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Development of oxygen selective adsorbents for gas separation and purification

D. Zhang · N. A. Stephenson

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Abstract Development, characterization, and testing of oxygen selective chemical adsorbents (chemisorbents) for cyclic gas separation and purification applications using pressure cycling are described herein. Three structurally related compositions, designated **IA-1**, **IA-2**, and **IA-3** offer high oxygen capacities and selectivities coupled with fast uptake kinetics. Extended lifetime tests for **IA-3** indicate a half-life of 17 years with 0.01 % oxygen at 60 °F under cycling conditions. Hazard testing results are presented and these data impose some restrictions on handling and use. For practical applications using packed beds of adsorbent in pressure-swing cycles, agglomeration is required to produce larger particles using formulations and methods that minimize the impact on oxygen binding. Methods are described herein using polymeric binders that provide the necessary physical features while maintaining adequate adsorption performance characteristics. Proof of concept oxygen removal test results are also described.

Keywords Oxygen-selective · Chemical adsorbent · Chemisorbent · Lifetime · Cobalt complex

D. Zhang
Vigor Gas Purification Technologies, 5100 Westheimer Road, Suite 200, Houston, TX 77056, USA

N. A. Stephenson (✉)
Adsorption R&D, Praxair Inc., 175 East Park Drive, Tonawanda, NY 14150, USA
e-mail: neil_stephenson@praxair.com
URL: www.praxair.com

1 Introduction

The interaction of molecules with surfaces is a continuum of behavior spanning weak intermolecular forces (physisorption) through irreversible chemisorption as illustrated with examples in Fig. 1.

Many have recognized that reversible chemisorption is desirable since it can offer very high selectivities without the need for a chemical regeneration step. Although practical systems exist for reversible CO chemisorbents (Xie et al. 1990; Peng et al. 1996; Huang et al. 1999) there are no broad commercial applications of reversible oxygen chemisorbents. This is in part due to the lack of compositions that meet all practical needs including working capacity and lifetime. Examples of compositions that exhibit reversible oxygen chemisorption in the solid state include a functionalized metalloporphyrin (Nishide et al. 1997), a Schiff base complex denoted “Fluomine” which exhibited a half-life of 10 months under cycling conditions (Adduci 1976), and a member of the lithium pentacyanocobaltate complex family which showed a half-life of 5 months (Ramprasad et al. 1992, 1997). In addition, several groups have reported supported and polymeric cobalt(II) coordination complexes that exhibit oxygen selective behavior (Mullhaupt et al. 1999; Hutson and Yang 2000; Wang et al. 2002). This manuscript describes compositions and characteristics for adsorbents that exhibit reversible oxygen chemisorption and the results of testing necessary for commercial use. These materials will be referred to as oxygen selective adsorbents.

The characteristics that are necessary for a practical commercial adsorbent include: high working capacity and selectivity, fast interaction kinetics, extended lifetime, and minimal hazards. Based on prior work for reversible oxygen binding in solution and in the solid state (Jones et al.

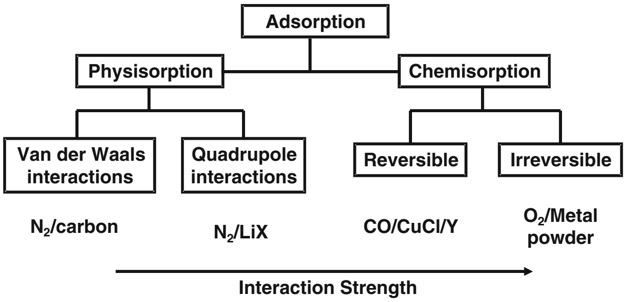


Fig. 1 Continuum of interactions between adsorbents and adsorbates

1979; Busch and Stephenson 1990), the development of a practical adsorbent requires structural features including: 5-coordinate metal center with a vacant site for oxygen with preferred superoxo binding ($M:O_2 = 1$), and with no acidic protons or peripheral sites susceptible to oxidation. The pentacyanocobaltate series represent an elegant approach to generate high concentrations of 5-coordinate active sites in 3-dimensional frameworks. A disadvantage of this approach is the modest structural modifications that can be applied to manipulate oxygen binding characteristics (isotherm shape). The current work describes oxygen selective adsorbents using cobalt(II) sites in coordinating ligands including materials development, characterization, and testing relating to their potential use in pressure swing adsorption (PSA) processes for industrial gas separations. The systems described combine structural variability and features that enable self-assembly to generate 3-dimensional microporous structures. Since the compositions contain a significant organic fraction, hazard testing was performed focusing on oxygen compatibility. The practical application of oxygen selective adsorbents in packed beds requires particle sizes >1 mm rather than as-synthesized powders. Therefore, agglomeration of as-synthesized powder to larger particles is described in a manner that provides adequate physical characteristics including low attrition and also minimizes impact on adsorption capacity and rate.

