI-Co-IW< AC-CoRu-IW< AC-HNO₃-Co-IW< AC-CoRe-IW< AC-Co-IW< AC-Co-US. Compared to previous studies [29] with conventional supported (Al₂O₃, SiC, TiO₂) cobalt dispersion in Co/AC-catalysts was quite competitive and in some cases rather high, especially with catalyst AC-Co-US dispersion of Co was even high as 10.1 %. Also, catalyst AC-Co-IW gave quite high values for the dispersion of cobalt metal, 8.6 %. Otherwise, it was expected, and as it was discussed in introduction part that oxidation treatment leads to a higher dispersion; treatment with HNO₃ did not lead any particularly high cobalt dispersion on the surface and the metal dispersion of catalyst AC-HNO₃-Co-IW was 3.4 %. The reason for this might be that treatment with HNO₃ did not increase the oxygen content of the AC. Instead, treatment with HCl increased oxygen content in the AC (see Table 3) but also in this case no higher metal dispersion was observed, in fact, HCl treated AC proved to have the lowest dispersion from prepared Co/AC-catalysts. According to CO-chemisorption results addition of promoter metals did not give any particularly high metal dispersion and Ru- and Re-promoted catalysts were measured to have a metal dispersions of 3.2 % (AC-CoRu-IW) and 5.8 % (AC-CoRe-IW) respectively.

263 Metal contents of the catalysts were measured by ICP analysis. The expected concentration of cobalt added 264 was 10 wt. % and concentration of ruthenium and rhenium were 0.2 wt. %. The measured concentrations of 265 metals are presented in Table 5. Cobalt concentrations in catalysts were at the expected level around 10 wt. 266 % except in catalyst AC-Co-IW which contained only 5.9 wt. % of cobalt. The reason for this might be the 267 preparation step and miscalculation the amount of cobalt. The concentration of promoter metals was 268 expected to be 0.2 wt. %. The concentration of promoter Ru was in desired concentration, 0.24 wt. %. 269 Measured value of Re was 0.39 wt. %. This double sized value must have caused the preparation step in 270 which the addition of a very small amount of liquid promoter was difficult. Other metals including calcium, 271 iron, potassium, sodium and magnesium were also measured to verify if some traces of metal were left from 272 the preparation process of AC. Acid treated catalysts AC-HCI-Co-IW and AC-HNO₃-Co-IW contained these 273 metals less than 0.02%. The concentration of metal Ca was 0.02 wt. % and concentration of metals Fe, Na, K 274 and Mg were 0.01 wt. % or less and could be expected that no interference from these metals should be 275 present in catalytic use. Other catalysts (AC-Co-IW, AC-CoRu-IW, AC-CoRe-IW, and AC-Co-US) contained Ca 276 <0.04 wt. %, Fe <0.06 wt. % and Mg <0.03 wt. % and these values were guite low. Instead, concentrations of 277 Na and K were higher; Na <0.35 wt. % and K <0.11 wt. %. These metals might be traces from pulping process 278 and might interfere the catalytic activity in a negative way. [30, 31]

SEM and TEM analyses were used to verify catalyst morphology. From FESEM and TEM images (Figure 2)
taken from the catalyst AC-Co-IW can be observed that Co-particles size were around 10-20 nm which was

quite close to results from CO-chemisorption in which average Co particle size was determined to be 11.6 nm (Table 4). TEM images of AC-Co-IW also highlighted that the active metal was present in the form of spherical particles with dimensions of about 10-20 nm guite well distributed on the support surface.

SEM-EDS analyses were performed for calcined Co/AC-catalysts. The point analyze were performed at different locations and marked in the SEM images. All elements were auto-detected using Oxford Instruments INCA software. Figure 3 showed the SEM-EDS analyze sites for catalyst AC-HNO₃-Co-IW. From SEM-EDS analyses, only major components (C, O and Co) are shown in Table 6. The SEM-EDS analyses also indicated the addition of Co on the catalyst surface.

