

REMOVAL OF VOLATILE METAL CARBONYLS FROM RAW SYNGAS

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Introduction

Industrial processes using carbon monoxide and/or hydrogen obtained from syngas can suffer from metal carbonyls originating from the feedstock used and the piping and reactor system. Nickel tetracarbonyl and iron pentacarbonyl, especially in combination with hydrogen sulfide, cause serious problems during the treatment of raw syngas and subsequent applications, mainly due to thermal and/or chemical carbonyl decomposition. For example, in gas treating processes using a liquid absorbent for the removal of acid gases, such as hydrogen sulfide and carbon dioxide in combination with a Claus plant, pressure build-ups, due to deposition of metal oxides/sulfides can be expected not only in the treating unit, but also throughout the Claus plant, especially on the catalyst bed of the first Claus reactor. In addition, downstream pressure-buildups may occur, as metal is being deposited on catalyst beds in syngas treating, e.g. COS hydrolysis and water gas shift. Furthermore, the active phase in the catalysts can become poisoned or show adversely changing activities and selectivity's due to the deposition of iron/nickel.

Generally, when CO is present in a gas stream as a reactant or (by) product in industrial processes, a suitable absorbent for nickel tetracarbonyl and iron pentacarbonyl often is imperative in order to eliminate or reduce the risk of catalyst poisoning, to extend plant operation life and to reduce the nickel and iron impurities in numerous chemical products originating from syngas.

In the research project described here, several high-surface oxides and zeolitic materials have been studied for their suitability to effectively remove metal carbonyls from raw syngas streams. The properties to be met with these materials are: applicable in a fixed bed, large capacity, regenerability and insensitivity for hydrogen sulfide and water.

Experimental

Absorbents

Several non-bindered zeolites and high-surface metal oxides have been studied for their ability to absorb iron and nickel carbonyls out of hydrogen sulfide and water containing syngas streams. High-surface SiO_2 , Al_2O_3 , Al_3PO_4 , and zeolitic materials including ZSM-5 (MFI), mordenite (MOR), Y (FAU), Beta (BEA), UTD and MCM-41 were used in our experiments. In addition, different samples of faujasite were used, exhibiting a silica alumina ratio (SAR) ranging from 3 to 91. Faujasites with a SAR value higher than 3 had been de-aluminized by steam treating. All zeolitic materials exhibited a total pore volume of about 0.5 ml/g.

The samples were pelletized using a pressure of 1 MPa and subsequently crushed. A sieve fraction of 0.425-0.800 mm was used for absorption experiments. Prior to a measurement, the samples were treated in air for 24 hours at 523 K. Dehydration of the samples took place for 18 hours at 723 K.

Hexamethyldisiloxane (HMDS) was used to modify the hydrophilic character of the alumina and silica samples. This was established through boiling these materials in HMDS for one hour. In addition, the surface of alumina was treated with phosphoric acid in order to study the influence of the surface acidity. This was established through boiling this material in phosphoric acid for one hour.

Absorption experiments

Metal carbonyl absorption experiments were carried out in a fully automated microflow apparatus. In our experiments, simulated syngas was used, consisting of 40 vol.% H_2 , 50 vol.% CO and 10 vol.% He. If required, water, hydrogen sulfide, metal carbonyl or a mixture of these components was added.

Prior to use, carbon monoxide was led at room temperature over a carbonyltrap consisting of zeolite Y. Water was introduced into the gas stream by means of a water saturator. Nickel tetracarbonyl was introduced into the gas stream by leading carbon monoxide over a reduced nickel catalyst (Ni/ Al_2O_3 , 70 wt.%) kept at 243 K. Iron pentacarbonyl was added to the feed by leading a controlled flow of helium through an iron pentacarbonyl saturator kept at 258 K. Helium 5.0, hydrogen 4.5, hydrogen sulfide 2.2 and carbon monoxide 4.7 were purchased from Hoek Loos b.v. Helium, hydrogen and hydrogen sulfide were used without further purification. The total gas flow was set at 100 ml/min, unless stated otherwise, so that an hourly linear space velocity was established of 6000 hr^{-1} . The iron pentacarbonyl and nickel tetracarbonyl partial pressures in the feed were varied between 0 and 30 Pa.

