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A COMPARISON OF PROPERTIES AND BEHAVIOR OF COAL-DERIVED, CARBON-SUPPORTED COPPER, POTASSIUM AND COBALT CATALYSTS

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Resumen-Abstract

Coal-based catalysts were prepared by adding a metal (Cu, Co, K) by ion exchange (IE) to chars obtained from pyrolysis of a subbituminous coal. The effects of pyrolysis temperature, between 550 and 1000 ºC, on some catalyst characteristics (e.g, BET surface area, XRD spectrum) are presented. Catalytic activities in C-O_2 and C-NO reactions are also compared. The BET surface area increased in the presence of the metals, especially Co, being 700 ºC the HTT for which the highest values were obtained. XRD results show that, except for Cu (which exhibits sharp Cu^0 peaks), the catalysts may be highly dispersed (or amorphous) on the carbon surface. For the C-O_2 reaction the order of activity is K >> Co > Cu. The catalytic activity for NO reduction is lower than that exhibited for the C-O_2 reaction. The K-C-IE catalyst appears to be the most promising catalyst showing similar activity as the Co- and Cu-loaded catalysts in spite of its lower metal content. Some surprising results regarding CO and CO_2 selectivity are finally shown, although their interpretation is still under study.

Introduction

Carbon has been a popular catalyst support for many years [1]. In some liquid-phase applications it is irreplaceable, because of its tolerance of both highly acidic and highly basic solutions. And yet the virtues and the flexibility of carbon supports have not been exploited to their fullest extent, mostly because of a lack of appreciation of the potentially widely varying surface chemistry of carbon materials [1, 2]. Another challenge is related to the ease of reproducible preparation and the cost of carbon-supported catalysts. We have recently initiated a research program that is meant to address both these issues, using inexpensive and abundant coal and biomass as precursors to carbon supports for several representative catalysts: potassium, copper and cobalt. As test reactions we selected H_2O_2 decomposition and NO reduction or decomposition, in which carbon can best exhibit its remarkable flexibility, not only as a support but also as a catalyst in its own right as well as a reducing agent. In addition to the practical importance of each one of these two reactions (the former is a key electron transfer step for the efficient use of batteries and fuel cells [3] and the latter is the key to effectively combating smog and acid rain), they are expected to share a crucial mechanistic feature, as summarized in the following reaction sequence:

$$2C_f + 2NO \rightarrow N_2 + 2C(O) \quad (1)$$
$$C_f + H_2O_2 \rightarrow C{-}O + H_2O \quad (2)$$
$$C(O) \leftrightarrow C{-}O \quad (3)$$
$$2C{-}O \rightarrow O_2 + 2C_f \quad (4)$$
$$2C(O) \rightarrow CO_2 + C_f \quad (5)$$

The reduction of NO (reactions 1,3,5) on the free carbon active sites (C_f) is known to follow the same general mechanism as both catalyzed and uncatalyzed carbon combustion or gasification [4]: the reactive intermediate (C(O)) is either in (temporary) equilibrium with the stable complex (C—O) or decomposes to CO_2 (at relatively low temperature, e.g., < 500 ºC; at higher temperatures CO is produced as well). In the often more desirable decomposition of NO (reactions 1,3,4), carbon acts as a true catalyst, and not also as a reducing agent. This is also a unique feature of H_2O_2 decomposition (reactions 2,4). The proposed mechanism highlights the critical importance of the surface chemistry of carbon, which in turn depends on both its pyrolysis (or heat treatment) conditions and the nature of its precursor: the relative abundance of C(O) vs. C—O surface species (e.g., at the edges of carbon crystallites and within the graphene layers, respectively) is expected to govern both carbon (re)activity and product selectivity. In the presence of an active metal catalyst (M) on the carbon support, the complementary reactions are the more effective adsorption of oxygen from NO or H_2O_2,

$$2M + 2NO \rightarrow N_2 + 2M(O) \quad (6)$$
$$M + H_2O_2 \rightarrow H_2O + M(O) \quad (7)$$

and the transfer ('spillover') of surface oxygen from the catalyst to the support

$$M(O) + C_f \rightarrow C(O) + M \quad (8)$$

In this communication we present our initial results on the preparation and characterization of such catalysts and some preliminary results of catalytic activity during NO reduction.

