Zeolites Modified by CuCl for Separating CO from Gas Mixtures Containing CO_2

YOUCHANG XIE, JIAPING ZHANG, JIANGUO QIU, XIANZHONG TONG,
JINPING FU, GE YANG, HAOJIE YAN AND YOUQI TANG
Department of Chemistry, Peking University, Beijing 100871, China

Abstract. Although zeolites such as NaY and 13X adsorb CO_2 much more than CO, the adsorption amount of CO_2 and CO can be reversed if the zeolites are modified with CuCl. When zeolite NaY or 13X is mixed with CuCl and heated, high CO adsorption selectivity and capacity can be obtained. Isotherms show the adsorbents have CO capacity much higher than CO_2. This is because CuCl has dispersed onto the surface of the zeolites to form a monolayer after the heat treatment and the monolayer dispersed CuCl can provide tremendous Cu(I) to selective adsorb CO and inhibit the CO_2 adsorption. The monolayer dispersion of CuCl is confirmed by XRD and EXAFS studies. The loading of CuCl on the zeolites has a threshold below which the CuCl forms monolayer after heating and crystalline phase of CuCl can not be detected by XRD. An adsorbent of CuCl/NaY with CuCl content closed to the monolayer capacity shows very high CO selective adsorbability for CO_2, N_2, H_2 and CH_4. At temperature higher than room temperature, the adsorbent has even better CO selectivity for CO_2. Using the adsorbent, a single-stage 4 beds PSA process, working at 70°C and 0.4 MPa to 0.013 MPa, can obtain CO product with purity >99.5% and yield >85%.

Keywords: CO adsorbent, CO_2 adsorption, zeolite modification, monolayer dispersion

Introduction

Carbon monoxide is a valuable raw material for the syntheses of variety of chemicals such as phosgene for polyurethanes and polycarbonate, acetic acid, fomic acid, propionic acid, dimethyl formamide, oxylates, acrylic acid and metal carbonyls etc. Separation and recovery of carbon monoxide from gas mixtures by adsorption is of great interest in recent years. There are many large scale CO sources such as off-gases from steel plants and other metallurgical plants, synthesis gas from steam reforming, CO_2 conversion and partial oxidation of hydrocarbon and coal gasification. In general, these gases contain CO together with CO_2, N_2, H_2, CH_4 and H_2O as impurities. For the recovery of CO from the gas mixtures, a two-stage adsorption process, consisting of a first PSA stage to remove CO_2 and moisture, and a second PSA stage to separate CO from the other gases, has been used (Beysel et al., 1988). This kind of process needs two adsorbents, which are

a CO_2 adsorbent to remove CO_2 and H_2O at first and a CO adsorbent to recover CO from the other gases. If an adsorbent with CO selectivity and capacity not only much higher than N_2, H_2 and CH_4 but also than CO_2 is available, a single-stage PSA process might use it to recover CO from the gas mixtures. Some studies have been reported in literature (Golden et al., 1991; Nishide et al., 1986; Tsuji et al., 1987). According to our long term study on CO adsorbents, we find that some zeolites modified by CuCl are better adsorbents for the application.

It was found (Xie and Youqi, 1990; Xie et al., 1984) in our laboratory that salts or oxides can disperse spontaneously onto the surface and pores of zeolites or other supports to form a monolayer or submonolayer, we call it solid/solid adsorption. This phenomenon is quite widespread and has been confirmed by many techniques such as XRD, XPS, ISS, EXAFS, NMR and Raman spectra, etc. For example, heating a mixture of CuCl and a Na-zeolite at a suitable temperature (lower

than the melting point of CuCl), the CuCl crystalline phase can disappear and change into monolayer dispersion state on the surface of the zeolite.

Since Cu^+ ions on the surface can selectively form coordination bonds with CO and weaken the basicity of the surface, if CuCl is heated and dispersed onto the surface of a Na-zeolite, an adsorbent with higher capacity and selectivity of CO than that of CO_2 might be obtained. This point has been confirmed in this work by the study on adsorbents by heating CuCl with NaY and 13X zeolites.