The gas composition upstream and downstream of the absorbent bed was analyzed with a Varian Cary 1E UV Vis spectrophotometer equipped with quartz gas flow cells with a length of 10 cm. The detection limit for iron pentacarbonyl was 0.01 Pa for iron pentacarbonyl, and for nickel tetracarbonyl 0.007 Pa. Furthermore, a Balzers quadrupole mass spectrometer was applied downstream of the bed for determination of the water and hydrogen sulfide partial pressures. 1 ml of absorbent sample (sieve fraction 0.425 to 0.800 mm) was placed in a quartz micro reactor tube (I.D. = 8 mm). If water and / or hydrogen sulfide were present in the gas stream, the absorbent bed was pre-saturated with water and/or hydrogen sulfide before the metal carbonyl was introduced in to the feed. Absorption profiles as a function of time were measured at 298 K. The total amount of metal carbonyl absorbed by the absorbent was calculated by integration of the metal carbonyl concentration difference up and downstream of the absorbent bed.

Absorbent Characterization

Pore size distributions and pore volumina were deduced from nitrogen absorption measurements with a Micromeretics 2000 gas absorption apparatus. The Horvath-Kawazoe model assuming a cylindrical pore geometry was applied.

Results and Discussion

To make a first selection, the suitability of a number of different absorbents was investigated. The influence of the chemical nature and the textural properties of the absorbent on the $\text{Fe}(\text{CO})_5$ absorption capacity was examined using high-surface silica, high-surface alumina, zeolite Beta and Faujasite. All samples exhibited surface areas of 400 to 700 m^2/g . Syngas, only containing 20 Pa of iron carbonyl, was led over the absorbent bed. The results are summarized in Figure 1. From these results, it is clear that the zeolitic materials absorb significantly more metal carbonyl than the metal oxides. The absorption capacities of HMDS treated Al_2O_3 and SiO_2 are comparable with the absorption capacities of their unmodified counterparts. Also, the absorption capacity of untreated alumina is comparable with the absorption capacity of phosphoric acid treated alumina.

The above findings led us to the conclusion that, when no additional compounds are present in the feed, the specific pore size and specific pore volume is far more important than the chemical nature of the surface for a suitable metal carbonyl absorbent.

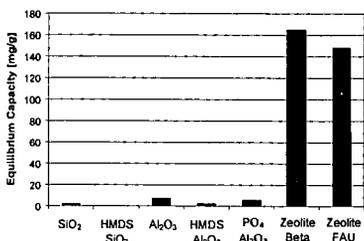


Figure 1: Equilibrium $\text{Fe}(\text{CO})_5$ absorption capacities for several types of materials at 298 K. Hexamethyldisiloxane-treated SiO_2 and Al_2O_3 are denoted as HMDS- SiO_2 or HMDS- Al_2O_3 , respectively. Al_2O_3 treated with phosphoric acid is denoted as PO_4 - Al_2O_3 .

Figure 2 displays the iron and nickel absorption capacity per gram of a number of zeolites as a function of pore size. Syngas, only containing 20 Pa of iron carbonyl or 16 Pa of nickel carbonylsulfide was led over the absorbent bed. From Figure 2 it becomes clear that zeolites exhibiting pores with a diameter less than 7 Å absorb only about 1 wt.% iron and nickel carbonyl. This suggests absorption to take place only at the external surface of these zeolite crystals. The kinetic diameter of the metal carbonyl molecules in the gas phase is about 7.4 Å, which is apparently too large to fit into the pore structure.

Zeolite Beta and Faujasite exhibit the largest absorption capacity. The pore (mouth) diameter of these materials is about the same size as the kinetic diameter of iron and nickel carbonyl. UTD and MCM, which have pores with a diameter larger than 8 Å, absorb significantly less. Their absorption capacity is found to be about one-third of the capacities for Beta and Faujasite. These results clearly reflect the

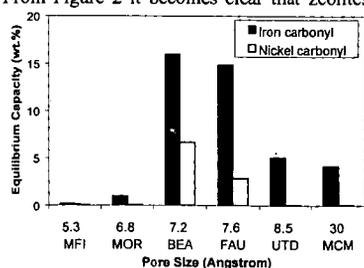


Figure 2: Equilibrium absorption capacity at 298 K for Iron pentacarbonyl and Nickel tetracarbonyl as a function of the pore size. The zeolites used in this experiment are ZSM-5 (MFI), Mordenite (MOR), Faujasite (FAU), UTD, and mesoporous MCM-41

influence of the pore diameter on metal carbonyl absorption. For the zeolites tested, the capacity for nickel carbonyl is less than the capacity for iron carbonyl, although the kinetic diameters of iron and nickel carbonyl are about the same. It is beyond the scope of this abstract to go into detail on this issue. For the remainder of this abstract, we confine ourselves to faujasites and absorption of iron pentacarbonyl.

A typical iron carbonyl absorption curve for a faujasite is displayed in Figure 3. Here, the carbonyl concentration downstream of the absorbent bed is plotted as a function of time. Syngas with 20 Pa of iron carbonyl was led over the absorbent bed. This breakthrough curve clearly shows that faujasites are capable of completely removing iron carbonyl out of a dry syngas stream.