2 Experimental

2.1 Adsorption measurements

All gases were purified prior to use using standard methods and equipment to remove residual moisture. Single component isotherms were recorded using custom-made pressure microbalance systems based on Sartorius balances readable to 0.1 μg and with a gas manifold and pressure transducers to introduce gases at predetermined pressures. The systems also include vacuum for pressure adjustment and heating capabilities to control temperature and perform in situ activation. All data are corrected for buoyancy effects using values determined experimentally for each sample using helium as a non-adsorbing gas. Thermogravimetric analysis (TGA) experiments were performed on TA Instruments 2050 units equipped with a TA Instruments Gas Switching Accessory connected to oxygen and nitrogen supplies. Pressure and flow control was accomplished using Alicat Scientific mass flow controllers and back-pressure regulators. To facilitate handling of air-sensitive samples and to minimize the impact of system leaks, the testing of active forms was performed in a nitrogen purged M Braun glove box equipped with a recirculating purifier. TGA studies for samples starting from the solvated precursor were performed without the glove box as a secondary atmosphere but using a heating sequence to provide in situ activation. Differential scanning calorimetry (DSC) studies were performed on a TA Instruments DSC 2010 unit connected to oxygen and nitrogen through manual valves. Samples were loaded in a solvated form and activated in situ. Volumetric adsorption measurements using carbon dioxide to examine microporosity of **IA-1** powder were performed using a Micromeritics ASAP 2010 unit and a cooling bath to maintain a temperature of 195 K.

2.2 Characterization studies

X-ray powder diffraction (XRD) data were collected using a Philips Xpert system. Atmosphere control was performed using an Anton Parr hot stage accessory connected to oxygen and nitrogen through manual valves. The sample was loaded in a solvated state and activated in situ by heating to 75 °C under nitrogen flow. The X-ray crystal structure of solvated **IA-1** was performed at the Hauptman-Woodward Medical Research Institute in Buffalo, New York to confirm structural ordering and the nature of intermolecular organization.

Magnetic susceptibility measurements were performed using a Johnson Matthey Magnetic Susceptibility Balance to monitor changes in magnetism resulting from storage in air. All values are reported in Bohr Magnetons (BM) and include a diamagnetic correction using Pascal's constants.

2.3 Hazard testing

Minimum ignition energy and chargeability tests for **IA-3** powders were performed by Chilworth Technology Inc. of New Jersey. Flammability tests related to UN Transport of Dangerous Goods were performed for **IA-3** at Stresau Laboratory Inc. of Wisconsin. Limiting oxygen concentration (LOC) tests were performed by the Materials Engineering Laboratory at Praxair.

2.4 Agglomeration

Agglomeration by extrusion was accomplished by dissolving candidate polymeric binders in reagent grade solvents then combining this solution with oxygen selective adsorbent powder. In all cases, the oxygen selective adsorbents were insoluble in the solvents selected for polymers. The resulting pastes were extruded using either a hand-made screw extruder, or an LCI Benchtop Granulator. Extruded materials were either allowed to dry by solvent evaporation or were added to a polymer non-solvent to induce phase separation followed by removal from the non-solvent and evaporative drying. After drying, samples were activated prior to testing to remove residual solvent as previously described.

2.5 Lifetime testing

A lifetime testing unit was constructed in-house to evaluate impact of temperature, oxygen concentration, and water content. This unit allowed 25 independent tubes containing **IA-3** to be automatically cycled between feed consisting of nitrogen containing defined oxygen and moisture contents and nitrogen every 10 min. The system pressure on the feed step was maintained at 100 psig using back pressure regulators and the regeneration purge was maintained at 2 psig. Feed oxygen concentrations of 1 and 0.1 % were introduced by mixing oxygen and nitrogen using mass flow controllers, while 0.01 % oxygen was introduced using permeation tubes supplied by Kin-Tec. Water was introduced into some of the streams as a test parameter at levels of 5, 1, and 0.1 ppm using Kin-Tec permeation tubes (Span-Pac Precision Standards Generator model 61 for water only, and model 61/171 for water and oxygen). The temperature of tubes containing adsorbent was controlled within ±0.5 °C using water baths. Samples of **IA-3** were removed periodically and adsorption behavior was assessed using a TGA unit within a glove box for sample transfer. The system was operated for 12 months to accurately define lifetimes over longer periods consistent with commercial use.

3 Results and discussion

3.1 Adsorbent synthesis and characterization

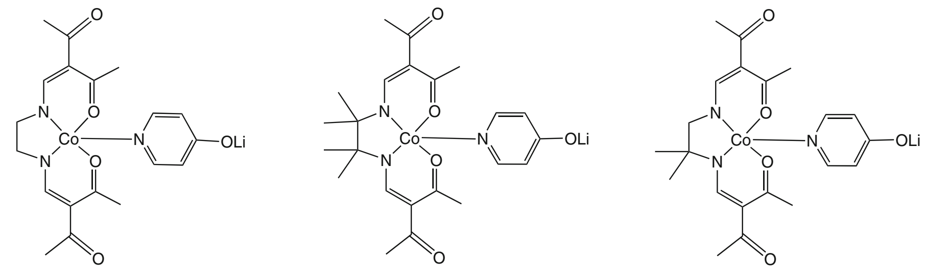
Oxygen selective adsorbents with suitable combinations of performance and lifetime are a key to achieving commercial success. In addition, the pressure dependence of oxygen uptake (oxygen isotherm) determines the suitability of a material for a particular application (separation or purification). A family of materials is described that uses peripheral groups for formation of extended arrays with 5-coordinate deoxy sites by "Intermolecular Assembly". The chemical structures of the three adsorbent compositions described herein are illustrated in Fig. 2 and differ in the substituents on the saturated 5-membered saturated chelate ring derived from a 1,2-diamine precursor. IA-1 is derived from ethylenediamine (en), IA-2 is derived from tetramethyl(ethylenediamine) (tmen), and IA-3 is derived from dimethylethylenediamine (dmen). The naming convention is described in detail elsewhere (Zhang and Stephenson 2006). These substituents have a major impact on adsorption characteristics and their suitability for oxygen separation and purification applications. The composition, designated **IA-1**, represents the simplest structure and was used in initial structural studies.