Experimental

Zeolite NaY was supplied by Lan Zhou Catalysts Factory, 13X by Shanghai Molecular Sieve Factory. Analytical grade CuCl was used. The purity of CO, CO_2, CH_4 and N_2 is >99.9%. Adsorbents are prepared by mixing and grinding CuCl with the zeolites then heating the mixtures at $350°C$ for four hours under nitrogen atmosphere.

Adsorption isotherms were measured volumetrically by using a glass apparatus.

X-ray diffraction (XRD) measurements were carried out on a BD-86 X-ray diffractometer with Ni-filtered CU $K\alpha$ radiation and a scintillation detector. Intensity of XRD peaks was measured by step scan mode.

Extended X-ray adsorption fine structure (EXAFS) spectra were obtained by using the SRL, BEPCNL (Synchrotron Radiation Laboratory, Beijing Electron Positron Collider National Laboratory) facilities in Beijing, China. The data were measured in transmission mode with a Si(111) double-crystal monochromator. Every EXAFS measurement was repeated two or three times. The EXAFS data were processed with standard procedure.

Results and Discussion

XRD Studies

Dispersion of CuCl onto zeolites by heating can be verified by using XRD. For example, Fig. 1 shows the XRD patterns of CuCl/NaY samples. A mixture of 0.31 g CuCl/g NaY before heating gives XRD pattern e with sharp peaks of crystalline CuCl phase. When the mixture is heated at 350°C for four hours, the peaks of crystalline CuCl disappear and the pattern e changes into f which is very much the same as the pattern of NaY (Fig. 1(a)). It indicates that CuCl has dispersed
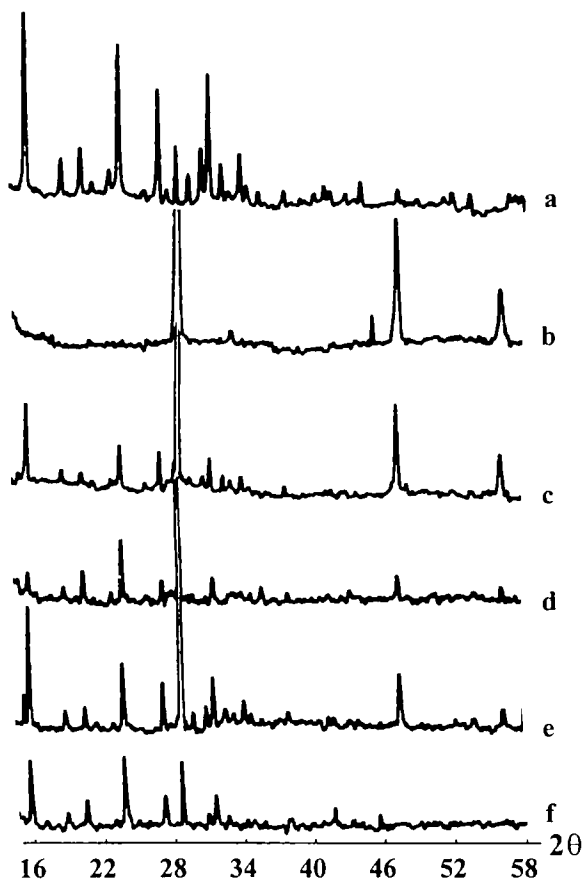

Figure 1. XRD patterns of CuCl/NaY samples: (a) NaY, (b) CuCl, (c) 0.83 g CuCl/g NaY before heating, (d) 0.83 g CuCl/g NaY 350° C, 4 hrs, (e) 0.31 g CuCl/g NaY before heating, (f) 0.31 g CuCl/g NaY 350°C, 4 hrs.

