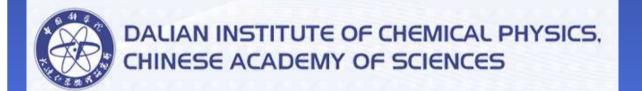
DICP Course - Dalian, 2012 Preparation of solid catalysts Exercises

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Ex.1. A transition alumina support has been prepared; the determination of the specific surface area (S_{BET}) and the porous volume (V_p) gave the following results:

$$S_{BET} = 200 \text{ m}^2 \text{ g}^{-1}$$
 $V_{p} = 1 \text{ mL g}^{-1}$

- a) Calculate the size of the pores (hint: use the cylindrical pore model with constant diameter)
- b) Is this alumina microporous, mesoporous or macroporous?
- c) What is the accuracy of the experimental data? (hint: the accuracy can be expressed as estimated relative standard deviation)

Ex.2. A transition alumina support display a specific surface area $S_{BET} = 180 \text{ m}^2 \text{ g}^{-1}$.

It is used for the preparation of platinum supported catalysts Pt/Al₂O₃.

The maximum loading of H_2PtCl_6 precursor is: 1.6 μ mol m⁻².

The number of surface hydroxyl groups is 8 OH nm⁻².

- a) Compare the number of surface OH groups able to adsorb the precursor to the total number of surface OH groups (assumption: the adsorption need one OH group per precursor molecule).
- b) Describe the different steps of the preparation procedure.
- c) Determine the maximum platinum loading (in term of mass percentage) that can be reach at the end of the catalyst preparation.
- d) What would you suggest for the surface loading for 10 g of support? Calculate the initial pH for different surface loadings. Conclusion.

Ex.3. We have prepared a catalyst Ir/Al_2O_3 for the decomposition of hydrazine for space propulsion. The characteristics of the catalyst are:

wt.-%
$$Ir = 40 \%$$

Specific surface area of the support = $100 \text{ m}^2 \text{ g}^{-1}$

Porous volume = 0.7 mL g^{-1}

Ir crystallite size = 2 nm

- a) Estimate the pore diameter of the support
- b) Calcultate the distance x_1 of Ir particles center to center on the surface
- c) Calculate the distance x_2 of Ir particles center to center in the porous volume

Ex.4. Preparation of a copper catalyst on silica (200 m² g⁻¹)

We prepare a solution containing the complex tetraamminecopper(II) [Cu(NH₃)₄]²⁺ by adding commercial concentrated ammonia (28 wt.-%, density 0.898 kg L⁻¹) to 50 mL of an aqueous solution containing copper nitrate 0.2 mol L⁻¹; the final pH is 12.

The pK_a of the acid-base couple NH₄+/NH₃ is 9.25

- a) Concentration of the commercial ammonia solution?
- b) Concentration of ammonia in an aqueous solution of pH 12?
- c) Volume of the commercial ammonia solution to be to be added to reach pH 12?
- d) Final volume, concentration of copper and pH? Conclusion

Exercice 4 (cont'd)

Ex.4. Preparation of a copper catalyst on silica (200 m² g⁻¹)

We dip 8.5 g of silica into the solution at room temperature and maintain agitation for 2 h. Then we remove the impregnated support by filtration, wash with water, dried, then calcined under air at 300 °C. We observe that 57 % of initial copper remains on the support as CuO.

- e) How can we obtain experimentally this value?
- f) Describe the silica surface in ammonia solution? Compare with the aqueous solution.
- g) What happen in the presence of the copper complex; what is the best procedure to impregnate silica?
- h) Determine the wt.-% of CuO and Cu in the sample. How can we obtain experimentally this value?

A sample of 100 mg is followed by H_2 TPR. At 300 °C, the H_2 consumption is 1.44 cm³ (20 °C, 1 bar); at 500 °C, the H_2 consumption is 1.55 cm³ (20 °C, 1 bar)

g) Determine the reduction rate for copper at both temperatures. What is the final wt.-% of Cu in the sample?

Ex.5. Study of a silica-supported copper catalyst Cu/SiO₂

Cu cubic cell, Bravais lattice F, a = 3.6147 Å

Loading level $x_m = 1$ wt.-% Cu Dispersion = 10 %

- a) Determine: (i) the diameter of a copper atom, (ii) the atom surface density for the three faces (100), (110) and (111), (iii) the mean density, and (iv) the average distance L_{Cu} between two Cu atoms.
- b) Determine: (i) the surface area of copper A_m (m^2 g^{-1}), (ii) the size of the copper particles d (nm), (iii) the number of copper particles (g^{-1}), the perimeter of the interface metal/support (hint: cubic particles with one face in contact with support, edge length d, surface density = mean density).
- c) Calculate: (i) the total number of copper atoms present in one particle; (ii) the number and percentage of Cu atoms on the edges and corners; (iii) the number and percentage of Cu atoms on the free faces and (iv) the number and percentage of atoms in contact with the support.

Ex.6. Characterization of a silica-supported copper catalyst Cu/SiO₂

hydrogen is adsorbed on copper at 25 °C without dissociation; the adsorption enthalpy is close to 40 kJ mol⁻¹.

a) Can we use hydrogen to determine the number of surface Cu atoms?

Nitrous oxide decomposes on copper between 25 and 80 °C following the reaction:

 $N_2O(g) + 2 Cu(surface) \rightarrow Cu-O-Cu(surface) + N_2(g)$

Using 150 mg of the catalyst, we obtain $0.43 \text{ cm}^3 \text{ N}_2 \text{ (STP)}$.

- b) Determine the dispersion of copper and the metallic surface area
- c) Calculate the size of the copper particles
- d) We use electron microscopy; how many copper particles can we expect to see on a picture 200 nm x 200 nm?

The copper atoms in contact with the support are more difficult to reduce.

e) How ca we explain the TPR results?