The synthetic pathway to cobalt(II) complexes from common raw materials is illustrated in Fig. 3 for the composition designated **IA-3**. Details of the synthesis have been described elsewhere (Zhang and Stephenson 2006). The overall yield of **IA-3** from the coordinating ligand precursor (3-step procedure) is 82 % and the oxygen uptake at 760 mmHg and 27 °C is 6.52 wt% (2.04 mmol/g). This uptake is close to the stoichiometric uptake of 2.14 mmol/g for **IA-3** (one oxygen molecule per cobalt, molecular weight 466.3) indicating that the experimental sample is relatively pure.

Confirmation of the intermolecular assembly was demonstrated for **IA-1** methanol solvate based on single crystal X-ray diffraction. Crystals suitable for study were obtained directly from a synthesis solution by slow evaporation of methanol solvent within an inert atmosphere glove box. Single crystals were transferred to thin-wall glass capillary tubes and mineral oil was used to temporarily seal the opening. Immediately after removal from the glove box, the tubes were sealed using a thin flame. The crystal structure indicated a space group of $P2_1/c$ with a = 11.951 Å, b = 15.988 Å, c = 12.825 Å and with beta 105.90°.

The structure (Fig. 4, left) illustrates the basic 5-coordinate cobalt unit comprising the chelating ligand providing N_2O_2 donors to the cobalt site, and the nitrogen atom of a substituted pyridine group. Further organization occurs whereby the peripheral OLi units of the substituted pyridine in neighboring units combine to form an Li_2O_2 square (Fig. 4, right) with additional coordination to lithium by the oxygen atoms of the methanol solvate. A fourth coordination site on lithium is occupied by the oxygen atom of an acetyl substituent on the ligand periphery of an adjacent unit. The details of the X-ray crystal structure for non-hydrogen atoms are summarized in Table 1.

Although it was not possible to obtain single crystals of **IA-1** in the absence of methanol solvate, reversible structural changes were demonstrated using X-ray powder



IA-1

Co(Me$_2$Ac$_2$H$_2$malen)(PyOLi), en refers to ethylenediamine (1,2-diaminoethane)

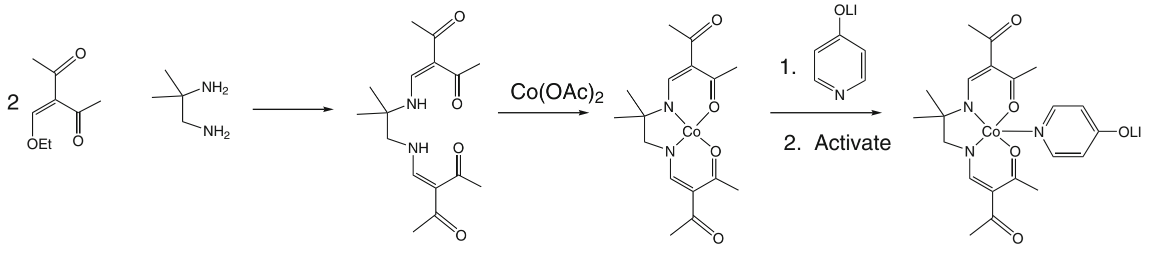
IA-2

Co(Me$_2$Ac$_2$H$_2$maltmen)(PyOLi), tmen refers to 1,1,2,2-tetramethylethylenediamine (2,3-diamino-2,3-dimethylbutane)

IA-3

Co(Me$_2$Ac$_2$H$_2$maldmen)(PyOLi), dmen refers to 1,1-dimethylethylenediamine (2-methyl-2,3-diaminopropane)

Fig. 2 Structures for oxygen selective compositions



IA-3

Fig. 3 Synthetic pathway for Adsorbent composition **IA-3**

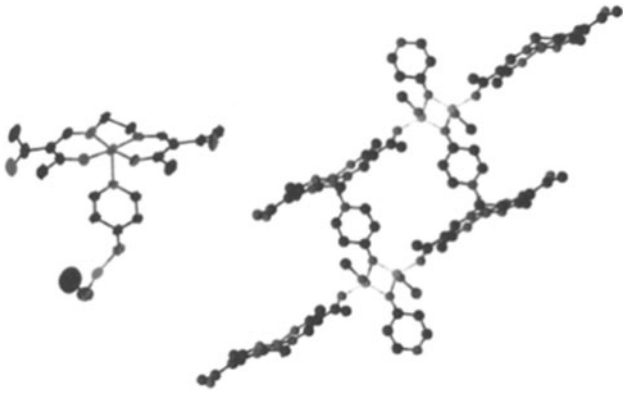


Fig. 4 Single crystal X-ray structure of **IA-1** illustrating subunit (*left*) and intermolecular packing (*right*)

diffraction. A powder sample of **IA-1** methanol solvate was loaded in an Anton Parr hot stage accessory and activated in situ using heat and nitrogen purge. Switching the atmosphere of the accessory between nitrogen and oxygen resulted in a reversible change in diffraction pattern (Fig. 5). These findings support a belief that the desolvated form of **IA-1** and the oxygenated form remain crystalline. The powder diffraction data were indexed and the best fit for both cases is monoclinic, space group C2 suggesting that there are subtle rather than large structural changes. Data are presented in Table 2. Under oxygen, the unit cell volume increases by 2.5 %. In spite of the modest structural changes, no hysteresis was observed on oxygen isotherms. A slow oxygen desorption for **IA-1** is attributed instead to its high oxygen affinity.