to the surface and pores of the zeolite after the heating. The mixture with more CuCl content, 0.83 g CuCl/g NaY before heating gives XRD pattern c, in which peaks of crystalline CuCl is higher than that in pattern e. After heating the mixture, XRD pattern c changes into d in which peaks of crystalline CuCl do not disappear but recede markedly. It suggests that a part of CuCl in the mixture have dispersed to the surface and pores of the zeolite, while the rest CuCl remains as residual crystalline phase. The amount of residual crystalline CuCl in the sample can be obtained from its XRD peak area. Measuring the quantity of residual crystalline CuCl by XRD quantitative phase analysis, we can get the dispersion capacity of CuCl on the zeolite. Figure 2 shows the amount of residual crystalline CuCl in CuCl/NaY samples after heating as a function of total CuCl content in the samples. In this plot, we
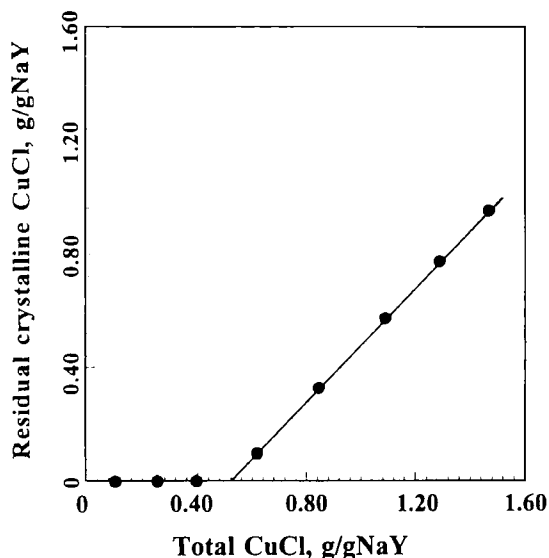
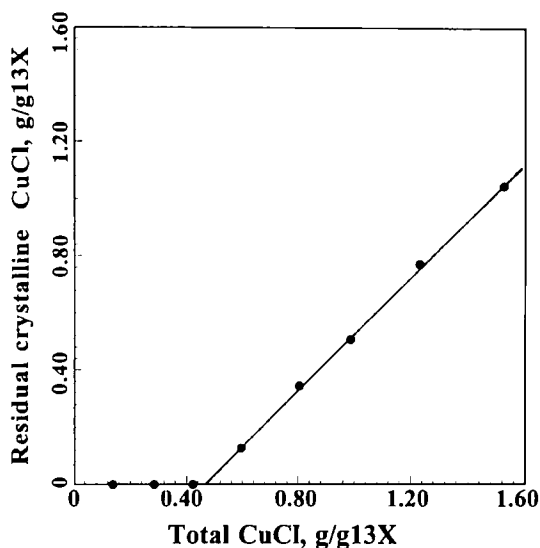*Figure 2.* Residual amount of crystalline CuCl versus total CuCl loading on NaY zeolite.

Figure 3. Residual amount of crystalline CuCl versus total CuCl loading on 13X zeolite.

can find a threshold value at 0.52 g CuCl/g NaY, which is the utmost dispersion capacity of CuCl on the NaY zeolite. If the loading of CuCl is lower than the threshold, all the CuCl can disperse atomically to the internal and external surface of the zeolite after heating, while higher than the threshold, there is residual crystalline phase of CuCl in the samples. From the dispersion threshold and the data of crystal structure of NaY zeolite, we can obtain that on an average, the dispersion of CuCl in NaY zeolite is 8.4 CuCl "molecules" per a supercage or a sodalite cage of NaY zeolite. Since the sodalite cage ($d = 6.6$ Å) is too small to accommodate 8.4 CuCl "molecules" ($d_{Cl^-} = 3.6$ Å, $d_{Cu^+} = 0.96$ Å), most of the CuCl should be on the surface of the suppercages ($d = 9$ Å). Only a small part of Cu^+ may result in ion-exchange with Na+ in the sodalite cages. Similar result has been obtained by using XRD for CuCl/13X systems as shown in Fig. 3. It gives a threshold of 0.47 g CuCl/g 13X.

