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# SOME PHYSICAL CHARACTERISTICS OF A METHANOL SYNTHESIS CATALYST

# ลักษณะทางกายภาพบางประการของตัวเร่งปฏิกิริยาสำหรับสังเคราะห์เมทิลแอลกอฮอล์

**Wiwut Tanthapanichakoon** วิวัฒน์ ตัณฑะพานิชกุล

**Arunwan Punyaporn** อรุณวรรณ ปัญญาภรณ์

**Tomoyuki Inui*** โทโมยูกิ อินุย

**Department of Chemical Engineering, Chulalongkorn University**
ภาควิชาวิศวกรรมเคมี จุฬาลงกรณ์มหาวิทยาลัย

## ABSTRACT

*A ternary methanol catalyst composed of $Cu-ZnO-Cr_2O_3$ (atomic ratios of Cu:Zn:Cr = 2:2:1) was prepared and used to synthesize methanol from synthesis gas ($CO:H_2$ = 1:2). Using a fresh sample of the activated catalyst, its BET surface area, ZnO crystal size and Cu crystal size were measured. The crystal sizes were determined by the X-ray diffraction method. For the fresh catalyst, CO adsorption and metal surface area were also determined.*

* Department of Hydrocarbon Chemistry, Kyoto University, Japan.

In this study a ternary catalyst of copper-zinc oxide promoted by chromium oxide is used for methanol synthesis from one part of CO and two parts of $H_2$. The composition of the prepared catalyst is Cu:Zn:Cr = 2:2:1 and was prepared from copper nitrate, zinc oxide and chromium oxide.

## MATERIALS AND METHODS

### Methanol synthesis experiments

Experiments were carried out under various conditions in a through-flow tubular reactor using a feed consisting of $H_2$ and CO at a ratio of 2 to 1. The reaction pressure was varied from 20-50 kgf/cm$^2$, reaction temperature, from 220-300°C; and the space velocity, from around 2,000-16,000 ml of synthesis gas/(ml cat. h).

Figure 1 shows a schematic diagram of the experimental apparatus, which was designed and constructed to withstand a maximum pressure of 50 kgf/cm$^2$.

Figure 2,3 show a few typical experimental results obtained with the above catalyst. It was found that, as expected, methanol selectivity generally increased with increasing pressure. It tended to rise at first with temperature before decreasing as temperature increased further. Space time yield (STY) of methanol increased with both pressure and temperature. With respect to space velocity, STY of methanol increased all the way with space velocity because its methanol selectivity decreased only slightly with space velocity. (Note that STY = space velocity × total CO conversion × methanol selectivity)

### BET surface area

A glass apparatus was used to measure the volume of gas adsorbed on a sample of the solid material. The apparatus operated at a low pressure which can be varied from near zero up to about 1 atm. The operating temperature was in the range of the normal boiling point of $N_2$. The procedure was to pass a gaseous mixture of known composition over the sample until equilibrium was reached, that is, until the solid catalyst had adsorbed an amount of nitrogen corresponding to equilibrium at its partial pressure in the mixture. Then the nitrogen was desorbed by heating the sample while a stream of pure helium flowed over it. The amount of desorbed $N_2$ was measured with a thermal-conductivity detector. Figure 4 taken from Smith[5] shows some isotherms obtained with this method.

Brunauer-Emmett-Teller[1] extended the monolayer Langmuir isotherm

$$\frac{P}{V} = \frac{1}{KV_m} + \frac{P}{V_m} \qquad \text{.....(2)}$$

to apply to multilayer adsorption and arrived at

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{cV_m P_0} \qquad \text{.....(3)}$$

*After the catalyst was used for the synthesis of methanol in a high pressure through-flow reactor for approximately 50 h at pressures ranging from 20-50 kg/cm$^2$ and temperatures from 220-300°C, the above physical properties of the used catalyst were determined for comparison with the fresh sample. It was found that the crystal size of ZnO increased from 931 Å to 2,600 Å with respect to face 100 and that of Cu increased from 170 Å to 2,300 Å with respect to face 111. The BET surface area decreased from 57.4 m$^2$/g to 46.2 m$^2$/g. For the fresh catalyst, its metal surface area and Cu particle sizes were 2.57 m$^2$/g cat. and 536.31 Å. This clearly indicated that appreciable sintering occured at 300°C and less, resulting in appreciable crystal growth and reduction of BET surface area. It also showed that Cu was more susceptible to sintering than ZnO.*

## บทคัดย่อ

การศึกษาคุณสมบัติทางกายภาพของตัวเร่งปฏิกิริยาในการสังเคราะห์เมทิลแอลกอฮอล์จากก๊าซสังเคราะห์ ($CO:H_2$ = 1:2) ซึ่งประกอบด้วย $Cu-ZnO-Cr_2O_3$ (อัตราส่วนอะตอม Cu:Zn:Cr = 2:2:1) โดยการหาพื้นที่ผิวของตัวเร่งปฏิกิริยาก่อนใช้งานโดยวิธีของ BET หาขนาดผลึกของ ZnO และ Cu โดยวิธี X-ray diffraction พร้อมทั้งทำการดูดซับก๊าซคาร์บอนมอนอกไซด์ และหาพื้นที่ผิวโลหะของตัวเร่งปฏิกิริยาก่อนใช้งาน และหลังจากที่ใช้ตัวเร่งปฏิกิริยาในการสังเคราะห์เมทิลแอลกอฮอล์ในเครื่องปฏิกรณ์ที่ความดัน 20 - 50 กก./ตร.ซม. และอุณหภูมิ 220 - 300°ซ. เป็นเวลาประมาณ 50 ชม. ได้นำตัวเร่งปฏิกิริยาไปหาคุณสมบัติทางกายภาพอีกครั้งหนึ่ง เพื่อเปรียบเทียบกับตัวเร่งก่อนทำปฏิกิริยา พบว่าขนาดของผลึก ZnO ด้าน (1, 0, 0) โตขึ้นจาก 931 Å เป็น 2,600 Å และด้าน (1, 1, 1) ของผลึก Cu เพิ่มจาก 170 Å เป็น 2,300 Å นอกจากนี้ พื้นที่ผิวที่หาโดยวิธีของ BET ก็ลดลงจาก 57.4 ตร.ม./ก. เป็น 46.2 ตร.ม./ก. และยังพบว่าตัวเร่งก่อนทำปฏิกิริยามีพื้นที่ผิวโลหะและขนาดของอนุภาค Cu บนผิวตัวเร่งเป็น 2.57 ตร.ม./ก. และ 536.31 Å ตามลำดับ ข้อมูลที่ได้จากงานวิจัยนี้ทำให้ทราบว่า ซินเทอริง (sintering) ของตัวเร่งปฏิกิริยาเกิดขึ้นได้ที่อุณหภูมิประมาณ 300°ซ. โดยจะเกิดขึ้นที่ Cu มากกว่า ZnO ผลก็คือขนาดผลึกโตขึ้น และพื้นที่ผิว BET ของตัวเร่งปฏิกิริยาลดลง

