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Preparation of carbon supported cobalt by electrostatic adsorption of $[Co(NH_3)_6]Cl_3$

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Abstract

Our previous paper [L. D'Souza, L. Jiao, J.R. Regalbuto, J.T. Miller, A.J. Kropf, J. Catal. 248 (2007) 165] presented the synthesis of cobalt catalysts on carbon (Timrex) and silica supports by strong electrostatic adsorption (SEA), using a cobalt hexaamine chloride ($[Co(NH_3)_6]Cl_3$, CoHA) precursor. The CoHA undergoes reductive deammination in an uncontrolled manner in the presence of NaOH and adsorbs as Co_3O_4 on carbon with broad size distribution. The present paper extends these studies toward the end of synthesizing well-dispersed Co oxide particles in a narrow size range on carbon supports using NH_4OH. Cobalt uptake versus pH was determined in NH_4OH and NaOH basified solutions over a number of carbons with varying point of zero charge (PZC). The resulting materials were characterized by ICP, powder XRD, XAS, TPR and STEM. CoHA in the presence of NH_4OH adsorbs as well dispersed as CoO, Co_3O_4 and $Co(OH)_4^{2-}$ depending upon the pH of the adsorption solution. These phases were undetectable by powder XRD and STEM Z-contrast imaging, but could be identified by XAS. Additionally, non-adsorbed CoHA complexes underwent transformation to $[Co(NH_3)_5Cl]Cl_2$ at $pH > 11$ in solution. After calcinations of 250 °C, particle sizes of Co_3O_4 range from 20–50 Å from NH_4OH and 50–200 Å from NaOH. Maximum metal uptake was approximately 3.3 and 2.7 μmol/m^2 in presence of NaOH and NH_4OH, respectively. The SEA method of preparation was compared with incipient wetness impregnation (IWI) of $Co(NO_3)_2{\cdot}6H_2O$; this method yields Co_3O_4 particles after 250 °C calcinations which are almost as small or in one case, smaller than the calcined SEA samples. Higher metal loadings can be achieved by the SEA method by successive adsorption steps with a little variation in particle size and distribution. However, the main advantage of SEA is in forming mono- or submonolayer of different Co oxide phases on carbon surface.

Keywords: Strong electrostatic adsorption; SEA; Point of zero charge; PZC; $[Co(NH_3)_6]Cl_3$; $[Co(NH_3)_5Cl]Cl_2$; Co_3O_4/C; CoO/C; Co/C; Fischer–Tropsch catalysts; Fuel cell catalysts

1. Introduction

The method of strong electrostatic adsorption (SEA) is a simple, rational method for the preparation of catalysts. Based on the "revised physical adsorption" model [2], it describes the adsorption of metals salts with the oxide support under differing pH of the adsorption solution and is successful in quantitatively predicting the Pt uptake on Al_2O_3 and SiO_2 [3–5] from the $PtCl_6^{2-}$ anion and $Pt(NH_3)_4^{2+}$ cation, respectively. The main consideration for the SEA method is whether support hydroxyl groups protonate or deprotonate at the pH of the impregnating solution. The pH at which the hydroxyl groups are neutral is termed as point of zero charge (PZC). Below this hydroxyl groups protonate and become positively charged and the surface can adsorb anionic metal complex ions such as $[PtCl_6]^{2-}$ and $[Pt(SO_4)_2]^{2-}$. Above the PZC, the hydroxyl groups deprotonate and become negatively charged, and cations such as $[Pt(NH_3)_4]^{2+}$ can strongly adsorb on the surface electrostatically. There exists a pH at which electrostatic force of attraction and hence metal complex adsorption is maximum and the catalysts prepared at that pH, followed by pretreatment, leads to nanoclusters, often between 10–20 Å, with near monodispersity (standard deviation <15% [6]).

There are a number of important applications for Co catalysts including water gas shift (WGS) [7–9], steam reforming of

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ethanol [10], Fischer–Tropsch [11,12] and methylamines [13] synthesis, and cyclocarbonylation of acetylenes [14]. Mixed cobalt oxide catalysts have also been widely used for the WGS reaction [15–17].

In our earlier work, we reported on Co/C and Co/SiO_2 catalyst synthesis by the SEA method, especially physico-chemical changes of CoHA ($[Co(NH_3)_6]Cl_3$ or hexaammine cobalt chloride) precursor during various preparation steps [1]. In that study, we found that cobalt on carbon particles are large with a broad size distribution and standard deviation. Co_3O_4/carbon catalysts with small particle size and narrow standard deviation is desirable prior to adsorption with noble metal complexes for bimetallic fuel cell catalysts [18]. The main goal of the present work is to find preparation protocol to synthesize small and near monodispersed Co_3O_4/carbon. Small unsupported cobalt particles are easy to produce and good synthetic protocols are known in colloidal chemistry especially by the thermal decomposition of carbonyl complexes [19]. But to date no well established protocols exist to synthesize near monodispersed supported Co oxide or metal nanoclusters (particle sizes between 10–100 Å [20]) from aqueous solutions with readily available metal salts. In the current work, it is shown that through control of the preparation variables, small cobat oxide particles can readily be prepared on a variety of carbon supports.