Experimental

Demineralization

A low-rank coal (Pecket, from southern Chile) was used as the carbon precursor. The results of its proximate analysis are listed in Table 1. The as-received particulate coal (AR-C) was ground and sieved to 53-180 μm. The size-graded coal was demineralized using the following protocol: ca. 30 g of AR-C and 200 mL of 5 N HCl was magnetically stirred at 55-65 °C for 1 h and filtered. The residue was stirred in 23 N HF (250 mL) at 55-65 °C for 1 h and filtered. This residue was stirred in 12 N HCl (200 mL) at 55-65 °C for 1 h and filtered. The filtered coal was rinsed with hot distilled water until Cl anions could not be detected (using 0.1 M $AgNO_3$ aqueous solution). The demineralized coal (H-C) was obtained after drying at 100 °C in an oven. The results of proximate analysis for H-C are also listed in Table 1.

Cation exchange treatment

Copper, potassium, and cobalt were added to H-coal by the ion-exchange method. The acetate salts of these metals, $Cu(Ac)_2$, KAc, and $Co(Ac)_2$, were used as catalyst precursors. Each H-C (35 g) with 300 mL of acetate aqueous solution (0.3 M for $Cu(Ac)_2$ and $Co(Ac)_2$, and 0.6 M for KAc) was magnetically stirred at 55-65 °C for 24 h. The pH of the suspension was not optimized. The slurry was filtered and washed with 2000 mL of the diluted acetate solution (0.01 M) and 500 mL of distilled water. The residual cation-exchanged coal was dried at 50 °C in a vacuum oven. These samples are denoted as Cu-C-IE, K-C-IE and Co-C-IE, respectively. Their metal content was determined by atomic absorption spectroscopy. For these experiments, the samples were burnt off to remove the carbon and then dissolved in HCl. The results are shown in Table 2, together with those of AR-C and H-C for comparison.

Carbonization

The cation-exchanged coal samples, as well as AR-C and H-C, were converted to chars at 550, 700, 850, and 1000 °C. An alumina boat-type crucible and a horizontal tubular furnace were used. The heating rate was 5 °C/min in a N_2 flow of 200 mL/min, and the final temperature was maintained for 1 h. The catalysts were obtained after cooling to 50 °C while maintaining the N_2 flow. The final heat-treatment temperature (HTT) is indicated by the last three or four digits in sample designation, e.g., Cu-C-IE-550.

Catalyst characterization

The catalysts were examined by means of elemental analysis, atomic absorption, thermal analysis, N_2 physisorption, and X-ray diffraction (XRD). For elemental analyses, C, H, N, and S contents were measured (Leco CHN-2000). Metal content after carbonization was determined by atomic absorption spectroscopy. Thermogravimetry (TG) and differential thermal analysis (DTA) experiments were carried out in air or N_2 flow (100 mL/min) from ambient temperature to 1000 °C at 5 °C/min (Netzsch STA 409 PC Luxx). Nitrogen adsorption isotherms were obtained at 77 K in a volumetric apparatus (Micromeritics Gemini 2360) after pretreatment at 150 °C and 20 Pa for 24 h. The XRD spectra were obtained using CuKα radiation (λ=0.1542 nm, Rigaku).

Catalytic activity for NO reduction

The reactivity of metal-loaded chars in NO was examined in a fixed-bed flow reactor at atmospheric pressure. The catalyst (ca. 100 mg) was sandwiched between quartz wools and exposed to a flow of NO in He (0.1%) at 500 mL/min. The temperature-programmed reaction (TPR) was carried out at 5 °C/min to 950 °C. The gaseous products were monitored using IR detectors for CO and CO_2 (Horiba PIR-2000) and a chemiluminescence analyzer for NO (Horiba).

Table 1. Proximate analyses of AR- and H-C coals (wt%).

	AR-C	H-C
Moisture	16.8	4.6
Ash	16.0	0.1
Volatile matter	35.3	44.8
Fixed carbon	31.9	50.5

Table 2. Metal contents in AR-C, H-C and the cation-exchanged coals (wt%).

Sample	AR-C	H-C	Cu-C-IE	K-C-IE	Co-C-IE
Na	0.23	<0.001			
Mg	0.19	< 0.01			
Fe	0.06	0.02			
Al	2.07	< 0.01			
Ca	1.29	< 0.02			
Cu	<0.01	< 0.01	3.65		
K	0.07	<0.001		1.85	
Co	<0.001	<0.001			3.35

Results and Discussion

The conventional approach to the preparation of carbon-supported catalysts is to independently produce a general-purpose activated carbon, with a maximum specific surface area and an optimum pore size distribution, and then to prepare the catalyst by selecting an adequate activated carbon support and devising a suitable metal loading procedure (e.g., dry mixing, atmospheric pressure or vacuum impregnation, ion exchange). While such an approach may have its advantages, here we have explored a more straightforward and in principle less expensive procedure.

