DICP Course - Dalian, 2012
Preparation of solid catalysts
Exercises

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Exercice 1

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:

$S_{BET} = 200\ m^2\ g^{-1}$

$V_p = 1\ mL\ g^{-1}$

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)

Exercice 2

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

It is used for the preparation of platinum supported catalysts Pt/Al_2O_3.

The maximum loading of H_2PtCl_6 precursor is: 1.6 µmol 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.

Exercice 3

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 $m^2\ g^{-1}$

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

Exercice 4

Ex.4. Preparation of a copper catalyst on silica (200 m^2 g^{-1})

We prepare a solution containing the complex tetraamminecopper(II) $[Cu(NH_3)_4]^{2+}$ 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 NH_4^+/NH_3 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 m^2 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 cm^3 (20 °C, 1 bar); at 500 °C, the H_2 consumption is 1.55 cm^3 (20 °C, 1 bar)

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

Exercice 5

Ex.5. Study of a silica-supported copper catalyst Cu/SiO_2

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.

Exercice 6

Ex.6. Characterization of a silica-supported copper catalyst Cu/SiO_2

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:

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

Using 150 mg of the catalyst, we obtain 0.43 cm^3 N_2 (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?