Carbon dioxide uptake measurements were performed for **IA-1** in an active (desolvated) state to investigate inherent crystal porosity. A sample of **IA-1** methanol solvate was activated by heating under vacuum at 75 °C for 3 h. The activated **IA-1** was transferred to a sample tube in a glove box and the sealed sample was loaded onto a volumetric adsorption unit (Micromeritics ASAP 2010). Data analysis for carbon dioxide adsorption measurements at 195 K indicated a BET surface area of 156 m^2/g and the Horvath-Kawazoe method provided a median pore diameter and maximum pore volume of 5.1 Å and 0.080 cc/g respectively.

3.2 Adsorption behavior

The oxygen interaction of the compositions **IA-1**, **IA-2**, and **IA-3** were obtained using single component measurements on a gravimetric system and differ significantly as summarized in Table 3. Oxygen isotherms for **IA-1** and **IA-3** are shown in Fig. 6. In all cases, no hysteresis was observed. Nitrogen uptake values for **IA-1** and **IA-3** are too low to measure accurately at low pressures. The nitrogen uptake values for **IA-1** and **IA-3** at 1,000 mmHg and 27 °C are

Table 1 X-ray crystallographic data for **IA-1** methanol solvate

ATOM	x	y	z	U11	U22	U33	U23	U13	U12
CO	0.038402	0.83206	0.48816	0.0703	0.0407	0.0579	0.00119	0.00565	−0.0013
C1A	0.091828	0.81811	0.71165	0.0934	0.0616	0.0529	−0.0049	0.00478	−0.0182
N2A	0.006567	0.7902	0.61169	0.0584	0.0632	0.0416	−0.0107	0.01461	−0.0007
C3A	−0.07358	0.73774	0.61782	0.0533	0.0635	0.0675	0.0093	0.01471	0.00128
C4A	−0.15935	0.7047	0.53042	0.0612	0.0558	0.0772	0.00645	0.01603	−0.0008
C5A	−0.15716	0.72161	0.42097	0.0592	0.0578	0.0724	−0.0066	0.01166	−0.005
O5A	−0.08341	0.76726	0.39705	0.0619	0.0573	0.0598	−0.0047	0.00498	−0.0084
C6A	−0.24478	0.68463	0.32414	0.1022	0.0861	0.0811	−0.0154	−0.0051	−0.0343
C7A	−0.24953	0.65142	0.54915	0.0565	0.047	0.0824	0.00845	0.0142	0.00645
O7A	−0.33937	0.6339	0.4814	0.0757	0.0979	0.1032	0.0201	0.00261	−0.025
C8A	−0.24032	0.61804	0.66191	0.1383	0.072	0.0802	0.00805	0.03441	−0.025
C1B	0.122577	0.90655	0.6893	0.103	0.0529	0.0631	−0.0133	0.01188	−0.0141
N2B	0.132279	0.91208	0.57809	0.0969	0.0415	0.0542	0.00094	−0.0014	−0.0115
C3B	0.195561	0.96736	0.55285	0.0884	0.0453	0.0749	0.0003	0.01215	−0.0089
C4B	0.208552	0.98017	0.44518	0.0725	0.0458	0.0893	0.00529	0.01656	−0.0024
C5B	0.133725	0.93984	0.35736	0.0828	0.0623	0.0681	0.00886	0.02801	0.00144
O5B	0.056019	0.88435	0.36143	0.0847	0.0674	0.0464	0.00116	0.01218	−0.0096
C6B	0.130777	0.95918	0.23996	0.1276	0.0907	0.0785	0.00811	0.0301	−0.0278
C7B	0.301403	1.03339	0.43032	0.0923	0.0656	0.1011	0.02985	0.01571	−0.0093
O7B	0.338277	1.03147	0.35069	0.125	0.1265	0.1138	0.03413	0.03616	−0.0351
C8B	0.363995	1.09371	0.52621	0.1377	0.0819	0.1458	0.00406	0.00075	−0.0439
LI	0.54234	0.55025	0.43566	0.0847	0.0539	0.1216	−0.0063	0.00762	−0.0107
N1	0.169071	0.7417	0.48965	0.0557	0.0556	0.0559	−0.0028	0.01416	−0.0005
C2	0.35826	0.69907	0.47566	0.0587	0.0562	0.1251	−0.0076	0.02043	−0.0024
C3	0.271216	0.75596	0.47508	0.0585	0.0578	0.0844	0.00063	0.01926	0.0067
C4	0.335297	0.6121	0.48896	0.0578	0.0525	0.0953	0.0009	0.01684	0.00362
O4	0.414276	0.55745	0.4906	0.0806	0.0554	0.1501	0.0087	0.03405	0.01771
C5	0.145509	0.65913	0.50047	0.0598	0.0595	0.0863	−0.003	0.01853	0.00509
C6	0.228014	0.59672	0.50062	0.072	0.0504	0.0972	0.00527	0.02937	0.00478
O1	0.508353	0.55042	0.27533	0.1199	0.1755	0.1045	−0.044	0.01753	−0.0278
C2	0.446271	0.63224	0.21874	0.1714	0.2709	0.2456	0.04489	−0.0447	0.00057

IA-1 ($C_{80}H_{104}N_{12}O_{24}Co_4Li_{-4}$) space group $P2_1/c$, a = 11.951 Å, b = 15.988 Å, c = 12.825 Å, beta = 105.90°