289 XRD measurements were performed for calcined but not reduced Co/AC-catalysts. XRD was used to confirm 290 the presence of cobalt in the catalysts and also to verify metal particle size. From XRD diffraction patterns, it 291 was observed that catalysts showed very broad peaks for Co oxides, indicating a high cobalt metal dispersion 292 and/or amorphous phase of support [32,33]. Since the broad peaks detected from XRD patterns calculation 293 of cobalt metal particle size, based on Scherrer equation was not reliable. However from the XRD diffraction 294 pattern (Figure 4) broad peaks indicated to CoO (111) at 2theta=36.7° and CoO (200) at 2theta=42.6°, 295 according to standard JCPDS file number (CoO 04-005-4912) which proved the presence of cobalt in catalysts.

296

297 3.2 Reducibility of catalysts

298 **3.2.1** Temperature programmed reduction (TPR)

According to the literature [34] from the H₂-TRP profile of Co/AC-catalysts three major peaks could be found; the first peak at around 320 °C corresponding the reduction of Co_3O_4 to CoO and second high-temperature peak at 450 °C related to the reduction of CoO to metallic cobalt, the third broad peak maximum around 600 °C is attributed to methane formation which is originated from the reduction of surface functional groups on the AC surface by H₂. From the H₂-TRP profile (Figure 5) in some cases, a small peak at 100 °C was detected which is due to desorption of residue moisture adsorbed on the catalysts surface. Also, the weak reduction peak at around 220 °C could be found and is due to decomposition of residual cobalt nitrate. The first reduction peak for all catalysts is found at temperature 320-380 °C and the intensity is about the same for all. With second peak reduction step corresponding to the reduction of CoO and cobalt oxides to Co^{0} there is more variety with reduction temperatures from 370 to 490 °C. A summary of H₂-TPR reduction temperature shifts is presented in Table 7. The treatment with HNO₃ (AC-HNO₃-Co-IW) seemed to shift the second reduction step to a lower temperature at 370 °C

311 The influence of support material and interaction between support and metal oxide can be observed when 312 AC supported catalysts was compared to the conventional SiO₂ supported catalyst synthesized and 313 characterized in a previous work [35]. Carbon supported catalysts presented little higher reduction 314 temperatures referred to the first reduction step with respect with traditional FT catalysts [36, 37]. The first 315 peak of reduction Co₃O₄ to CoO was around 260 °C for silica supported (SiO₂-Co) and 320-380 °C for AC 316 supported Co-catalysts while second peak related to the reduction of CoO to metallic cobalt showed 317 remarkable lower temperature for AC supported catalysts compared to silica supported catalyst (SiO₂-Co), in 318 fact, the average temperature of carbon supported catalyst is around T= 420 °C, while the reduction 319 temperature for the transition from CoO to Co presented by the SiO₂ supported catalysts is equal to T=780320 °C due to the presence of Co-silicates species, which are hard reducible species [38].

321

322 **3.2.2** Temperature programmed oxidation (TPO)

The degree of reduction (Table 8) was calculated from the theoretical value of moles of oxygen per consumed moles of oxygen using the measured Co metal content value from the ICP analysis (see Table 5). The addition of Re seemed to affect the reduction degree of the catalyst AC-CoRe-IW with the highest degree of reduction 72 %. Catalyst AC-HNO₃-Co-IW oxidized with HNO₃ had a degree of reduction 66 %. With catalyst AC-CoRe-IW, the degree of reduction was higher when compared to conventional CoRe-catalyst supported on Al₂O₃ from literature [39]. The lowest degree of reduction was calculated on catalysts AC-Co-US and it was equal to 25 %. Low values of reduction were measured also with catalysts AC-CoRu-IW (38 %) and AC-Co-IW (39 330 %). One of the reasons for the low degree of reduction might be explained due to rather small cobalt particle
331 sizes, which are harder to reduce. Overall, these values were well comparable with other tested Co/AC332 catalysts from the literature [40].