## INTRODUCTION

At present, methanol is commercially produced by catalytic hydrogenation of carbon monoxide under pressure, as follows:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \text{.....(1)}$$

where $P_0$ = saturation or vapor pressure of $N_2$ at liquid $N_2$ temperature, 77.3 K
$c$ = constant for the particular temperature
$V$ = volume of $N_2$ (NTP) adsorbed by the sample
$P$ = $N_2$ pressure in equilibrium with the surface
$V_m$ = The volume of one monomolecular layer of gas

**Crystal size via X-ray diffraction**

A Bragg-Brentano powder diffractometer allows a range of diffraction angle $\theta$ values to be scanned. The photon detector rotates at twice the angular speed of the specimen, thereby maintaining the required geometrical condition. Since the specimen consists of a random distribution of crystallites, the appropriate planes are in the correct orientation to diffract the wavelength $\lambda$ each time the Bragg condition is satisfied. Thus in X-ray diffraction, each peak angle value corresponds to a certain d spacing. With the wavelength-dispersive spectrometer, a single crystal of known d spacing is used to disperse the polychromatic beam of characteristic wavelength of the sample, such that wavelength diffracts at a discrete angle. Figure 6 shows an example X-ray diffractometer system.[3]

The crystallite size can be found with the equation defined by P. Sherrer in 1918.[2]

$$\beta = K\lambda/L\cos\theta$$

where $\beta$ = the peak breadth in radians at half-maximum intensity due only to the small crystallite size,
$K$ = a constant conveniently equal to unity,
$\lambda$ = X-ray wavelength,
$L$ = average crystallite dimension normal to the diffracting plane,
$\theta$ = the diffraction angle.

The observed peak breadth at half-maximum intensity is measured in degree $2\theta$. If the particular peak occurs at relatively low $2\theta$ angles, the measured breadth must be corrected for broadening caused by the instrument.

**Metal surface area and Cu particle sizes via CO adsorption**

The common adsorbates used in selective chemisorption are $H_2$, CO, $O_2$, $N_2O$ and $C_6H_6$. First of all the correct experimental condition for the formation of a monolayer must be determined: temperature, pressure, time required for equilibrium. Usually, the measurements must be corrected for, because of adsorption on the support, adsorption inside the metal, or a weak chemisorption on the metal itself. The first use of selective chemisorption is that of Emmelt and Brunauer who used CO to determine the number of iron atom at the surface of a catalyst.[1]

## RESULT

### Determination of BET surface area of methanol synthesis catalyst

**Fresh sample**

1. Set He carrier gas flow = 30 ml/min (room temperature = 25°C).
2. Add $N_2$ gas and increase flow to 41.1 ml/min.
3. Since total flow ($N_2$ + He) = 41.10 ml/min

$$P_a = \frac{N_2}{He+N_2} = \frac{41.10-30}{41.10} = 0.270$$

4. Sample + paper = 332.87 mg
   paper = 266.19 mg
   sample = 66.68 mg
   desorption temp. = 300°C
   area counts under desorption peak = 1,041,756
   area counts per 1 cc of $N_2$ = 921,617

Analysis of data (fresh catalyst)

Since c $\gg$50, the BET equation may be approximated by

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m}\frac{P}{P_0} \qquad \text{.....(1)}$$

In this research BET measurement

$P_0$ = 1.1 atm, $P = P_aP_b$

$$P_b = \left(\frac{273.16}{273.16 + \text{room temp.}}\right) \times P_t$$

$P_t$ = 1 atm, $\therefore P_b = \left(\frac{273.16}{273.16+25}\right) \times 1 = 0.916$ atm

$\therefore P = (0.270)(0.916) = 0.247$ atm

$$\text{Since } V = \frac{\text{desorption peak area}}{\text{calibration area for 1 cc}}$$

where desorption peak area = 1,041,756
calibration area for 1 cc = 921,617

$$\therefore V = \frac{1,041,756}{921,617} = 1.13 \text{ cc}$$

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m}\frac{P}{P_0}$$

$$\frac{0.247}{1.13\,(1.1-0.247)} = \frac{1}{V_m} \times \frac{0.247}{1.1}$$

$V_m$ = 0.876 ml for 0.06668 g adsorbent

$S_g$ = $4.37 \times V_m$ $m^2$/g solid adsorbent

= (4.37)(0.876) $m^2$/0.06668 g catalyst

$\therefore$ total surface = 57.41 $m^2$/g catalyst

**Used catalyst**

sample + paper = 477.87 mg

paper = 265.04 mg

sample = 212.83 mg

desorption temp. = 300°C

area counts under desorption peak = 2,673,419

area counts per 1 cc of $N_2$ = 921,576

Analysis of data (used catalyst)

since c $\gg$50, the BET equation may be simplified as

$$\frac{P}{V(P_0-P)} = \frac{1P}{V_m P_0}$$

$P_0$ = 1.1 atm

P = 0.247 atm

since $V = \frac{2,673,419}{921,570}$ = 2.90 cc

$$\frac{0.247}{2.9(1.1-0.247)} = \frac{1(0.247)}{V_m(1.1)}$$

$V_m$ = 2.25 cc

$S_g$ = $4.37 \times V_m$ $m^2$/g solid adsorbent

= $4.37 \times 2.25$ $m^2$/0.2128 g

= 46.2 $m^2$/g cat.