All site occupancy factors fixed at 1. R1 = 0.1069 for 1333 Fo > 4sig (Fo), and 0.2434 for all 3,471 data

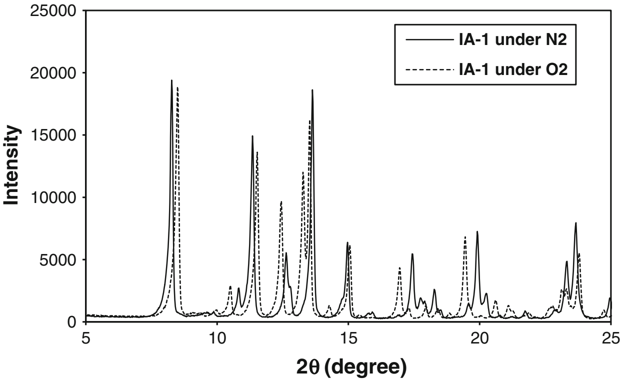


Fig. 5 Changes in X-ray powder diffraction with oxygen exposure of **IA-1**

0.012 and 0.035 mmol/g respectively. Nitrogen isotherms are assumed to be linear for selectivity calculations and this is supported by additional nitrogen data to higher pressures. Calculated selectivities for oxygen over nitrogen from single component uptake data at 10 mmHg are >1,000 consistent with a chemisorption mechanism and sites specific for oxygen.

The half-saturation pressure is a useful feature to describe materials that exhibit Langmuir behavior since it represents the pressure at which half the sites are oxygenated and reflects the shape of the oxygen isotherm. Materials with low half-saturation pressures have high affinities for oxygen and can be difficult to regenerate. For example, regeneration of the composition **IA-1** requires vacuum or extended purge

Table 2 Indexed powder diffraction data for **IA-1**

Sample	a (Å)	b (Å)	c (Å)	Â (°)	Volume (Å^3)	Space group
IA-1 N_2	13.138	16.357	15.873	137.4	2309.0	C2
IA-1 O_2	13.390	16.905	16.198	139.8	2366.7	C2

Table 3 Summary of oxygen binding characteristics for **IA-1**, **IA-2**, and **IA-3** at 27 °C

	IA-1	IA-3	IA-2[a]
O_2 half-saturation pressure (mmHg)	1	2	100–750
O_2 capacity @ 10 mmHg (mmol/g)	2	1.67	0.5–1.5[b]
O_2/N_2 selectivity @ 10 mmHg	17,000	4,700	100–300

[a] Pretreatment dependent

[b] Capacity range at 750 mmHg

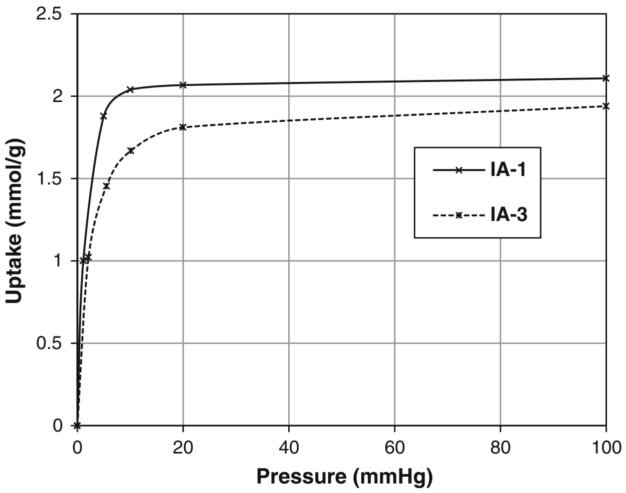


Fig. 6 Oxygen isotherms for **IA-1** and **IA-3**

which limits the practical applications for a reversible operating mode. Similarly, the practical use of an adsorbent reflects the working capacity between partial pressures that are achievable within reasonable economic constraints of vacuum and compression equipment. The isotherm shape for **IA-3** at temperatures near ambient indicate saturation at relatively low partial pressures making it better suited to purification applications.

A combination of DSC and TGA tests provided a direct measurement of the heat of adsorption for **IA-3** upon switching from nitrogen to oxygen. The value obtained of −14.3 kcal/mol(O_2) is consistent with ranges reported in the literature for cobalt(II) complexes (Jones et al. 1979; Busch and Stephenson 1990).

The oxygen uptake for **IA-2** is strongly dependent on the oxygen pretreatment, particularly the temperature, oxygen pressure, and duration. For example, exposure of **IA-2** to 10,000 mmHg oxygen at 27 °C changes the subsequent sorption performance, with longer exposure providing higher oxygen loadings in the low pressure region. The optimal activation procedure employs modest oxygen pressures at subambient temperatures. Repeated exposure of **IA-2** to 760 mmHg oxygen at low temperature (0 to −50 °C) provided the maximum oxygen capacity at modest pressures. The binding mode for oxygen with **IA-2** after oxygen pretreatment was examined using infrared spectroscopy. Exposure to oxygen resulted in a new signal at 1,143 cm^{-1} which is consistent with superoxide (Jones et al. 1979). This superoxo binding mode is typical of cobalt(II) complexes and was observed for other materials described herein.