EXAFS Studies

The structure of dispersed CuCl on the surface of NaY zeolite has been studied by using EXAFS. Fourier transforms of EXAFS of Cu-K edge for CuCl, Cu_2O and three heat-dispersion CuCl/NaY samples with different CuCl loading are shown in Fig. 4. In comparison with the curves of CuCl and Cu_2O, the CuCl/NaY
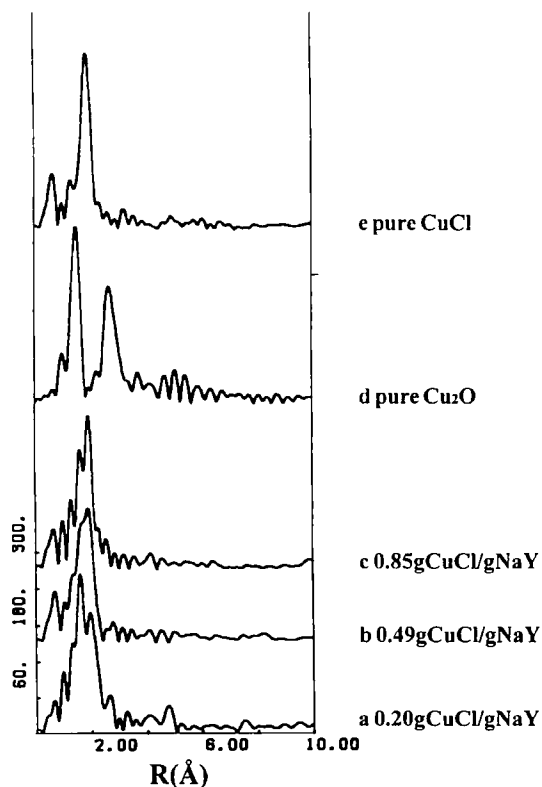

Figure 4. Fourier transforms (k^3, $\Delta k = 2.5–16.2$ Å^{-1}) of EXAFS spectra of CuCl/NaY samples, pure Cu_2O and pure CuCl.

curves have both Cu-Cl and Cu-O peaks. It indicates that the Cu^+ ions in the CuCl/NaY samples not only contact Cl^- but also O^{2-} ions. This is because the CuCl had already dispersed to the zeolite. The neighbours of Cu^+ ion in the CuCl/NaY samples will be very different from that in the crystalline CuCl, in which Cu^+ only has Cl^- as neighbours. Since there are great amount of O^{2-} ions on the surface of zeolite, the Cu^+ ions dispersed in CuCl/NaY has not only Cl^- but also O^{2-} as neighbours. The number of oxygen neighbour of Cu^+ ions will increase when the CuCl loading in NaY decreases. This is in agreement with the relative height of Cu-O and Cu-Cl peaks on the spectra of Fourier transforms of EXAFS of CuCl/NaY samples in Fig. 4. The curves, a, b, c show that the lower CuCl loading, the lower the ratio of the Cu-Cl peak height to the Cu-O peak height.

