

# A fluidized bed reactor for low temperature deposition

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## Abstract

A new reactor system was designed and constructed for controlled gas-phase preparation of heterogeneous catalysts. The reactor operates at low temperatures (25–200°C) and under inert atmospheres, allowing the use of volatile, air-sensitive precursors like metal carbonyls. Accurate temperature control in the different parts of the reactor system, and effective particle mixing in the fluidized bed, enable controlled preparation. Test results confirmed the usefulness of the reactor in the preparation of Co/SiO<sub>2</sub> samples from Co<sub>2</sub>(CO)<sub>8</sub> precursor. © 1997 Elsevier Science B.V.

*Keywords:* Fluidized bed reactor; Gas-phase preparation; Low temperature; Silica support; Metal carbonyl

## 1. Introduction

Heterogeneous catalysts consisting of active metal components supported on porous high surface area supports are widely used in the chemical industry. Various techniques are available for deposition of the active components, and the activity and selectivity of the resulting catalyst may vary widely according to the choice. To be able to control the preparation steps is consequently of considerable importance.

Impregnation is the standard technique for preparing supported metal catalysts. Several steps are involved, however, including reductions and oxidation at high temperatures. The preparation of catalyst is difficult to control, because the solvent may block the adsorption

sites on the support preventing the surface area of the support from being fully used. The objective is to manufacture structurally well-defined catalysts, and to obtain surface species of known structure and electronic properties, the active metal species need to be bound on the support in a controlled manner. To control the preparation of heterogeneous catalyst several gas-phase preparation methods have been developed. One of them is chemical vapor deposition (CVD), in which the active phase is deposited on the catalyst support from gaseous metal precursors. Another useful gas-phase method is atomic layer epitaxy (ALE) [1–4], in which growth is controlled by the surface itself, and the desired surface structure is formed in chemisorption reactions. Optimally, both methods will result in catalysts with high metal or metal oxide dispersion.

Customized reactor systems are often used in the preparation of heterogeneous catalysts on

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highly porous supports by gas-phase methods. In investigations of the potential of low pressure organometallic chemical vapor deposition (OMCVD) for the preparation of rhodium supported catalysts, Serp et al. [5–7] obtained high metal dispersion in a single step in a fluidized bed reactor. Similar techniques have been used in vapor-phase adsorption by several other groups [8–11].

The above-cited studies have confirmed the usefulness of a fluidized bed in obtaining homogeneous deposition on supports. In the present work we describe a new reactor system which allows controlled stepwise preparation of heterogeneous catalysts. The reactor has been designed to operate at low temperatures and inert atmospheres. These requirements are appropriate because sintering of the support and migration of metal species can be avoided at low temperatures and air-sensitive precursor complexes can be used in inert atmospheres. The reactor was tested in the preparation of Co/SiO<sub>2</sub> samples where Co<sub>2</sub>(CO)<sub>8</sub> was used as precursor.

## 2. Experimental

### 2.1. Reactor construction

Fig. 1 shows a schematic view of the reactor system. The heart of the system is the fluidized bed reactor (a) and the sublimation chamber (b), which are surrounded by separate thermally controlled environments (e). The catalyst can be prepared without exposure to air by using a glovebox to pack the precursor into the sublimation chamber and the support into the fluidized bed reactor.

The fluidized bed reactor was chosen because it allows accurate temperature control and effective mixing. The reactor (a) is made of glass in the shape of a cone, and gas is introduced through a sintered glass filter disc. Another porous filter is placed on top of the reactor to prevent the outflow of particles with the carrier

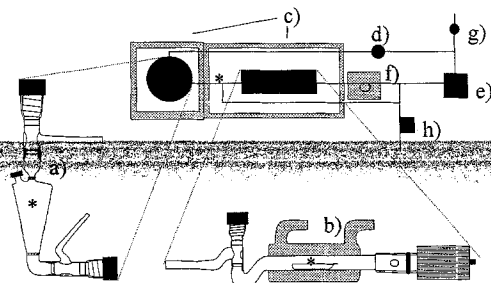


Fig. 1. A fluidized bed reactor system for low temperature deposition: (a) fluidized bed, (b) sublimation chamber, (c) separate thermally controlled environments, (d) cold trap, (e) gas circulation pump, (f) gas tube circle in a warm bath, (g) mercury bubbler and pressure gauge. Thermoelements are denoted by \*.

gas. The support material is packed into the bed through a sidearm. The inlet and outlet of the reactor can be closed with stopcocks to prevent contact with air.