Significantly, the **IA-2** oxygen pretreatment can be adjusted to prepare oxygen isotherms between the extreme cases that remain stable on cycling over several months. The impact of pretreatment on oxygen binding is illustrated in Fig. 7. The origin of this oxygen isotherm tuning remains unclear. Gravimetric data indicate no net weight change during the pretreatment ruling out either ligand oxidation or more thorough solvent removal. The observations support a change in crystal structure to a metastable form that provides greater access to oxygen binding sites. No X-ray data were obtained to support this hypothesis. Extended cycling tests for **IA-2** at 27 °C resulted in a slow performance decline (12 % in 2 months), possibly due to decay of the active phase. The oxygen uptake behavior of **IA-2** following pretreatment is more suitable for bulk air separation than **IA-1** and **IA-3** since the working capacities under reasonable feed and regeneration conditions is higher.

3.3 Hazard assessment

Since the intended application of oxygen selective adsorbents involves oxygen exposure, and the structures contain a significant organic component and a transition metal

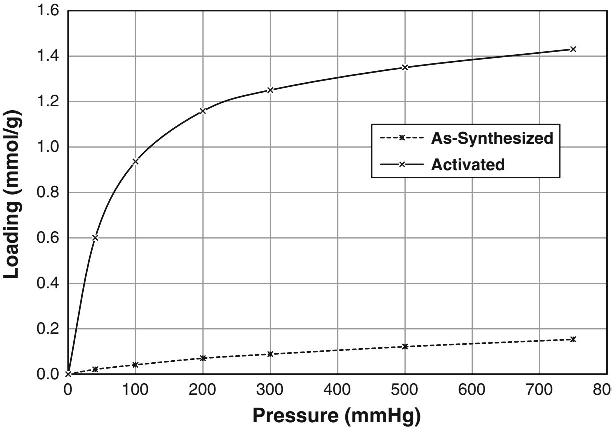


Fig. 7 Impact of pretreatment on **IA-2** oxygen binding at 27 °C

center capable of activating oxygen, it is important to understand any limitations that may exist for handling and application of these adsorbent structures. In all hazard tests, adsorbent powders were used and samples were pretreated as necessary to ensure that they were in their active form capable of binding oxygen. The use of active powders is viewed as a worst case for conditions that may be encountered in material preparation and use. Initial screening studies were performed using TGA methods for candidate samples in air and oxygen using a heating rate of 1 °C/min. The composition designated **IA-1** showed weight loss in air consistent with ligand degradation above 200 °C and loss of temperature ramp and rapid weight loss consistent with combustion at 360 °C. These values decreased under oxygen purge to initial weight loss near 180 °C and combustion at 300 °C. For the composition designated **IA-3**, the initial weight loss in air occurred at 200 °C with combustion at 390 °C. Under an oxygen purge **IA-3** showed an initial weight loss at 190 °C and combustion at 370 °C. These screening tests using small quantities (<100 mg) of **IA-3** as a shallow layer did not highlight specific concerns. Oxygen compatibility testing was expanded to include larger quantities of **IA-3** including dust clouds. Autothermal ignition testing for **IA-3** under static conditions with 35 psig oxygen indicated a value of 130 °C with self-heating from 6 to 65 °C/min. This value is low compared to many common materials such as oils.

Tests were performed for **IA-3** powder in air relating to the U.N. Transport of Dangerous Goods. Ignition of an unbroken strip of **IA-3** powder 250 mm long by 20 mm wide by 10 mm high on a cool, impervious base plate resulted in a propagation time over a 100 mm length of 7.6 s (average of 6 runs). Use of a wetting agent (Triton 100 surfactant) applied across the strip at a point past the timing zone did not stop propagation. These data indicate that **IA-3** meets the definition of a Division 4.1 Flammable solid, Packing group II.

Additional tests were performed to examine the LOC which is the minimum concentration of oxygen necessary to support combustion. This test helps to define the conditions that are necessary for safe use and storage. At atmospheric pressure, **IA-3** bulk powder has an LOC value of 13 % oxygen indicating that the material will burn in air. At elevated pressures up to 400 psig, the LOC for **IA-3** bulk powder is 9 % oxygen with onset of adiabatic self-heating at 85 °C. Based on these data, the recommended maximum storage or process temperature for **IA-3** bulk powder in oxygen purities at or above the LOC is 60 °C.

Hazard testing results indicate that the hazards associated with **IA-3** dust clouds are substantially greater than for **IA-3** powder. **IA-3** dust has an LOC value of 2–5 % oxygen. The minimum ignition energy of 5–10 millijoules was measured using a 63 mm internal diameter vertical tube of acrylic/glass with total volume approximately 1 L equipped with a compressed air dust dispersion system and 2 mm brass electrodes to generate capacitive sparks of known energy. This range indicates a high sensitivity to ignition and requires special attention during handling of powders. Autoignition of **IA-3** dust occurs at a temperature of 340–360 °C. Based on these test results, **IA-3** dust is ranked as a 'strong explosive' at or above its LOC (2–5 % oxygen) and with dust concentrations of 250–1,250 g/m^3. At dust concentrations from 125 to 1,500 g/m^3 the rating dropped to a 'weak explosive'. Chargeability tests were performed under low relative humidity conditions by pneumatically conveying a known amount of powder using air velocities of 15 and 20 m/s through tubes of different materials, collecting the powder in a Faraday cup, and measuring the charge using an electrometer. Average chargeability values based on multiple runs are $+4.5 \times 10^{-6}$ C/kg (stainless steel), $+1.2 \times 10^{-7}$ C/kg (polypropylene), and $+8.4 \times 10^{-8}$ C/kg (glass). The values for stainless steel and polypropylene are considered to have moderate chargeability, while the value for glass indicates low chargeability. The chargeability coupled with a low ignition energy pose a handling concern at or above the LOC.