Adsorption Studies

We have reported that adsorbents with high adsorption capacity of CO can be obtained by heating mixtures of CuCl and zeolites (Xie et al., 1990; Xie et al., 1992). Figure 5 shows that the CuCl/NaY adsorbents have the highest CO adsorption at the composition close to its dispersion threshold, 0.52 g CuCl/g NaY, obtained by the XRD measurement mentioned above. The result is in good agreement with the monolayer dispersion
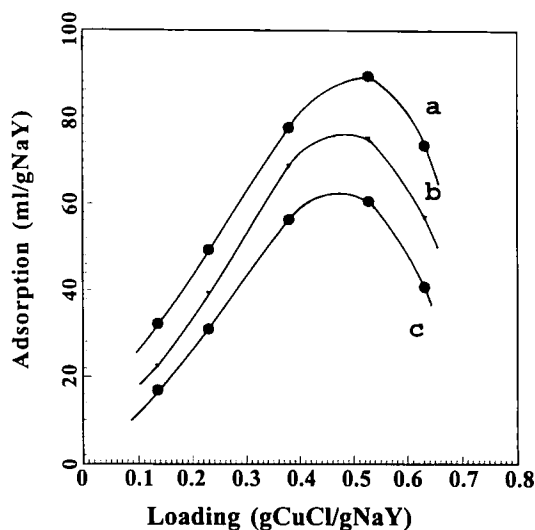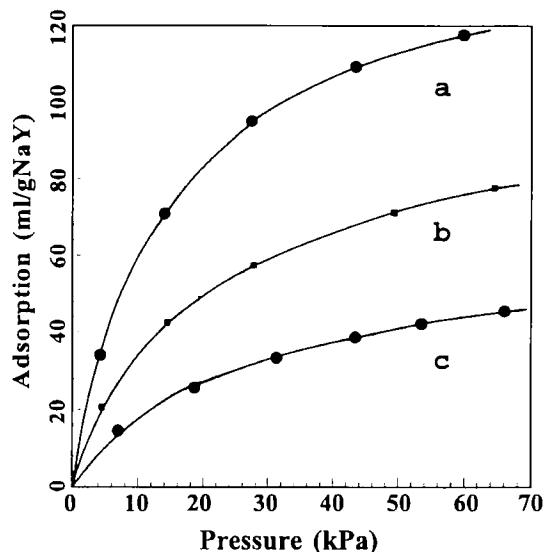

Figure 6. Adsorption isotherms of CO_2 on NaY and CuCl/NaY at 30°C: (a) NaY, (b) 0.384 g CuCl/g NaY, (c) 0.554 g CuCl/g NaY.

of CuCl on the zeolite. Figure 6 gives the adsorption isotherms of carbon dioxide at 30°C for CuCl/NaY adsorbents with various CuCl loading. The capacity of CO_2 is calculated on per gram support (Na-zeolite). The isotherms show that the CO_2 adsorption on the CuCl/NaY adsorbents decreases as the CuCl loading increases. The CO_2 amount adsorbed on CuCl/NaY is much less than that on the NaY adsorbent, because the surface property of CuCl/NaY is very different from that of NaY. Since Na aluminosilicates has weak basicity and CO_2 has weak acidity, NaY can adsorb CO_2 strongly. CuCl has weak acidity. When CuCl dispersed on NaY, the surface basicity decline and acidity increase, therefore the more the coverage of CuCl on the zeolite surface, the less the adsorption capacity of CO_2.

Figure 7 gives the isotherms of CO_2 and CO on NaY and a CuCl/NaY adsorbent with loading (0.554 g CuCl/g NaY) close to the monolayer dispersion threshold (0.52 g CuCl/g NaY). It shows that the CuCl/NaY adsorbent has CO adsorption much higher and CO_2 adsorption much less than NaY, and on the CuCl/NaY adsorbent the adsorption of CO is higher than that of CO_2.

Similar results have also been observed for the adsorbents of CuCl/13X which is also prepared by heating the mixtures of CuCl and 13X. The adsorption isotherms of CO and CO_2 on a CuCl/13X adsorbent are
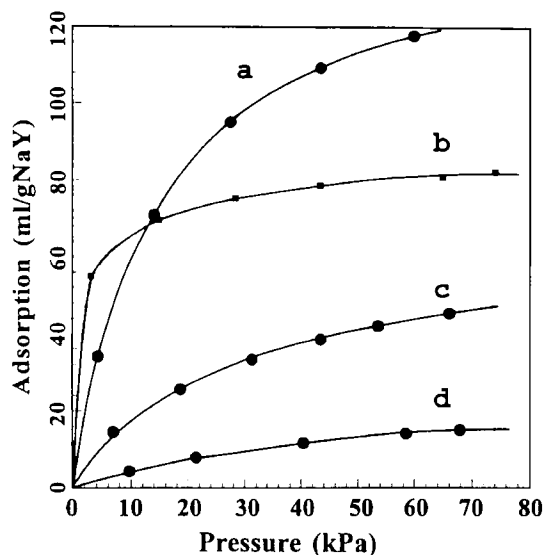

Figure 5. Adsorption of CO as a function of CuCl content in CuCl/NaY at 30°C: (a) $P_{CO} = 66.5$ kPa, (b) $P_{CO} = 26.6$ kPa, (c) $P_{CO} = 2.66$ kPa.