Catalyst characterization

The summary presented in Table 3 shows the effectiveness of the ion exchange catalyst loading procedure. For example, with a 50% carbonization yield, 7.5% Cu means that close to 100% of the carboxyl groups were exchanged at the unadjusted pH of the solution. (Many low-rank coals are known to have ca. 1 mmol carboxyl groups/g.) The relatively low K content may reflect its higher volatility and its loss from the sample during the ashing step in the elemental analysis procedure. The BET surface area is seen to increase in the presence of the metals, especially Co. In Table 4 it is seen that HTT of 700 ºC is optimal for the Co catalyst from the standpoint of maximizing its support surface area.

Table 3. Properties of carbon-supported catalysts prepared at 850 ºC.

	H-C-850	Cu-C-IE-850	K-C-IE-850	Co-C-IE-850
Metal content (wt%)	0.20 (Ash)	7.52 (Cu)	(2.72) (K)	7.33 (Co)
BET area (m^2/g)	19	66	21	122
Ignition temp. (°C)	471	383	316	343

Despite the relatively low BET surface areas, the XRD results (Figures 1 and 3) suggest that, except for Cu (which exhibits sharp Cu^0 peaks), the catalysts may be highly dispersed (or amorphous) on the carbon surface: the most prominent feature of the spectra are the very broad (002) and (10) peaks of the highly disordered non-graphitic coal-derived carbon.

Table 4. Properties of carbon-supported Co catalysts prepared at 550-1000 ºC.

	Co-C-IE-550	Co-C-IE-700	Co-C-IE-850	Co-C-IE-1000
Co content (wt%)	6.71	7.28	7.33	7.47
BET area (m^2/g)	268	337	122	<10
Ignition temp. (°C)	323	303	343	441

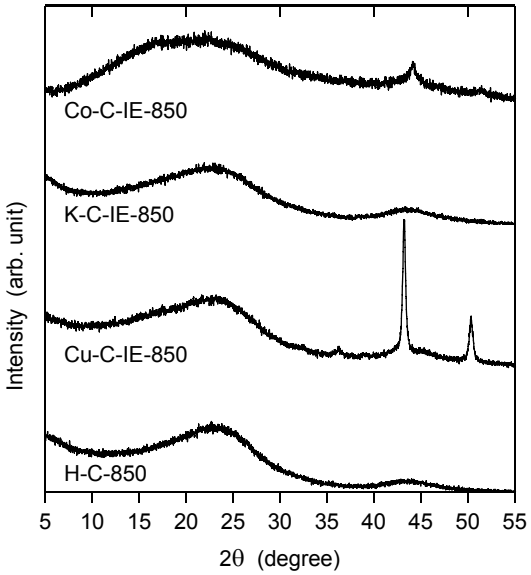

Figure 1. XRD patterns of carbon-supported catalysts prepared at 850 °C.

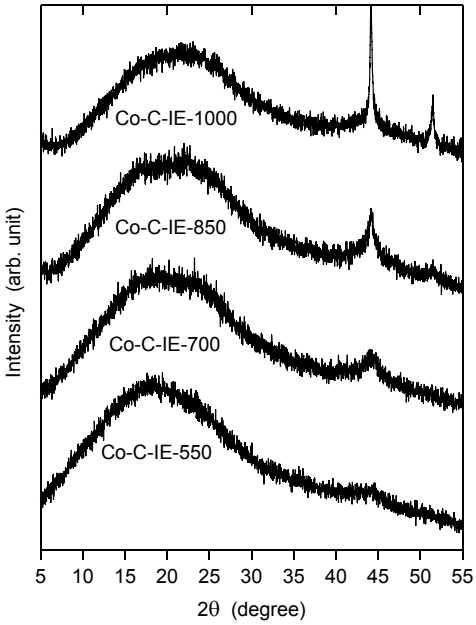

Figure 3. XRD patterns of carbon-supported Co catalysts.

Catalytic activity

The ignition temperatures shown in Tables 3 and 4 illustrate the high catalytic activity for the C-O_2 reaction. The order of activity here is K >> Co > Cu. It is interesting to note that for Co the optimum HTT (for highest catalytic activity) is 700 ºC. Figure 3 show that above 700 ºC there is dominant formation of Co^0, and the observed crystallite growth is consistent with the decrease in catalytic activity reported in Table 4.