It is evident that **IA-3** dusts are potentially more hazardous than bulk powder. It is therefore important to control, minimize, or eliminate dust formation and to ensure adequate atmosphere control. Methods to mitigate combustion and control dusting are critical. In addition, it is apparent that purification applications represent a lower risk than bulk air separation in view of the oxygen partial pressures involved.

3.4 Agglomeration methods

Agglomeration of oxygen selective adsorbent powder must be accomplished in a manner that minimizes impact on oxygen binding equilibria and kinetics while maintaining adequate physical characteristics including crush strength and attrition. In light of the results of hazard assessment tests for **IA-3** dusts, a screening test was developed to assess the attrition of **IA-3** agglomerates. This test involves shaking a preweighed sample of agglomerated particles in a glass vessel for days and weighing the amount of fines.

A brief survey of agglomeration technologies revealed that many common methods are not applicable to the current compositions. For example, clay binders commonly used for agglomeration of zeolite adsorbents require processing temperatures >500 °C which exceeds the thermal stability limits for **IA-3**. Compaction methods were evaluated including additives such as microgranular cellulose, Acrawax C and poly(phenylene oxide) (PPO) with contents from 10 to 30 %. Although tablets can be prepared that meet physical requirements and maintain oxygen equilibria (consistent with fraction of active material), the relatively high compaction forces required (2,000–6,000 lbF) resulted in slower oxygen uptake and release rates. Additives such as Nylon or Rayon fibers can dramatically increase the strength of compacts at equivalent force and result in compression and deformation rather than breakage. Due to concerns associated with the rate decrease and the potential cost of large scale production, alternative approaches were examined.

The agglomeration of oxygen selective adsorbents using polymeric binders was achieved by mixing adsorbent powder with binder solution to form a paste, which is dried to obtain beads. Extrusion of dough-like mixtures of **IA-3** with 10 % polymeric binder results in samples that combine good physical strength, equilibrium performance, and relative oxygen uptake and release rates. Polymer selection was explored, but it is evident that conventional low-cost polymers such as poly(phenylene oxide) (PPO), poly(vinyl chloride), and poly(vinyl acetate) can fulfill the agglomeration needs. Comparison of evaporative drying of extrudates with wet-dry phase inversion using a polymer non-solvent showed that the former is preferred based on piece density and crush strength. **IA-3** extrudates with 10 % PPO prepared by extrusion/evaporation showed minimal degradation in extended attrition tests. The fragments tended to be large enough that formation of a dust cloud would be unlikely.

The properties of **IA-3** samples produced with high molecular weight PPO using different agglomeration methods are compared in Table 4. Some minor capacity variations reflect the quality of the initial **IA-3** powder that was used. The relative oxygen uptake and release rates were obtained directly from TGA measurements switching to oxygen then nitrogen using initial slopes following gas composition changes. Crush strength values above 10 lbF are acceptable for most applications. Extrusion followed by solvent evaporation appears to give the best combinations of capacity, rate, density, and crush strength.

Parametric studies were performed to optimize porosity, density, and capacity using a hand-operated extruder. The best procedure uses 10 % poly(phenylene oxide) as a binder, toluene as the polymer solvent, and evaporative drying. Attrition is very low based on in-house extended attrition evaluations, and the extrudate piece densities as determined by mercury porosimetry are near 0.7 cc/g. These methods were extended using an LCI Benchtop Granulator to prepare 1 lb of agglomerated **IA-3** for extended lifetime studies.

3.5 Lifetime studies

The initial lifetime studies were performed using **IA-1** powder. Storage of **IA-1** powder in ambient air caused a 50 % loss in oxygen capacity over 2 days versus a fresh sample, but the capacity stabilized at this level. For **IA-3**, storage in ambient air at room temperature resulted in a complete loss in oxygen capacity after 42 days and a drop in magnetic moment from 1.95 to 1.19 BM. Typical ranges of effective magnetic moment for low spin cobalt(II) are from 2.0 to 2.7 BM. The potential role of hydroxyl groups (such as from water) in the room temperature decomposition of **IA-3** is also noted from cycling experiments, particularly the effect of pretreatment. The half-life of **IA-3** at 27 °C based on TGA cycling between oxygen and nitrogen increases by a factor of 2 to 400 days on increasing the in situ activation temperature from 75 to 150 °C. This is consistent with a more thorough removal of methanol solvate from the microporous solid. As with **IA-1**, increasing the cycling temperature following rigorous activation resulted in reduced half-life. The observed half-life is 3.3 days at 60 °C and 0.49 days at 80 °C.

The magnetic susceptibility measurements and oxygen capacity decay based on TGA studies at room temperature are consistent with oxidation of half the metal centers to cobalt(III). In contrast, heating **IA-1** at 85 °C under oxygen for 4 days resulted in complete loss of oxygen capacity, and the magnetic moment increased by 40 %. This suggests that the decomposition mechanism at elevated temperature is different from that in ambient air at room temperature. We propose that the ambient temperature degradation is water promoted to give cobalt(III). This finding is significant since it implies that reducing water content in the feed could increase the lifetime of oxygen selective adsorbents.

Analytical tests were performed to establish the origin of the performance loss for a sample of **IA-3** that had undergone cycling for approximately 6 months. Based on a combination of mass spectrometry and NMR spectra, we found no evidence of ligand-centered oxidation implying that the performance degradation is due to metal-centered oxidation.