333

334 3.3 Surface functional groups

335 Functional groups of activated carbon surface were determined by diffuse reflectance Fourier transformed 336 IR (DRIFT) analysis and it was possible to identify some of the oxygen-containing functionality. One of the 337 problems using infrared spectroscopy (FTIR) of carbonaceous materials is that they are effective black body 338 absorbers and are too opaque for direct transmission analysis on the mid-infrared spectral region. The 339 addition of KBr intensifies the signal but the signal is still too weak to obtain. An alternative technique is to 340 use (DRIFT) [41, 42]. Although IR spectroscopy does not provide quantitative information about carbon 341 surface chemistry, it can identify groups created or destroyed. Produced AC's were compared with 342 commercial AC. Main peaks at area 3400 cm⁻¹, 1620 cm⁻¹ and 1620 cm⁻¹ can be found from all AC's. From the 343 spectrum (Figure 6), few changes with different AC's peaks can be detected at the area 1000-2000 cm⁻¹. 344 Notable changes with peaks from AC treated with HNO₃ were at area 1760 cm⁻¹ (carbonyl stretching of 345 guinones and carboxylic acids), 1590 cm⁻¹ (C=C stretching in the form of aromatic rings) and 1240 cm⁻¹ (C-O 346 stretches presumably from both carboxylic acid groups and phenolic hydroxyls) [43, 44]. Peaks at 1570 cm⁻¹, 1380 cm⁻¹ and 1240 cm⁻¹ might also indicate to C=N structure[23]. 347

348 XPS measurements were performed for calcined but not reduced Co/AC-catalysts to get more specific 349 information from functional groups on activated carbon, especially carbon-oxygen, and cobalt complexes.

Figure 7a shows the high resolution C1s-spectra and reveals components corresponding carbidic carbon (*BE*= 282.6-282.9 eV); graphitic or aliphatic carbon (*BE*= 284.6-285.1 eV); carbon species in alcohol or ether groups (*BE*= 286.3-287.0 eV); carbon in carbonyl groups (*BE*= 287.5-288.1 eV); carbon in carboxyl or ester groups (*BE*= 289.3-290.0 eV); and shake-up satellite due π - π * transition in aromatic rings (*BE*= 291.2-292.1 eV). Peaks in the region 286.3-287.5 eV may also present of structures C-N [45, 46]. From Table 9 can be seen that most
of the carbon atoms present in the catalyst are graphitic/aliphatic and about 15-20 % is in carbon-oxygen (or
C-N) compounds.

357 XPS spectrum of O1s-scans is presented in Figure 7b. and represents the oxygen groups on the surface of the 358 catalyst. In the O1s-spectra functional oxygen groups are divided in three different peaks representing double 359 bonded oxygen (C=O) to carbon in carbonyl, carboxyl, oxygen of quinone groups (BE= 530.4-530.8 eV); single 360 bonded oxygen (C-O) in alcohol or ester groups (BE= 532.4-533.1 eV) and chemisorbed oxygen or water (BE= 361 534.8-535.6 eV). Results showed that oxygen is in the form of double bonded oxygen and single bonded 362 oxygen quite evenly (Table 9). Moreover, catalyst AC-Co-US contained more of double bonded oxygen 363 (carbonyl/carboxyl) compounds than other catalysts while catalyst AC-HNO₃-Co-IW contained the least 364 oxygen-containing groups from the catalysts.

365 XPS results of N1s-scans are presented in Table 9. The intensities of peaks from N1s spectrum was low but 366 showed that catalysts AC-Co-PR and AC-HNO₃-Co-IW contained more nitrogen than other catalysts.

The Co2p-scan XPS results of the catalysts (Figure 7c) highlighted that, as already confirmed by the TPR, Co is present in its oxidized forms Co_3O_4 , Co_2O_3 and CoO (BE= 779-782 eV) and no Co⁰ (*BE*= 778 eV) has been found in any of the catalysts [47]. The lack of metallic Co is attributable to the fact that the Co-precursor used has an oxidation state equal to +3 and no further reduction treatments have been applied before XPS analysis.