Figure 2 shows that the catalytic activity for NO reduction is lower than that exhibited for the C-O_2 reaction. The relative effectiveness of the catalysts appears to be the same, however, when taking into account the much lower K content. Thus, for example, 10% NO reduction is achieved with Co at ca. 600 ºC, with K at ca. 620 ºC and with Cu at ca. 670 ºC. The CO evolution results are of particular interest: (a) It is intriguing that CO is desorbed in preference to CO_2, suggesting (see Eq. 5) a relatively low oxygen surface coverage. (b) The appearance of smaller amounts of CO_2 at the higher temperatures is also intriguing. (c) In the case of Cu, CO evolution starts -- and is maintained at a relatively low level -- much earlier than in the case of the more active K and Co catalysts. (d) There are significant differences in the offset between NO disappearance and CO appearance; it is least pronounced in the case of Cu and most in the case of K. Their mechanistic implications (see Eqs. 1-8) will be discussed elsewhere.

The oscillatory behavior at the higher temperatures is observed only, and consistently so, in the case of Co catalysts and it is shown in more detail in Figure 4. As the reaction temperature increases, the CO and CO_2 peaks decrease; this is confirmed by an oxygen mass balance, which also shows that in each pulse more oxygen evolves as CO than as CO_2. And as the sample HTT increases, the intensity of the peaks exhibits a maximum. Because of the opposite slopes of CO and CO_2 evolution at this stage of the reaction, the obvious possible explanation is the Co-catalyzed carbon gasification by CO_2. It is well known that transition metals lose their catalytic activity when oxidized [5]. Therefore, the intriguing (and indeed dramatic!) results shown in Figures 2 and 4 are thought to be the net effect of the following three reactions:

$$C + CO_2 \leftrightarrow 2CO$$
$$Co + CO_2 \leftrightarrow CoO + CO$$
$$CoO + C \leftrightarrow Co + CO$$

A confirmation of this proposal and the implications of these results for the design of more effective coal-based NO reduction catalysts are the subject of our ongoing research.

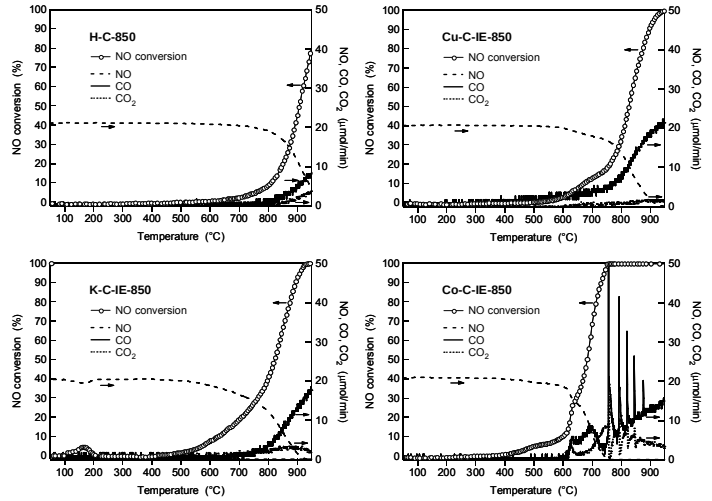

Figure 2. NO reduction behavior of carbon-supported catalysts prepared at 850 °C.

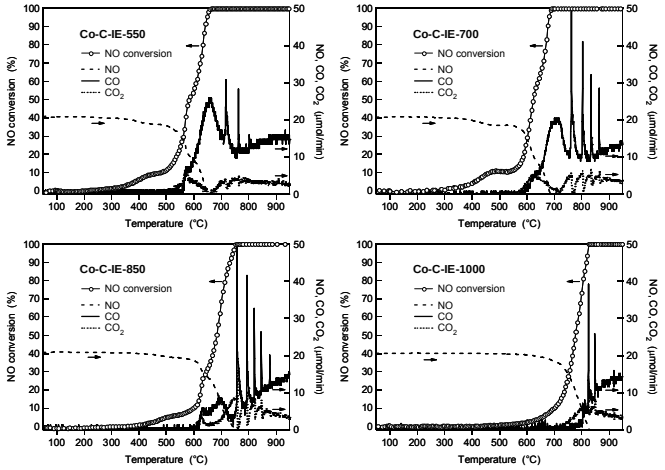

Figure 4. NO reduction behavior of carbon-supported Co catalysts prepared at 850 °C

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