Table 4 Performance comparison of **IA-3**/PPO prepared by different methods

Method	% PPO	O_2 uptake (mmol/g)	Adsorption rate (mmol/g/s)	Desorption rate (μmol/g/s)	Piece density (g/cc)	Median pore diameter (μm)	Crush strength (lbF)
Physical mixture	10	1.12	0.138	1.45	–	–	–
Extrusion/evaporation	10	1.75	0.15	1.78	0.7	0.35	12
Extrusion/hexane quench	10	1.88	0.13	–	0.53	0.42	Deforms
Extrusion/evaporation	5	1.83	0.2	2.2	0.69	0.41	11
Compaction, 2,000 lbF	10	1.13	0.047	0.74	1.05	–	24

Lifetime under conditions of use is a key performance characteristic that will dramatically change process economic projections. Therefore, a test system was developed to evaluate the influence of temperature, moisture, and oxygen partial pressure on lifetime of **IA-3** under conditions that would be experienced in an adsorbent bed for a purification application. The test system allowed extended cycling of extruded **IA-3** samples in 25 independent parallel packed bed tests to enable experiments that were parametric in oxygen content of the feed (1.0, 0.1, and 0.01 %), moisture content (5, 1, 0.1 and 0 ppm), and bed temperature (100, 80, 60, and 40 °F). Feed pressures for the oxygen containing stream was 100 psig in all cases. Regeneration was performed each cycle using nitrogen purge in a cocurrent direction. Periodically, samples were withdrawn from each test bed and the oxygen capacity was determined using a TGA method. The test system was operated for more than 1 year and indicated that moisture in the feed over the range tested is not a critical parameter. However, the lifetime of **IA-3** is very sensitive to temperature and the feed oxygen content. Data summarizing the results of lifetime studies are presented in Table 5. Adsorbent lifetime is a factor in commercial economics and it will be necessary to evaluate cost of replacement versus operating costs associated with lower temperature operation. The potential role of water coordinating to lithium sites and disrupting the structure cannot be excluded since changes in crystallinity were not examined.

The collective data support a mechanism with electron transfer as illustrated in Fig. 8. If one out of 1,000,000 molecules takes pathway B per 2 min cycle, the projected half-life is 2.6 years.

Table 5 Impact of temperature and oxygen content on **IA-3** lifetime

Temperature (°F)	Projected half-life (years)		
	1 % O_2	0.1 % O_2	0.01 % O_2
40	4.8	6.1	21
60	2	3.2	17
80	1	2	10
100	0.3	–	–

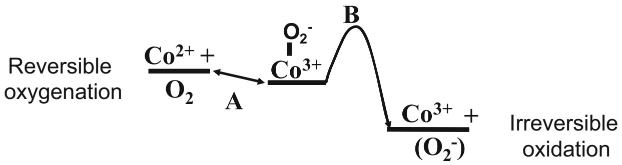


Fig. 8 Potential pathway to irreversible oxidation

3.6 Potential application of **IA-3**

The results of oxygen compatibility studies suggest that the best applications for oxygen selective adsorbents described are purifications where the feed oxygen concentration is <1 %. Of the compositions described, the composition **IA-3** is best suited to this application. In addition, extended lifetimes of **IA-3** are anticipated for relatively dry feeds. A potential application that can take advantage of these characteristics is oxygen removal from crude nitrogen. Both polymeric membrane of carbon molecular sieve PSA processes can provide dry nitrogen with oxygen content <1 %. The carbon molecular sieve PSA units have the potential to produce higher purities but do so by sacrificing nitrogen recovery. An adsorptive unit specifically designed to reject oxygen from a crude stream offers the potential to exploit synergies between the rate selective (carbon molecular sieve) and equilibrium selective (oxygen selective adsorbent) materials.

Breakthrough tests were performed using packed beds of **IA-3** extrudate (7.5 gm, bed ID 0.37”, length 11”) with 1.02 % oxygen in nitrogen at 22 °C with a feed flow of 0.5 scfh at 750 mmHg. Breakthrough of oxygen to 100 ppm occurred in 77 min and full breakthrough occurred in 124 min. Proof of concept testing was performed using in a bench-scale 2-bed system using a nitrogen feed containing 1 % oxygen at 10 psig and 15 gm of **IA-3** extrudates. At a feed flow of 0.21 scfh and with 10 min adsorption and desorption step times, an average product oxygen purity <10 ppb was obtained. Vacuum/purge combinations were shown to reduce the volumes of purge gas that are necessary for regeneration.

4 Conclusion

The results described herein illustrate a series of structurally related oxygen selective adsorbents wherein the substituents modify the oxygen interaction leading to materials that are suited to both separation and purification processes. Hazard testing data for **IA-3** indicate that the bulk powder is flammable and, at atmospheric pressure, can burn at oxygen concentrations greater than 13 %. In addition, **IA-3** dust clouds exhibit a low ignition energy and is ranked as a 'strong explosive' at or above its LOC (2–5 % oxygen) and with dust concentrations of 250–1,250 g/m^3. These results shifted emphasis to purification application where oxygen partial pressures are low and highlighted a need for agglomeration methods that minimize attrition. The preferred composition for purification applications is **IA-3** based on capacity and ease of regeneration (isotherm shape). Extrusion of **IA-3** pastes containing solutions of polymeric binders followed by solvent evaporation is shown to have extremely low tendency for dust formation. In addition, the formulation and methods minimizes the impact agglomeration on oxygen capacity and rate. Proof of concept demonstration of oxygen removal from nitrogen is presented from percent down to ppb levels.

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