The sublimation chamber (b) is made of glass and is air-tight. The entire sublimation chamber and the gas lines between the chamber and the fluidized bed are bathed in thermally controlled air. This arrangement ensures that there are no cold spots between the chamber and the bed where the precursor could crystallize. Furthermore, fluids circulating in the double jacket around the chamber (hatched area, Fig. 1) can be heated or cooled to ensure effective and constant evaporation of the precursor during the sublimation period. The precursor is packed in the small boat and placed into the chamber. The spherical shape of the walls of the chamber ensures good heat transfer from chamber to boat.

Carrier gases are circulated in the reactor system by a pump (e) to minimize the gas consumption. The circulation also permits collection of excess precursor in a cold trap (d) behind the fluidized bed. During sublimation and decarbonylation, a slow overflow of the carrier gas through a mercury bubbler (g) prevents the build-up of excess pressure in the reactor. The gas line has been constructed so that the tube between the fluidized bed and the sublimation chamber can also be evacuated.

During evacuation a pressure gauge (h) will indicate any leaks in the lines.

Stable temperatures are critically important in the controlled preparation of heterogeneous catalysts. Moreover, temperatures will often need to be different in the fluidized bed and the chamber. The bed and chamber are therefore isolated from each other, in separate thermally controlled environments, which can be adjusted to an accuracy of within 0.1°C. The upper limit of the working temperature in both the fluidized bed and the sublimation chamber is about 230°C. Preheating of the carrier gases (f) before they enter the sublimation chamber further stabilizes temperature differences in the chamber.

## 2.2. Reactor testing

Temperatures inside the fluidized bed and sublimation chamber and of the air surrounding them were measured with a Line Seiki thermometer TC-1100. Fig. 1 shows the positions of the thermoelements in the reactor system. Controlled low temperature preparation of Co/SiO<sub>2</sub> involved thermal pretreatment of the support, deposition of the vaporized Co<sub>2</sub>(CO)<sub>8</sub> at 40–50°C for a given period of time, and decarbonylation of the adsorbate by increasing the fluidized bed temperature to 100°C. Deposition times were long due to low vapor pressures of Co<sub>2</sub>(CO)<sub>8</sub> at reaction temperatures. The upper limit for the adsorption is 50°C because Co<sub>2</sub>(CO)<sub>8</sub> decomposes at 51°C.

## 2.3. Reactants

Co<sub>2</sub>(CO)<sub>8</sub> was supplied by Fluka Chemie Ag and used without further purification. Due to its sensitivity to air it was stored under nitrogen and packed into the sublimation chamber through a glovebox. Nitrogen (99.999%, Aga) and CO (99.997%, Aga) were used as carrier gases. The silica support, GRACE 432 (GRACE Davison, 320 m<sup>2</sup>/g, particle size 0.5–1 mm), was crushed and sieved to 200–500 μm to facilitate homogeneous fluidization. The support

was calcined at 300°C under vacuum for 10 h to remove physisorbed water and to control the number of OH-species on the surface. After calcination it was stored in a glovebox, and from there packed into the fluidized bed reactor, without exposure to air.

## 2.4. Conditions of controlled preparation

During the deposition the fluidized bed was heated to 40, 45 or 50°C (at 51°C Co<sub>2</sub>(CO)<sub>8</sub> decomposes) and the sublimation chamber to 35, 40 or 45°C. In all cases the temperature of the bed was 5°C higher than that of the reactant supply in order to control deposition of Co<sub>2</sub>(CO)<sub>8</sub> on the support surface. Carrier gas (CO) flowed through the chamber, transporting the sublimed carbonyl compound to the reactor, where it was adsorbed on the surface sites of the support. Deposition times were long due to low vapor pressures of Co<sub>2</sub>(CO)<sub>8</sub> at the reaction temperatures. For decarbonylation the chamber was replaced by a gas tube, the bed was heated to 100°C and nitrogen was used as carrier gas. When the fluidized bed contained about 7 g of silica the consumption of gas was about 20 ml/min. The silica support was of relatively large particle size, so the velocity of the carrier gas was increased with the gas circulation up to 700–1200 ml/min, depending on the metal loading on the support. Sufficient fluidization in the gas stream mixes the particles and homogeneous deposition is achieved throughout the fluidized bed.