Figure 8 highlights that the treatment with ultrasound causes a huge decrease in the content of graphitic or aliphatic carbon in AC-Co-US catalyst. It is wide discussed that ultrasounds are capable of degrading carbonyls and moreover a suitable technique to degrade graphite into other compounds [48, 49].

375 4. Conclusions

A series of Co-based catalysts supported on activated carbon and eventually promoted with Ru or Re have
been synthesized and characterized. Different pretreatments and metal addition procedures seemed to have
a high impact to the prepared Co-catalyst.

Prepared carbon support seemed to have many attractive properties including high specific surface area, proper pore distribution and high volume of mesopores and rather low ash value, which could be decreased even to zero by acid treatment. Acid treatment seemed to be important for removing inorganic compounds e.g. metals from the carbon support, which might affect to catalytic activity. Analyses including ICP-OES, SEM, TEM and XRD indicated that cobalt was successfully added onto carbon support in all catalyst preparation cases.

385 Some of the prepared Co-catalysts seemed to have good qualities (for FT-catalyst). Rather high dispersion 386 (10.1 %) of the active metal (cobalt) was measured with Co-catalyst prepared by ultrasonic assisted 387 impregnation method. Otherwise, there was an indication that a small metal particle size was difficult to 388 reduce (TPO). TPR results highlighted that carbon supported cobalt catalysts proved to have lower reduction 389 temperatures referred to the second reduction step of cobalt oxide to metallic cobalt if compared with SiO₂ 390 supported FT catalyst. Moreover, pretreatment with HNO₃ seemed to have a positive effect on reduction 391 temperatures and to a degree of reduction compared to other prepared Co/AC-catalysts. Also, the addition 392 of the promoter Re did seem to improve the reduction degree of cobalt as measured in the TPO 393 measurements. According to XPS analyses, different preparation techniques seemed to have an impact on 394 the catalyst surface structure. Further, these prepared cobalt catalysts needs a thorough testing in the pilot 395 scale FT plant.

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397 5. Acknowledgements

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401 6. References

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477	Lahti <i>et al</i> . Table captions
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479	Table 1. A summary of catalyst denotation: precursor salts, impregnation methods and calcination.
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Catalyst	Metal content	Metal salts used	Impregnation method used	Calcination
AC-Co-IW	10 wt. % Co	$Co(NO_3)_2 \cdot 6H_2O$	incipient wetness	320°C, 16h, N ₂ -flow
AC-HCI-Co-IW*	10 wt. % Co	$Co(NO_3)_2 \cdot 6H_2O$	incipient wetness	320°C, 16h, N ₂ -flow
AC-HNO ₃ -Co-IW**	10 wt. % Co	Co(NO ₃) ₂ ·6H ₂ O	incipient wetness	320°C, 16h, N ₂ -flow
AC-CoRu-IW	10 wt. % Co 0.2 wt. % Ru	Co(NO ₃) ₂ ·6H ₂ O Ru(NO)(NO ₃) ₃	one-step incipient wetness	320°C, 16h, N ₂ -flow
AC-CoRe-IW	10wt. % Co 0.2 wt. % Re	Co(NO₃)₂·6H₂O ReO₄H	one-step incipient wetness	320°C, 16h, N ₂ -flow
AC-Co-PR	10 wt. % Co	$Co(NO_3)_2 \cdot 6H_2O$	precipitation with urea	320°C, 16h, N ₂ -flow
AC-Co-US	10 wt. % Co	Co(NO₃)₂·6H₂O	ultrasonic assisted incipient wetness	320°C, 16h, N ₂ -flow

*) AC demineralized with HCl and **) AC oxidized with HNO₃ before impregnation.