Thus it was found that the BET surface area decreased from 57.4 to 46.2 $m^2$/g after the catalyst had been used in methanol synthesis.

**Determination of crystal sizes of methanol synthesis catalyst**

**Fresh catalyst**

Using a fresh sample of the above catalyst, its X-ray diffraction pattern was obtained.

Procedure

1. Take 0.1 g of catalyst.
2. Grind in a mortar for about 5 min.

3. Mix with vaseline and smooth out on sample glass plate.
4. Take record from 70° – 10° (diffraction angle).

a) ZnO crystal (fresh catalyst)

$$\text{Data } 2\theta = 31.8°, \text{ half-height width} = \frac{6\text{ mm}}{20\text{ mm}} \times 1 = 0.30° = B_0$$

$$\theta = 15.9°$$

$$\Delta = \frac{2(\lambda_2 - \lambda_1)}{\lambda_1} \sin\theta \times \frac{180}{\pi} = 4.94 \times 10^{-3} \sin\theta \times \frac{180}{\pi} \text{ (degrees)}$$

$$\because \lambda_1 = 1.5405, \quad \lambda_2 = 1.5443$$

$$\text{Now } \Delta = 0.0775° \quad \frac{\Delta}{B_0} = 0.258°$$

$$\text{From Figure 8 } \frac{B}{B_0} = 0.925 \Rightarrow B = 0.278°$$

$$\text{Standard quartz b} = 0.188° \text{ at } 2\theta = 31.8°$$

$$\therefore \frac{b}{B} = 0.676$$

$$\text{From Figure 9 } \beta/B = 0.32 \Rightarrow \beta = 0.32 \times 0.278 = 0.0890°$$
$$= 0.00155 \text{ (rad)}$$

$$L = \frac{K\lambda}{\beta \cos\theta}$$

$$K = 0.9 \quad \lambda = 1.5418 \text{ Å}$$

$$\therefore L = \frac{(0.9)(1.5418)\text{ Å}}{(0.00155)\cos 15.9°} = 931 \text{ Å}$$

Thus particle size of ZnO = 931 Å with respect to face 100

**Used catalyst**

b) ZnO crystal (used catalyst)

$$\text{After reaction } 2\theta = 31.8° \Rightarrow \theta = 15.9°$$

$$\text{Half-height width } B_0 = \frac{4.8}{20} \times 1 = 0.24°$$

$$\Delta = 0.0775° \text{ (as before)} \Rightarrow \frac{\Delta}{B_0} = 0.323$$

$$\text{From Figure 8 } \frac{B}{B_0} = 0.89 \Rightarrow B = (0.89)(0.24) = 0.214°$$

$$b = 0.188° \Rightarrow \frac{b}{B} = 0.880$$

$$\text{From Figure 9 } \frac{\beta}{B} = 0.15 \Rightarrow \beta = (0.15)(0.214) = 0.0321°$$
$$= 0.000560 \text{ (rad)}$$

$$L = \frac{K\lambda}{\beta \cos\theta}$$

$$L = \frac{(0.9)(1.5418)}{(0.000560)\cos 15.9} = 2600 \text{ Å}$$

Thus particle size of ZnO (used catalyst) = 2600 Å with respect to face 100. From the above, the crystal size of ZnO increased from 931 Å to 2600 Å with respect to face 100. Similary, it was found that Cu crystal size increased from 170 Å to 2300 Å with respect to face 111 after the catalyst had been used for methanol synthesis.

**Determination of metal surface area and Cu particle sizes**

**Before reaction (fresh catalyst)**

1. Paper = 279.85 mg
   Paper + sample = 386.99 mg
   ∴ sample = 107.14 mg
2. Set up sample in adsorption tube.
3. Pass He gas (5 kg/cm$^2$) through GC columns:
   flow 1 = 40 ml/min
   flow 2 = 40 ml/min.
4. After GC enter steady state, pour liquid $N_2$ into trap.
5. Turn on "current" of GC.
6. After GC reach steady state, turn off "current" (turn on "current" only to detect CO).
7. Start reduction of metal surface by introducing $H_2$ (about 1 kg/cm$^2$) into He ($H_2$ 10% vol.) and heating up from room temperature to 400°C, holding at 400°C for 10 min.
8. Stop flow of $H_2$, flow He for another 5 min.
   Cool system down rapidly using electric fan.
9. Set GC "current on". Introduce CO (20 $\mu$l) at 1-min interval (approx.). Use no packing in GC columns.

**Data analysis procedure**

1. From Table 1 read areas under peaks $s_1, s_2, \ldots, s_n = s_0$
2. Compute $s_i - s_0$ (i = 1, 2, ..., n) as follows:

$$\sum_{i=1}^{n} (s_i - s_0) = s = 454{,}468$$

$$\text{CO (20 } \mu\text{l)} \propto s_0 = 48{,}000$$

$$\text{CO adsorbed} = \frac{s}{s_0} \times 0.02 \times \left( \frac{273}{273 + \text{room temp.}} \right) \text{ ml NTP}$$

$$= \frac{454{,}468}{48{,}000} \times 0.02 \times \left( \frac{273}{273 + 400} \right)$$

$$= 0.07681387 \text{ ml NTP/sample weight}$$

From experiment paper + sample = 386.99 mg

paper = 279.85 mg

$\therefore$ sample = 107.14 mg

3. Find CO ads./g cat. = 0.07681387 ml NTP/107.49 mg
   = 0.7351 ml NTP/g cat. = a

4. Find surface area of metal/g cat. Since CO 1 molecule = 13 sq. Å

$$S \text{ metal} = \frac{a}{22{,}400} \times (6.02 \times 10^{23})^* \times (13 \times 10^{-20}) \text{ m}^2/\text{g cat.}$$