## 2.5. Characterization

Cobalt carbonyl/silica samples were characterized with a Nicolet Impact 400 D Fourier transform infrared spectrometer equipped with a diffuse reflectance accessory (DRIFT). The spectrometer was placed under the glove box so that the IR spectra could be run under nitrogen atmosphere [11]. Cobalt content was determined by atomic absorption spectroscopy (AAS) and energy dispersive X-ray fluorescence (ACAX

300 EDXRF). The AAS results and XRF results together were used to calculate the cobalt content of other samples measured only by XRF.

### 3. Results and discussion

#### 3.1. Temperature conditions

Temperature conditions affect the vapor pressure of the precursor, metal content and dispersion on the support, and the reaction on the support. Precursors for gas-phase deposition reactions must be sufficiently volatile and stable at the reaction temperature. Precursors that vaporize at low temperatures will be difficult to work with,  $\text{Co}_2(\text{CO})_8$  sublimates readily, and its vapor pressure at  $50^\circ\text{C}$  is about 0.6 Torr (80 Pa), but it decomposes slowly even at room temperature and melts at  $51^\circ\text{C}$  [12]. The thermal decomposition of cobalt carbonyl can be prevented, at least below the melting point by using CO as carrier gas. Equally important is the accurate control of temperature in the evaporation of the precursor and the deposition that leads to the controlled adsorption reaction between the precursor and the support. Choice of just the proper reaction temperature prevents decomposition of the reactant and condensation of it or its decomposition products on the support, which would result in poor metal dispersion.

Temperatures in the different parts of the reactor system were monitored and carefully controlled during the deposition process (Fig. 2). It is most important that the preset temperatures remain stable and that, at the beginning of the reaction, a temperature difference is maintained between the sublimation chamber (curve e) and the rest of the reactor. Cold liquid flow in the double jacket around the chamber made possible the lower temperature. Evaporation of the precursor was thus prevented until other parts of the reactor system had reached the target temperatures. Change from cold liquid to thermostated hot liquid warmed the chamber

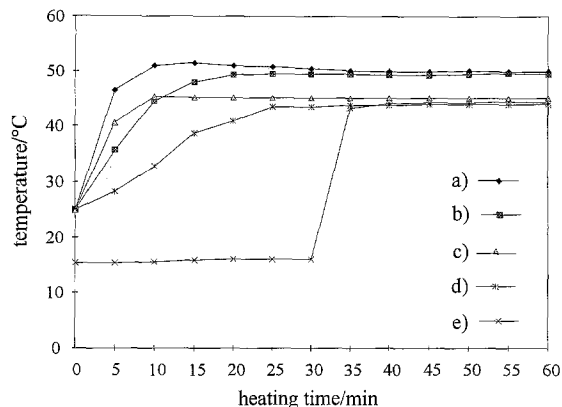


Fig. 2. Temperatures in different parts of the reactor system: (a) first heating unit (preset temperature  $50^\circ\text{C}$ ), (b) inside the fluidized bed reactor, (c) second heating unit (preset temperature  $45^\circ\text{C}$ ), (d) air between the bed and chamber and (e) inside the sublimation chamber.

and caused the precursor to evaporate. The target temperatures of the air bathing the reactor and chamber (curves a and c) were reached in ten minutes. Temperature stabilization inside the fluidized bed (curve b) and in the space between the chamber and bed (curve d) took a little longer.

#### 3.2. IR spectra

Deposition and decarbonylation were followed by IR spectroscopy. Cobalt carbonyl/silica sample easily oxidizes in air, so they were handled under  $\text{N}_2$  atmosphere. Under CO atmosphere the sample was orange brown, but under  $\text{N}_2$  it immediately became dark brown or black. After decarbonylation  $\text{Co}/\text{SiO}_2$  was grey, and in air the sample turned blue.