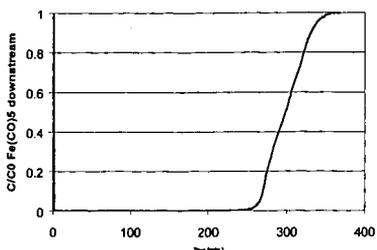


Figure 3: $Fe(CO)_5$ concentration downstream of an absorbent bed consisting of faujasite with a SAR value of 91.

Raw syngas contains also noticeable amounts of water and hydrogen sulfide. The question is, whether faujasites preferentially absorb water, hydrogen sulfide or metal carbonyl. Zeolite Y, a faujasite with a SAR value of 2.6, is known for its property to absorb water and, thus, it is used to dry gas streams. Therefore, it is imperative to study the influence of the SAR value on the absorption properties of faujasite for water, hydrogen sulfide and metal carbonyl separately, and in combination.

Syngas, containing both hydrogen sulfide (0.15 vol.%) and water (1.5 vol.%), but no metal carbonyls, was led over an absorbent bed consisting of faujasite with a SAR of 2.6 and 91, respectively. In Figure 4, both the H_2O and H_2S concentrations downstream of the absorbent bed are plotted as a function of time for both faujasites. For the faujasite with a SAR value of 2.6 it shows that initially both water and hydrogen sulfide are absorbed. However, as time progresses, hydrogen sulfide is desorbed from the zeolite and is expelled due to the absorption of water. A subsequently executed temperature-programmed desorption experiment showed only water to be present in the zeolite, the amount of which corresponds to complete pore filling. This result suggests that H_2O exhibits a considerably higher absorption energy than H_2S .

With the faujasite with a SAR value of 91, it turned out that only a small amount of water is absorbed, and no H_2S , since no desorption of H_2S due to absorption of water is measured.

A subsequent temperature-programmed desorption experiment showed that about 2 wt.% water is absorbed, and no hydrogen sulfide. These results demonstrate that from a gas stream containing both water and hydrogen sulfide, water is preferentially absorbed by faujasites.

The amount of water absorbed by the faujasite with a high SAR value, resembles a pore filling of only 4 percent. Therefore, we can conclude that only water might interfere with carbonyl absorption. Of course the extent of interference will be a function of the H_2O partial pressure.

De-aluminized faujasites are good candidates indeed for absorption of metal carbonyl from water and hydrogen sulfide containing gas streams. Additional absorption experiments showed no influence of hydrogen sulfide on the absorption kinetics of iron carbonyl.

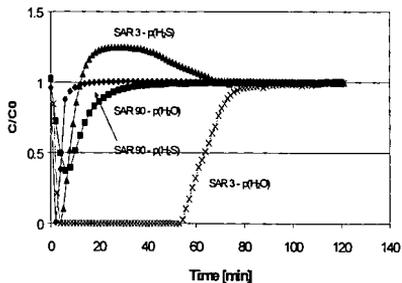


Figure 4: H_2O and H_2S concentrations downstream of the absorbent bed at 298 K, as a function of time onstream for two types of faujasites. The faujasites exhibit a silica alumina ratio of 2.6 and 91, respectively. C_0 is the concentration of H_2O and H_2S , respectively. $c(H_2O)=1.5$ vol.%, $c(H_2S)=0.15$ vol.%.

More information about the influence of water on the metal carbonyl absorption as a function of the SAR we obtained with the following experiments. Syngas, containing 20 Pa of iron carbonyl and either 0, 1.5 or 3 kPa of water, was led over the absorbent bed at 298 K. Figure 5 shows the equilibrium amount of absorbed iron carbonyl as a function of the SAR value, for a number of different H₂O partial pressures.

From these results we can conclude that at relatively low SAR values, H₂O is preferentially absorbed in faujasites. Therefore, these faujasites exhibit little or no metal carbonyl capacity. However, at increasing SAR values, the influence of water on the amount of iron carbonyl absorbed decreases sharply. Typically, the equilibrium amount of Fe(CO)₅ absorbed by a faujasite with a SAR value of 91 is about 21 wt.%, regardless of the presence of water. The amount of water absorbed at p(H₂O)/P₀=1 for faujasites with SAR values of 3.6 and 91 is 31 wt.% and 17 wt.%, respectively. Apparently, at an increasing SAR value, the absorption energy of water in the micro pores decreases and metal carbonyl can get in. A high SAR value is therefore of major importance to effective metal carbonyl absorption. In other words, the SAR value is related to the hydrophobicity of the pores, and therefore of importance for lowering of the absorption energy of water. Also, a high SAR value appears to have a positive influence on the metal carbonyl absorption of the faujasites, probably due to textural changes by de-aluminization.