$$= \frac{0.7351}{22{,}400} \times 6.02 \times 10^{23} \times (13 \times 10^{-20})$$

$$= 2.568 \text{ m}^2/\text{g cat.}$$

Mole ratio of catalyst = Cu:Zn:Cr = 2:2:1

Atomic weight ratio = $63.54 \times 2 : 65.37 \times 2 : 51.996 \times 1$

= 127.08 : 130.74 : 51.996

5. Find metal surface area per g Cu = 2.568 $m^2$/0.41 g Cu

= 6.263 $m^2$/g Cu = b

6. Find average radius of Cu particles (n = number of particles)

$$\frac{4}{3}\pi r^3 \rho_{Cu} \cdot n = 1 \text{ g}$$

$$4\pi r^2 \cdot n = b = 6.264 \text{ m}^2/\text{g Cu}$$

$$r_{av} = \frac{3}{b\rho_{Cu}}, \quad \rho_{Cu} = 8.93 \text{ g/cm}^3$$

$$= \frac{3}{6.264 \times 8.93 \text{ g/cm}^3}$$

$$= 5.363 \times 10^{-8} \text{ m} = 536.31 \text{ Å}$$

The above results showed that metal surface area of fresh catalyst is 2.57 $m^2$/g catalyst and average Cu particle size is 536.31 Å.

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* Avogadro number

## CONCLUSION

The above experimental results indicate that the crystal size of ZnO increased from 931 Å to 2,600 Å with respect to face 100 and that of Cu increased from 170 Å to 2,300 Å with respect to face 111. The BET surface area decreased from 57.4 to 46.2 $m^2/g$. Thus it may be concluded that appreciable sintering occurred at 300°C and less. Changes in the surface structure of the catalyst were due to prolonged exposure to elevated temperature in the reacting atmosphere, resulting in crystal growth and reduction of BET surface area. We also conclude that Cu was more susceptible to sintering than ZnO.

## ACKNOWLEDGEMENT

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**Table 1. CO adsorption on methanol synthesis catalyst**

| time (second) | area (counts) |
|---|---|
| 116 | $S_1$ = 3,828 |
| 204 | $S_2$ = 3,826 |
| 285 | $S_3$ = 6,284 |
| 362 | $S_4$ = 10,308 |
| 454 | $S_5$ = 10,994 |
| 522 | $S_6$ = 15,918 |
| 591 | $S_7$ = 20,170 |
| 668 | $S_8$ = 24,344 |
| 764 | $S_9$ = 23,175 |
| 849 | $S_{10}$ = 25,546 |
| 943 | $S_{11}$ = 25,715 |
| 1,036 | $S_{12}$ = 35,409 |
| 1,182 | $S_{13}$ = 22,184 |
| 1,266 | $S_{14}$ = 34,857 |
| 1,406 | $S_{15}$ = 30,915 |
| 1,531 | $S_{16}$ = 20,059 |
| 1,623 | $S_{17}$ = 48,000 |