2. Experimental

2.1. Chemicals

$[Co(NH_3)_6]Cl_3$ (CoHA), $Co(NO_3)_2{\cdot}6H_2O$ and CoO (product No. 343153, −325 mesh, average particle size <10 μm) and Co_3O_4 (product No. 203114, 99.995%) were obtained from Aldrich. Commercially available carbons were obtained from the manufacturers. Their designation, surface area and points of zero charge are given in Table 1. KB-600, KB-300, BP and VXC are carbon blacks obtained by pyrolysis of natural gas or oil fraction from petroleum processing [21]. AS is natural graphite and TX is graphite produced from petroleum coke [22]. KBB and CA are activated carbons obtained through chemical activation from coconut shells, wood, peat or coal [23]. High surface area Co_3O_4 (BET surface area 38 m^2/g) was prepared from $Co(CO_3)_2$ and supplied by UOP, Des Plaines, IL.

Table 1
Physical characteristics of different carbons

Carbon source	Abbreviation	Surface area (m^2/g)	Pore vol. (ml/g)	PZC
Norit CA-1, NC 99006, Norit Americas Inc., USA	CA	1400	1.7	2.6
Timrex 04088 N754, Timcal graphite and carbon, Switzerland	TX	280	1.0	4.5
Darco KB-B, Norit Americas Inc., USA	KBB	1500	4.0	4.8
Asbury grade 4827, The Asbury Graphite Mills, Inc., USA	AS	115		5.2
Keitzen black EC 600JD, Akzo Nobel, USA	KB	1250	9.0	9.4
Vulcan XC 72, GP-3845, Cabot Corporation, USA	VXC	254	2.0	8.9
Black pearls 2000, Cabot Corporation, USA	BP	1475	7.1	9.5

2.2. Catalyst preparation

The equilibrium adsorption uptake of CoHA onto carbon was determined as a function of pH, from solutions of constant metal concentration. Adsorption experiments were conducted with an excess of liquid to prevent large shifts in the solution pH due to the oxide buffering effect [24]. The surface loading is the amount of support surface area per liter of adsorption solution. For example, 0.1 g of 250 m^2/g carbon in 50 ml of solution yields a surface loading of 500 m^2/L, or about a 500-fold excess of the TX pore volume. The 50 ml polypropylene bottles containing 200 ppm CoHA solutions and support were shaken for 1 h, after which 3–4 ml filtered solution was analyzed by inductively coupled plasma (ICP) for Co remaining in the solution. The cobalt uptake was determined as the difference in Co concentrations in the initial and post-contacted solutions. The pH was adjusted with HCl, HNO_3, NH_4OH and NaOH. The error in ICP measurement is ±5%.

Larger samples (1 g) of catalysts were prepared at the pH of maximum uptake, which corresponds to optimal condition for strong electrostatic adsorption. The filtered solids were air-dried overnight and calcined at 200–250 °C in a muffle furnace for 1 h.

Cobalt catalysts were also prepared by IWI method using CoHA or $Co(NO_3)_2{\cdot}6H_2O$. Several portions of this highly concentrated solution were added to the carbon supports with frequent mixing of the wet powder. The slurry was dried at room temperature for 24 h, followed by drying in oven at 100 °C for 12 h and finally calcined at 250 °C for 1 h.

2.3. Characterization

Powder X-ray diffraction analyses were performed using a Siemens D5000 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å) operating at 30 kV and 40 mA, operating in Bragg–Brentano geometry. A 'locked coupled' scan mode in the 20–70° 2θ range, step size of 0.01° and 2.5 s exposure for each point were used.

UV–visible spectra were recorded at a scan rate of 100 $nm\,min^{-1}$ using Perkin–Elmer spectrometer with Win Lab 5.1.4.0630 software.

Barrett–Johner–Halenda 'BJH' adsorption average pore width was calculated from N_2 adsorption experiment using Surface area and porosity analyzer, supplied by Micromeritics, model ASAP 2020.

Temperature programmed reduction (50 ml/min 10% H_2 in Ar and 50 mg of sample) and desorption (50 ml/min 100% Ar) (TPR and TPD, respectively) were conducted using AutoChem II instrument supplied by Micromeritics. A ramp rate of 10 °C/min was used in all experiments. No special gases were adsorbed prior to the TPD experiment, rather evolution of