518 Lahti *et al.* Table captions

519	Table 2. Surface area, pore volume, pore size, pore distribution, total carbon content and ash content of
520	the raw lignin, activated carbon and acid treated activated carbons.
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539 Lahti et al. Tab 2.

	Sample	BET			BJH I	pore distril	oution		
		Surface	Pore	Pore	Micro-	Meso-	Macro-	Carbon	Ash
		area	volume	size	pores	pores	pores	content	
		(m²/g)	(cm ³ /g)	(nm)	(%)	(%)	(%)	(%)	(%)
	Lignin, untreated	4.6	0.02	18	n.d.	n.d.	n.d.	65	n.d.
	AC	810	0.41	2	32	62	6	96	6.1
	AC, treated with HCl	822	0.41	2	34	60	6	95	4.8
	AC, treated with HNO₃	714	0.35	2	33	61	6	85	0.0
541	n.d. = not determine	ed							
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556	Table 3. Elemental analysis (C, H, O, N) for activated carbon supports.
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Sample	Treatment	C (%)	H (%)	O (%)	N (%)
AC	Untreated	86.4	0.7	2.2	0.6
AC	30% HNO₃, reflux 3h	59.6	1.9	0	1.4
AC	30% HCl, reflux 3h	79.8	1.2	4.3	0.5
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592	Table 4. Surface area, pore volume, pore size, cobalt metal dispersion, metal particle size and metal surface
593	area of Co/AC-catalysts.
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	BET	Pore	Average	Co metal	Co metal	Co metal	Co metal
Catalyst*	Surface	volume	pore size	dispersion	particle size	surface	surface
Catalyst	area	(cm ³ /g)	(nm)	(%)	(nm)	area	area
	(m²/g)					(m²/g	(m ² /g of
						sample)	metal)
AC-Co-IW	710	0.35	2	8.6	11.6	5.8	58.1
AC- HCI-Co-IW	610	0.30	2	0.7	138.5	0.5	4.9
AC-HNO ₃ -Co-IW	640	0.32	2	3.4	29.8	2.3	22.7
AC-CoRu-IW	640	0.29	2	3.2	31.0	2.2	21.8
AC-CoRe-IW	630	0.31	2	5.8	17.2	3.9	39.2
AC-Co-PR	680	0.34	2	n.d.	n.d.	n.d.	n.d.
AC-Co-US	600	0.28	2	10.1	9.8	6.9	68.6

614 *) Preparation methods presented in Table 1.

615 n.d. = not determined

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629	Table 5. Metal content in catalysts from ICP analysis.
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655 Lahti et al. Table 5.

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_	Catalyst	Со	Ru	Re	Са	Fe	Na	К	Mg
	Caldiysi	wt.%	wt.%						
-	AC-Co-IW	5.9			0.02	0.02	0.30	0.11	< 0.01
	AC-HCI-Co-IW	11.1			0.02	0.01	0.01	<0.01	<0.01
	AC-HNO ₃ -Co-IW	8.3			0.02	0.01	0.01	<0.01	<0.01
	AC-CoRe-IW	9.1		0.39	0.03	0.03	0.35	0.10	0.02
	AC-CoRu-IW	9.3	0.24		0.04	0.06	0.13	0.07	0.03
	AC-Co-PR	9.2			0.01	0.02	0.25	0.09	<0.01
_	AC-Co-US	9.8			0.04	0.06	0.21	0.07	0.03
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674	Table 6. SEM-EDS spectrum labels from catalyst AC-HNO ₃ -Co-IW.
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Lahti et al. Tab 6.