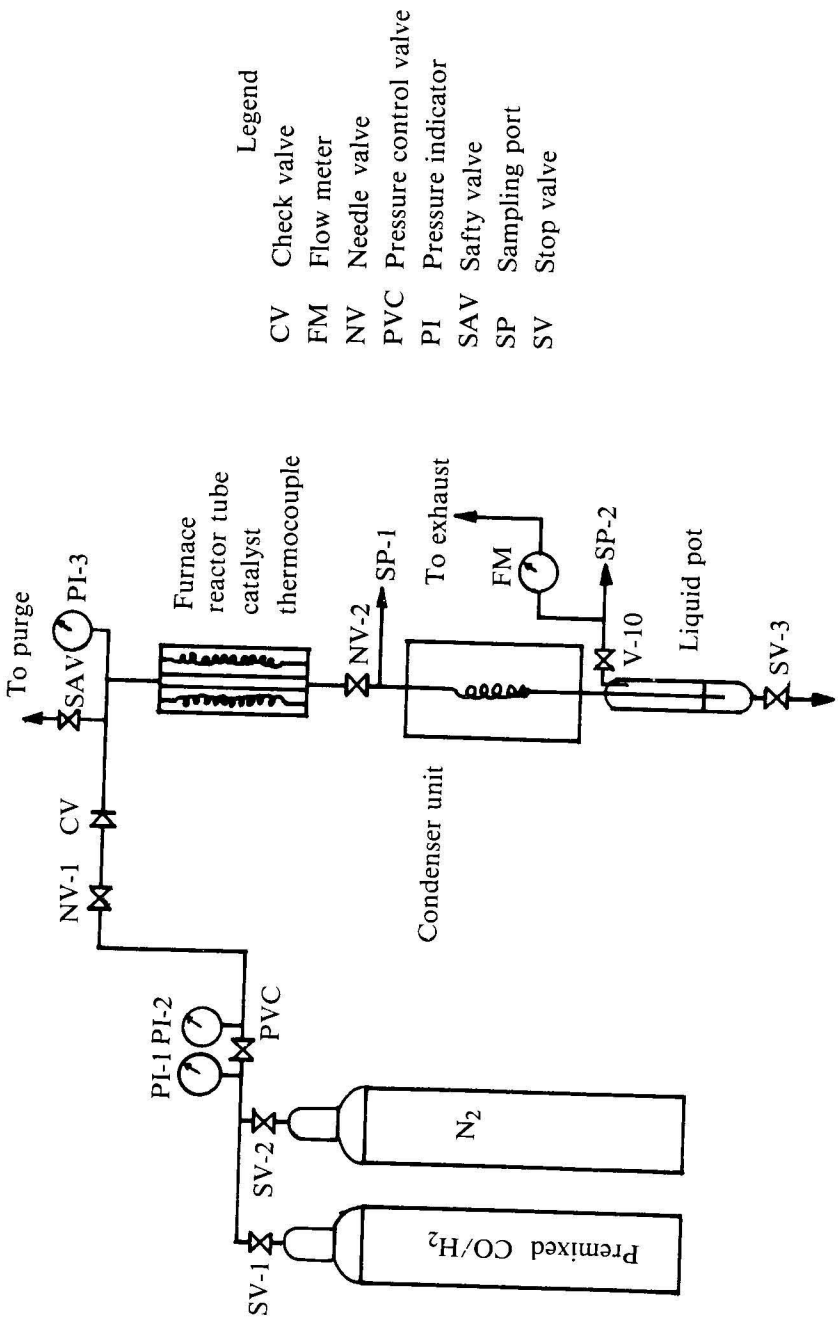


**Fig. 1 Schematic diagram of the experimental apparatus**

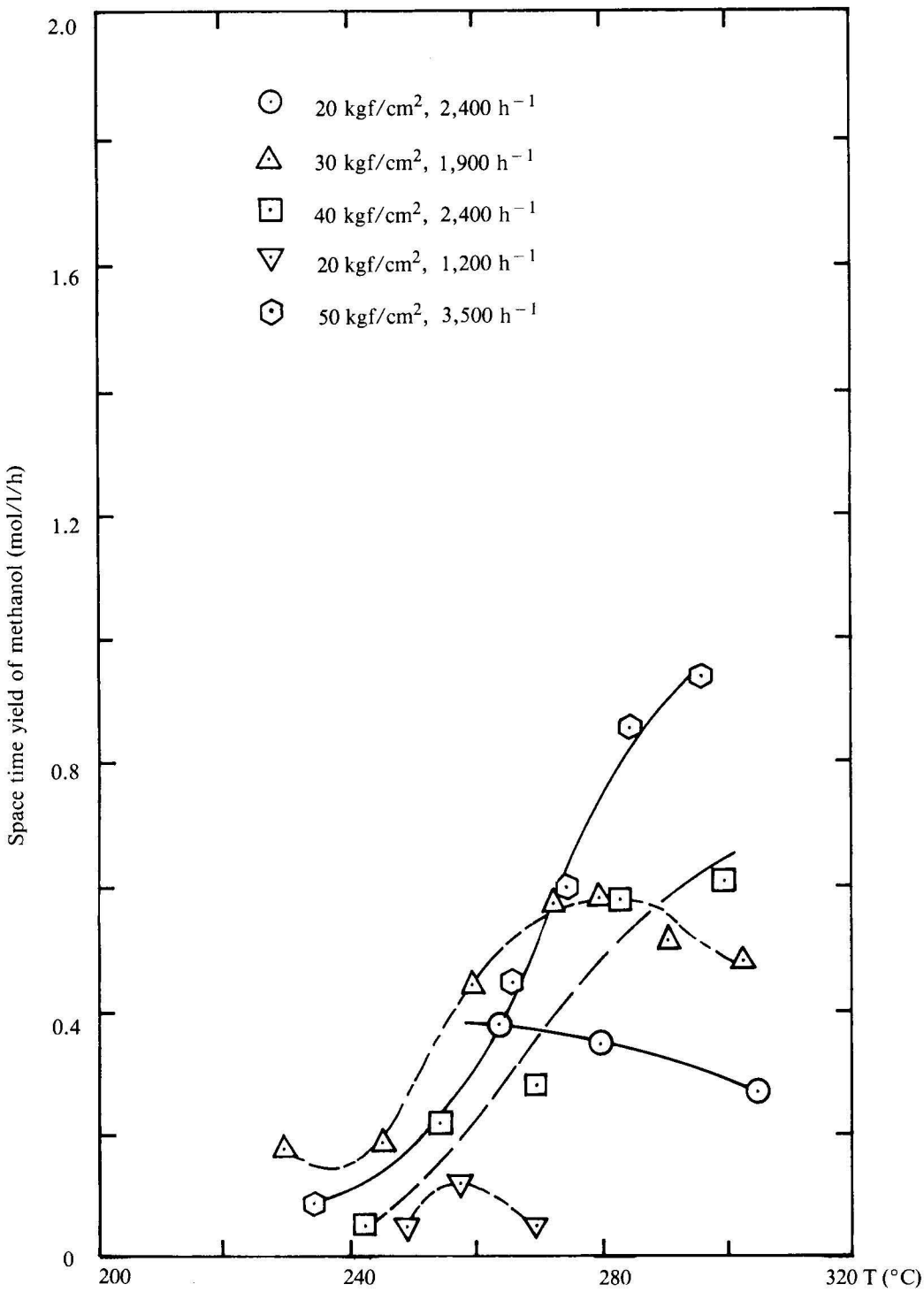


**Fig. 2 Effect of temperature (200 – 300°C), pressure (20 – 50 kgf/cm$^2$) and space velocity (2,400 – 3,500 h$^{-1}$) on space time yield of methanol**