However, it can be expected that the presence of absorbed water for faujasites with a SAR value higher than about 60, obstructs the uptake rate of iron carbonyl to some extent. Lowering of the gas hourly space velocity (GHSV) could neutralize this effect. For the faujasite with a SAR value of 91, we assessed the influence of the GHSV on the iron carbonyl absorption kinetics in the presence of water.

Syngas, containing 3 kPa of water and 20 Pa of iron carbonyl, was led over the absorbent bed at 298 K. In Figure 6 the carbonyl concentration, downstream of the absorbent bed, is plotted as a function of the time for a GHSV of 6000/hr and 1500/hr, respectively. At a GHSV of 6000/hr, iron carbonyl was detected immediately. This was not the case for the dry faujasite at the same GHSV, as can be seen from Figure 3. After a steady state condition had been reached, the metal carbonyl concentration rose from 1.6 to about 2.2 Pa in 230 minutes. Finally, the concentration of metal carbonyl increased sharply, which indicated that the absorbent almost was saturated with iron carbonyl.

Lowering of the gas hourly space velocity from 6000/hr to 1500/hr, resulted in complete removal of iron carbonyl from the gas stream, as is usual for the dry faujasite at a GHSV value of 6000/hr. For both space velocities, the uptake of iron carbonyl remains 21 wt.%, corresponding with a micro pore filling of 65%. The uptake of water remains 17 wt.%.

The results above led us to the conclusion that lowering of the GHSV neutralizes the retarding effect of water on the uptake rate of iron carbonyl. This retarding effect of water can only be explained by assuming that either water is rather easily expelled from the micro pore system of the faujasite due to absorption of iron carbonyl, or water is preferentially absorbed outside the micro pores. The exact nature of the influence of water on carbonyl absorption by de-aluminized faujasites goes beyond the scope of this abstract and will not be discussed here.

Finally, for application in an industrial process, these materials need to be regenerable. Bath [1] and Golden [2] already showed for zeolite Y that gentle heating restores completely the initial absorption capacity. Eijkhoudt et al. [3] showed the same for de-aluminized faujasites.

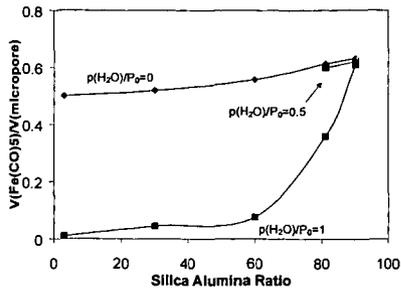


Figure 5: Volume Fe(CO)₅ absorbed in faujasite at 298 K, normalized on micro pore volume, as a function of silica alumina ratio and water partial pressure. For pore-filling calculations, it is assumed that Fe(CO)₅ absorbed in the micro pores has the same density as the bulk fluid.

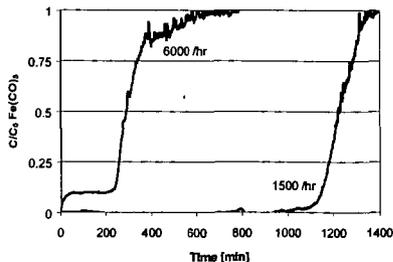


Figure 6: Fe(CO)₅ breakthrough curves at 298 K for a faujasite with a SAR value of 91, previously saturated with water. The gas hourly space velocity is varied between 6000 and 1500/hr.

Conclusions

When carbon monoxide is present in a gas stream as a reactant or (by) product in industrial processes, a suitable absorbent for nickel tetracarbonyl and iron pentacarbonyl often is imperative. Faujasites with a silica alumina ratio of 60 and higher prove to be excellent metal carbonyl absorbents with regenerable capacities up to 21 wt.%, which corresponds to a micro pore filling of 65 %. Under the conditions applied, our experiments show that the metal carbonyl absorption capacity of these faujasites is influenced neither by hydrogen sulfide nor water. However, water retards the uptake rate of metal carbonyl to some extent. This retarding effect is easily neutralized by lowering of the gas hourly space velocity.

Consequently, these absorbents can be used to remove volatile metal carbonyls from raw syngas streams.

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1 B. L. Bhatt, *Sep. Sci. and Techn.* 26 (1991), 1559.

2 T.C. Golden, *Ind. Eng. Chem. Res.*, 30 (1991), 502.

3 R. Eijkhoudt, "*Formation and Removal of volatile Metal carbonyls*", thesis, to be published.