Fig. 3a shows the IR spectrum of  $\text{Co}_2(\text{CO})_8$  deposited onto silica at  $50^\circ\text{C}$  for 5 h with CO flow. Both linear ( $2120\text{--}2000\text{ cm}^{-1}$ ) and bridging ( $1900\text{--}1800\text{ cm}^{-1}$ ) carbonyls can be seen in the spectrum. The cobalt carbonyl complex on the silica support seems to be  $\text{Co}_4(\text{CO})_{12}$  indicating  $\text{Co}_2(\text{CO})_8$  dimerization. The same findings were made by Schneider et al. [13] and Rao et al. [14] in their investigations with in situ FTIR of  $\text{Co}_2(\text{CO})_8$  deposition on silica surface

under CO and N<sub>2</sub> atmospheres. The IR spectrum in Fig. 3b represents the situation after decarbonylation at 100°C for 3 h in N<sub>2</sub> flow. All bridging carbonyls have disappeared and a very weak linear carbonyl remains. Both spectra (a and b) show how deposition can be achieved with the carbonyl ligands intact, and how with a relatively low heat treatment the ligands can be removed. The IR spectra of cobalt carbonyl on silica will be discussed in more detail in a forthcoming publication.

### 3.3. Control of the cobalt content

In general, the surface reaction on a support will be chemisorption or physisorption depending on the temperature. In chemisorption, a chemical bond is formed when the reaction temperature is high enough to overcome the activation energy needed for bond formation. At such a temperature, surface saturation will be achieved when the gaseous reactant is in excess of the number of bonding sites energetically available. In physisorption, there is a van der Waals interaction between the adsorbate and the support and the metal content increases linearly. When Co<sub>2</sub>(CO)<sub>8</sub> is deposited onto partially hydroxylated silica, hydrogen-bonding occurs between bridging CO groups and the weakly acidic

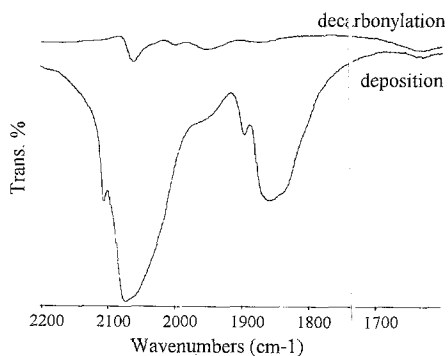


Fig. 3. (a) IR spectrum of Co<sub>2</sub>(CO)<sub>8</sub> deposited at 50°C for 5 h with CO flow onto silica preheated at 300°C in vacuum. (b) IR spectrum of sample (a) after decarbonylation at 100°C for 3 h with N<sub>2</sub> flow.

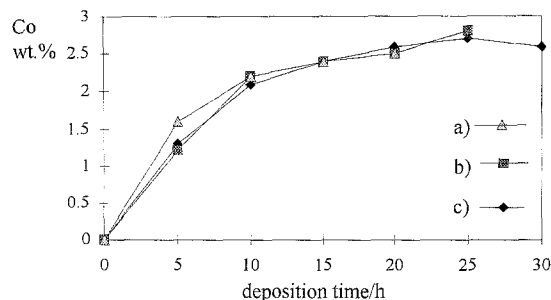


Fig. 4. Cobalt content (wt%) on the support versus deposition time, at preparation temperature: (a) 50°C, (b) 45°C and (c) 40°C.

surface hydroxyls [13,14]. This weak interaction takes place after physisorption of cobalt carbonyl on the surface. Fig. 4 shows the cobalt content (wt%) on the support plotted against deposition time at 40, 45 and 50°C. In all three cases, the cobalt content reached a saturation level, which means that the deposition was controlled by physisorption. The physisorption reaction leads to only partial surface coverage and can be achieved under controlled conditions at low temperature. At low temperature and appropriate vapor pressure, particles physisorbed on the support surface are able to move to vacant bonding sites inside the pores. When the dose of the vaporized reactant is sufficient, full saturation is achieved independent of time. Partial saturation can be achieved with the variation of the deposition time.

## 4. Conclusions

The results show the usefulness of the reactor system in the gas-phase preparation of heterogeneous catalysts at low temperature. The main advantages are an ability to handle air-sensitive precursors and products, accurate temperature control in different parts of the reactor system, and effective particle mixing in the fluidized bed. The gas circulation system reduces gas consumption, and the reactor system is inexpensive to construct and easy to run.

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