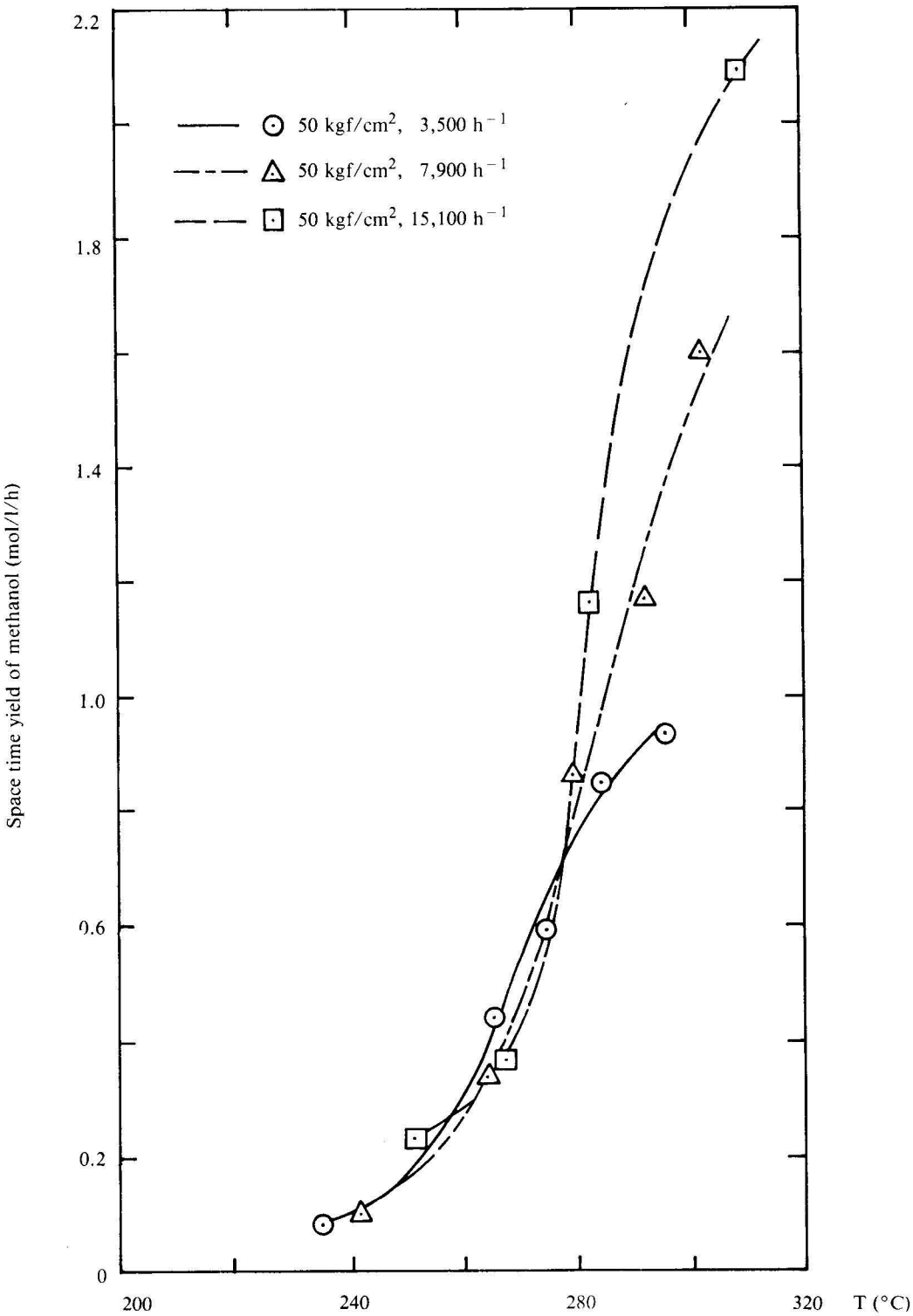


**Fig. 3 Effect of temperature (200 – 300°C) and space velocity (3,500 – 15,100 $h^{-1}$) on space time yield of methanol**