	Spectrum Label	S147	S148	S149	S150	S151	S152	S153	S154	S155	S156
	С	26.22	20.98	35.43	20.39	27.05	63.41	22.03	24.76	35.54	22.52
	0	1.06	20.11	2.40	0.71	1.40	8.44	0.85	0.99	15.91	0.84
	Со	71.82	58.53	60.49	75.82	70.36	27.39	76.10	72.67	48.19	75.32
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711	Table 7. Temperatures (°C) for reduction steps and total H_2 -consumption.
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Catalyst	Phase tran T (Total	
Catalyst	Co₃O₄→CoO	CoO→Co ⁰	(mmol/g _{cat})
AC-Co-IW	330	480	4.0
AC-HCl-Co-IW	350	410	3.3
AC-HNO3-Co-IW	320	370	6.3
AC-CoRu-IW	330	420	7.0
AC-CoRe-IW	380	480	5.2
AC-Co-PR	340	470	5.0
AC-Co-US	340	490	5.7
Co-SiO ₂	260	780	n.d.

742	Lahti <i>et al</i> . Table captions
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744	Table 8. The degree of reduction at 350°C and volume of O_2 adsorbed on the catalyst surface.
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	Catalyst	O ₂ -consumption (ml/g _{cat})	Degree of reduction (%)
	AC-Co-IW	1.2	39
	AC-HCI-Co-IW	2.2	37
	AC-HNO ₃ -Co-IW	1.9	66
	AC-CoRu-IW	1.9	38
	AC-CoRe-IW	2.2	72
	AC-Co-PR	1.8	45
	AC-Co-US	1.3	25
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779	Table 9. Spectral parameters of C1s-, O1s-, Co2p- and N1s-scans of catalysts.
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801 Lahti et al. Tab 9.

Scan	Binding Energy (eV)	AC- Co- IW (A%)	AC- HCl- Co-IW (A%)	AC- HNO ₃ - Co-IW (A%)	AC- CoRu- IW (A%)	AC- CoRe- IW (A%)	AC- Co- PR (A%)	AC- Co- US (A%)
C1s Scan								
carbidic carbon	282				7.0			
graphitic or aliphatic carbon	284–285	47.6	47.8	50.7	36.2	28.8	46.8	19.8
carbon in ethers, alcohols, phenols, amines, carbonyls, quinones, carboxyl or ester groups	286–291	12.6	13.0	21.9	14.7	9.8	11.8	7.9
π - π * shake-up peaks	291–292	12.7	12.5	9.3	14.0	7.9	11.2	10.0
O1s Scan	O1s Scan							
C=O groups	530	9.1	10.6	9.5	11.3	25.3	12.0	32.8
C-OH, C-O-C groups	532–533	10.0	8.4	2.9	9.0	14.7	9.1	11.0
chemisorbed O or water	534–536	3.6	2.4	0.9	3.5	4.2	2.9	5.9
Co2p Scan	779–782	4.0	4.8	0.9	4.6	6.0	4.8	13.8
N1s Scan	399	0.4	0.4	1.0	0.5	0.5	1.9	0.3

803 The peak area is calculated for each sample as atomic percent ratio

807	Lahti <i>et al</i> . Figure captions
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809	Figure 1. Scheme for the preparation methods of cobalt catalysts on activated carbon support.
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832 Lahti et al. Figure captions

833 Figure 2. FESEM (left) and TEM (right) images of catalyst AC-Co-IW.

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866 Lahti *et al*. Figure captions

- 867 Figure 3. SEM-EDS spectrum from catalyst AC-HNO₃-Co-IW.



898 Lahti *et al*. Figure captions

Lahti et al. Fig 4.



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927 Figure 5. H₂-TPR profiles for AC supported and SiO₂ supported Co-catalysts.

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Lahti et al. Figure captions

- Figure 6. DRIFTs spectrum for commercial AC, prepared AC and AC treated with HNO₃.

971 Lahti et al. Fig 6.



983 Lahti et al. Figure captions

984	Figure 7. High-resolution XPS spectrum of (a) C1s scans, (b) O1s scans, (c) Co2p -scans from Co/AC-catalysts.
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1007 Lahti et al. Figure captions

1008 Figure 8. Functional groups on carbon surface from C1s, O1s, and Co2p -scans.

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1038 Lahti et al. Fig 8.



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