Figure 7. Adsorption isotherms of CO, CO_2 on NaY and CuCl/NaY (0.554 g/g) at 30 C: (a) CO_2 on NaY, (b) CO on CuCl/NaY, (c) CO_2 on CuCl/NaY, (d) CO on NaY.
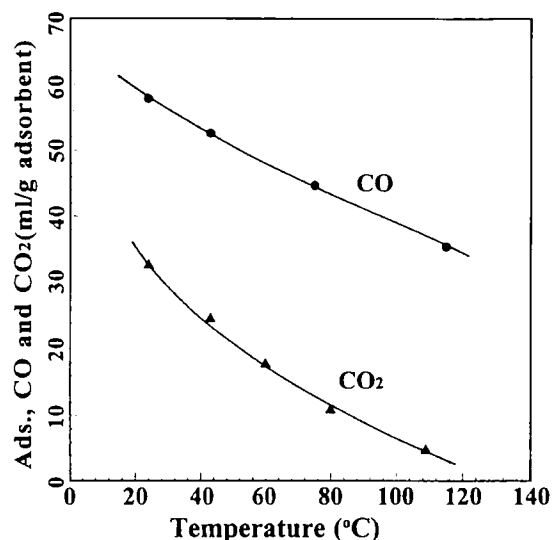

Figure 9. Adsorption isobars of CO and CO_2 for the adsorbent of of 0.554 g CuCl/NaY at 60.0 kPa.
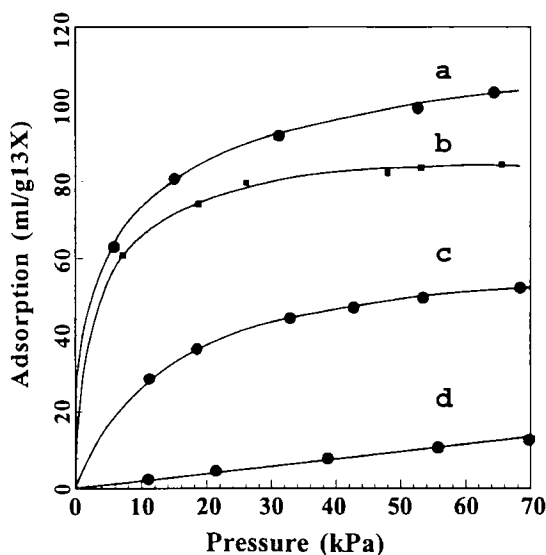

Figure 8. Adsorption isotherms of CO and CO_2 on 13X and CuCl/13X (0.523 g/g) at 30°C: (a) CO_2 on 13X, (b) CO on CuCl/13X, (c) CO_2 on CuCl/13X, (d) CO on 13X.

Figure 10. Adsorption of CO and CO_2 at 0.1 MPa for regenerated adsorbent (regenerated at 1.32 kPa).

shown in Fig. 8. The adsorbent also has CO adsorbtion higher than CO_2.

Figure 9 shows the isobars of CO and CO_2 on a CuCl/NaY adsorbent with the optimal composition of 0.554 g CuCl/g NaY and 20% binder. It is interesting to note that the decline of CO adsorption with increasing
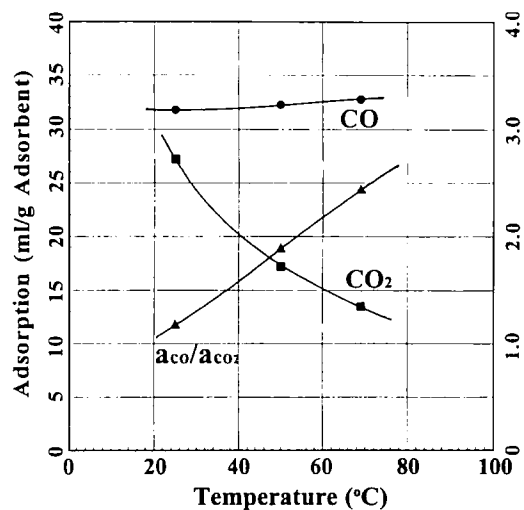
temperature is much slower than that of CO_2 adsorption. It indicates that the CuCl/NaY adsorbent would have higher separation coefficient for CO and CO_2 at a reasonable higher temperature than at room temperature.