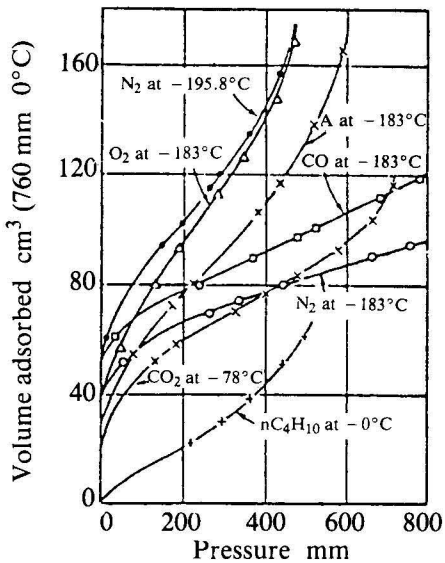


**Fig. 4 Adsorption isotherms for various gases on a 0.606 g sample of silica gel[5]**

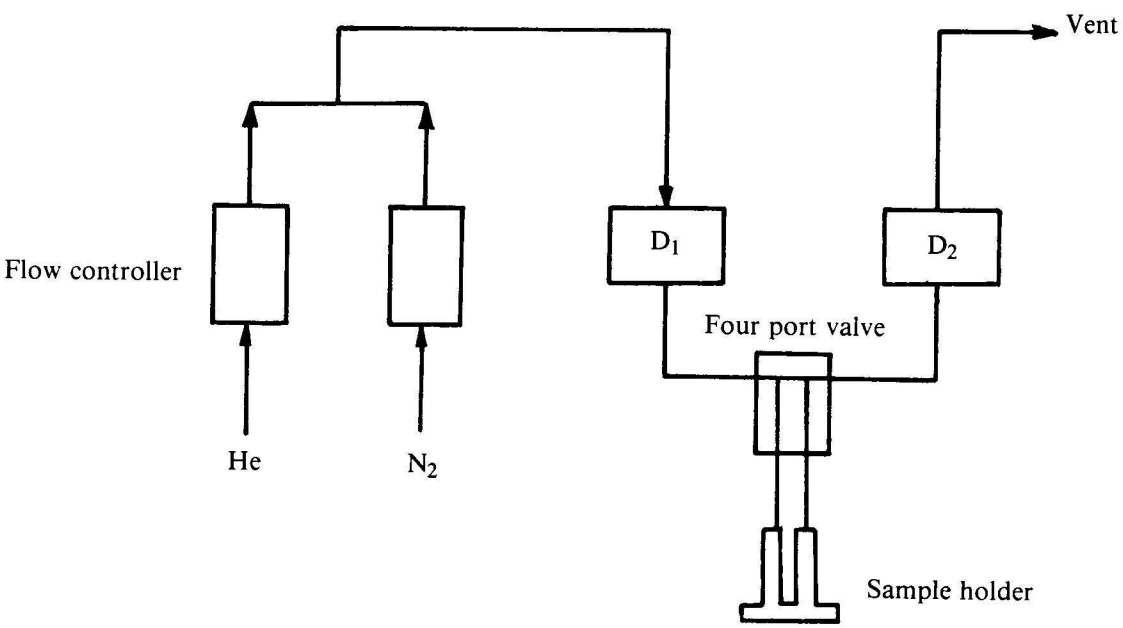


**Fig. 5 BET surface area analyzer[4]**

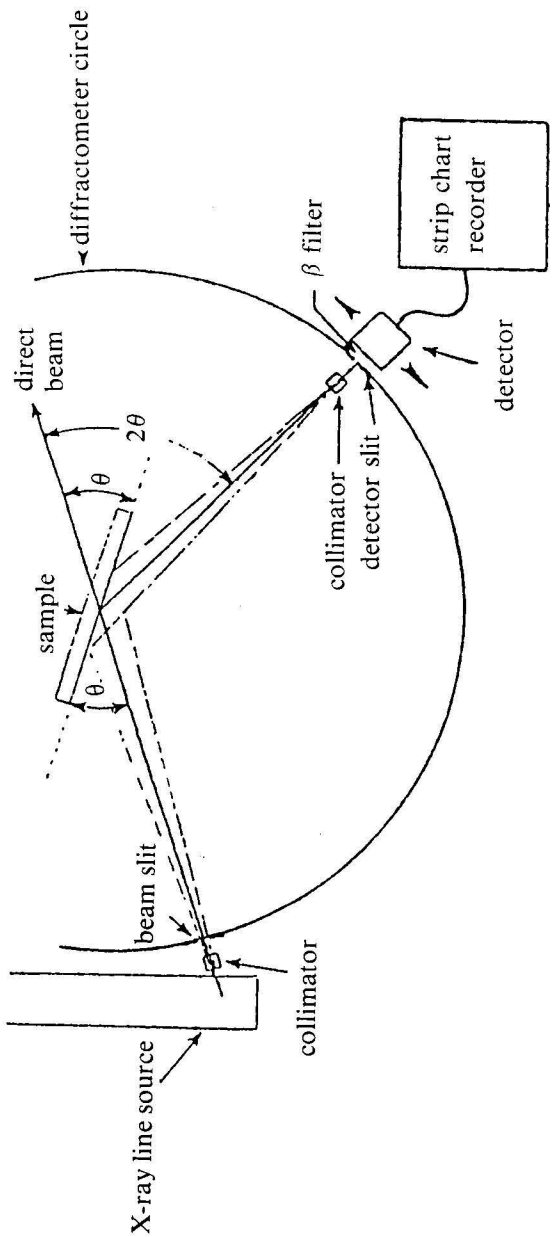


**Fig. 6 Typical X-ray diffractometer system**[3]

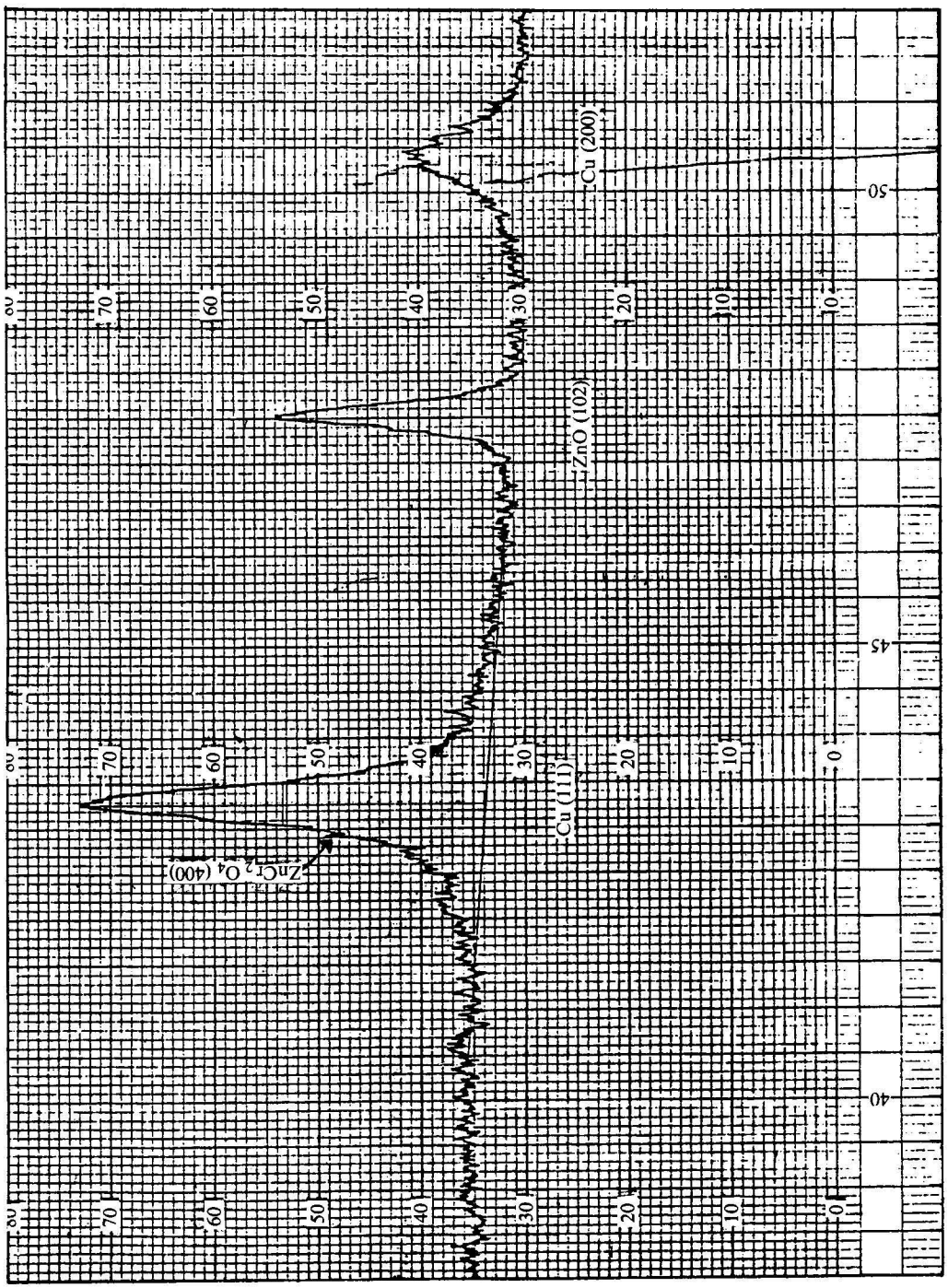


Fig. 7 X-ray diffraction pattern

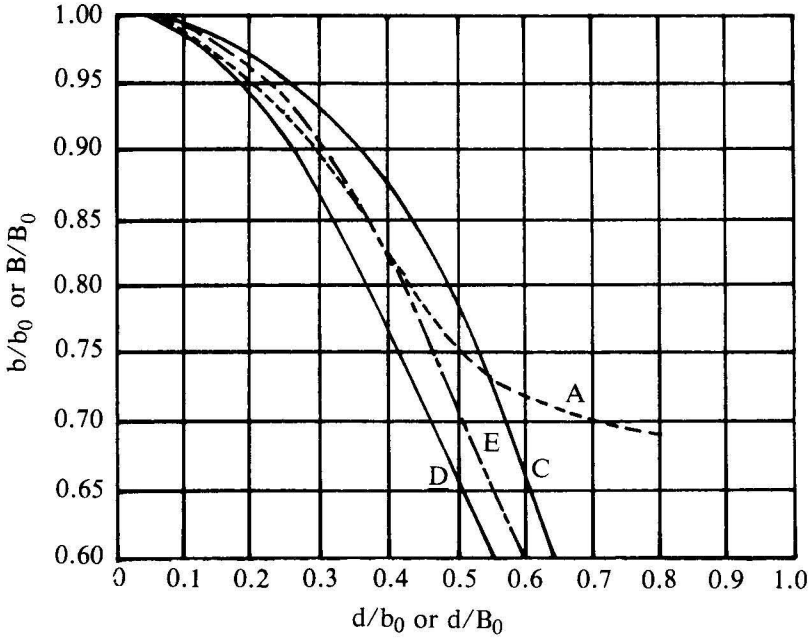


**Fig. 8 Curve for correcting line breadth**[5]

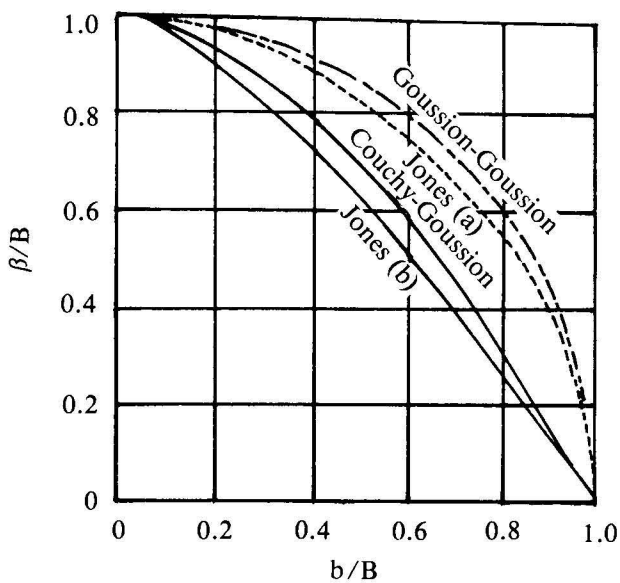


**Fig. 9 Curve for correcting integrate breadth**[5]

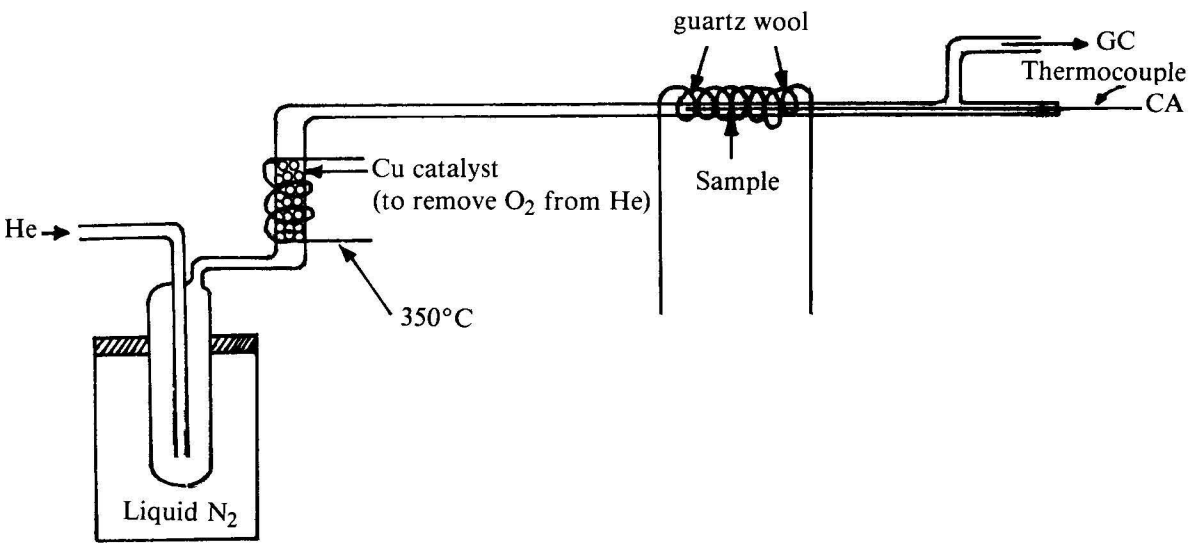


**Fig. 10 Diagram of CO adsorption set**