Figure 10 shows the working adsorption amount of pure CO and CO_2 at 0.1 MPa for the CuCl/NaY adsorbent which has been regenerated at 1.32 kPa after a first adsorption of CO and CO_2. It shows that,
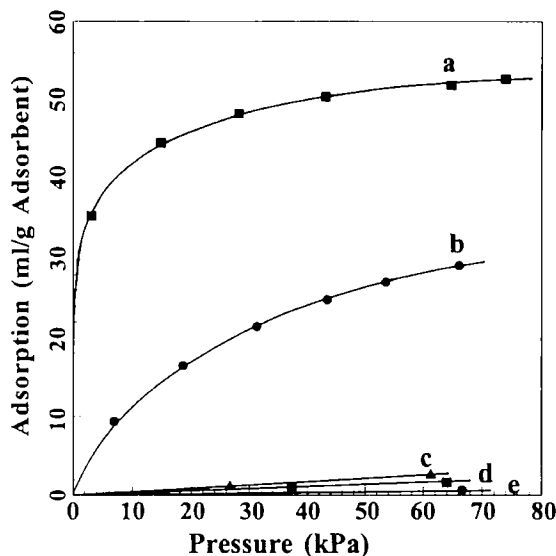
Figure 11. Adsorption isotherms of various gases on CuCl/NaY (0.554 g/g) adsorbent at 30 C: (a) CO, (b) CO_2, (c) CH_4, (d) N_2, (e) H_2.

with adsorption temperature increasing, the working adsorption capacity of CO changes very little, while that of CO_2 declines rapidly, i.e. the separation coefficients of CO and CO_2 (a_{CO}/a_{CO_2}) increases with increasing temperature. It means that a PSA process using the adsorbent, operating at a reasonable higher temperature, will have higher separating efficiency for CO and CO_2 than at room temperature.

Figure 11 gives the isotherms of CO, CO_2, CH_4, N_2 and H_2 on the CuCl/NaY adsorbent. It shows that its CO selective adsorbability for CO_2, CH_4, N_2 and H_2 is high and the adsorbent can be used for the separation of CO from gas mixtures containing CO_2, CH_4, N_2, H_2 and CO.

Using this adsorbent, a single-stage four beds ($\phi 50 \times$ 800 mm) PSA pilot test for the separation of CO from a simulated synthesis gas has been carried out. Each bed has a cycle of processes consisting of adsorption, pressure equalization, purge by CO product, evacuation for recovering CO and pressure build-up. Using a feed containing CO 31.5%, CO_2 10.3%, N_2 3.8%, H_2 50.2% CH_4 4.2% and H_2O < 0.1%, and operating at 70°C 1.5 MPa to 0.013 MPa and cycle time 15~20 mins, the

PSA test can obtain CO product of purity >99.5%, impurities CO_2 < 4000 ppm, CH_4 < 100 ppm and H_2 < 500 ppm, yield > 85% and productivity >0.30 mol/cycle kg adsorbent.

Conclusion

By heating CuCl with NaY and 13X zeolite at a suitable temperature, CuCl can disperse onto the surface and pores of the zeolites to form a monolayer or submonolayer. This point has been confirmed by XRD and EXAFS studies. Dispersed CuCl changes the surface basicity of the zeolites and decreases the CO_2 adsorption capacity on the zeolite. In comparison with the Na-zeolites, the CuCl modified Na-zeolites have CO capacity and selectivity much higher than CO_2, CH_4, N_2 and H_2. An adsorbent of CuCl/NaY has been used in a single stage PSA pilot test successfully to separate CO from a synthesis gas.

Acknowledgment

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