Synthesis of Heterogeneous Catalysts and Related Materials

Exam

10 April 2018

Time: 17.00 – 20.00

Answer in English

Use separate answer sheets for questions 1-3 and 4-6

Success!!!

The exam consists of six questions. Questions 1-3 are mainly focused on the synthesis of support materials (total 100 points), while questions 4-6 are focused on the synthesis of metal supported catalysts (total 100 points).

The number of points for each question is indicated in the brackets.

Question 1 – Mesoporous materials [max. 35 points]

(Ordered) mesoporous materials have received widespread interest because of their potential for a variety of applications such as catalysis, gas storage, separation, sensing, selective and adsorption.

a) Mention 3 properties of mesoporous materials that make them suitable for these applications. *[5 points]*
b) Mesoporous metal oxides are commonly prepared by sol-gel method. Using silica as an example, describe with an equation the two main reactions that are involved in the preparation of silica. *[10 points]*
c) Describe (not more than 3 sentences) the effect of pH on these reactions. *[10 points]*
d) For the synthesis of ordered mesoporous SiO_2 via cooperative self-assembly, what are the two mostly encountered interactions that cause the self-assembly into ordered structures? How does the difference in these interaction influence the structure and porosity of the two most widely reported ordered mesoporous silica materials: SBA-15 and MCM-41? *[10 points]*

Question 2 – Zeolites and MOFs [max. 35 points]

a) One of the important properties of zeolites in heterogeneous catalysis is its acidity, explain the 3 main factors that determine the acidity of a zeolite. *[5 points]*
b) What are the reasons for introducing mesopores in zeolite catalysts? Give short description of 3 approaches to introduce mesopores in zeolites. *[10 points]*
c) Molecular materials (MOFs, ZIFs, and COFs) have recently attracted attention as new class of micro-/mesoporous materials. What are the differences and similarities between MOFs, ZIFs, and COFs? *[10 points]*
d) Why are ZIFs considered to be analogues to zeolites, and what is the main difference between ZIFs and zeolites? *[10 points]*

Question 3 – Catalyst shaping [max. 30 points]

For industrial reactors, which are meters high, metal-oxide supports are usually shaped into larger particles, of a few mm in size (“catalyst bodies”).

a) Why is shaping of catalysts relevant for applications in industry? *[10 points]*
b) Name at least three aspects that have to be taken into account upon formulating the composition, size and the shape of the catalyst bodies. *[10 points]*
c) Fluid catalytic cracking (FCC) reaction takes place in fluidized bed reactors. Zeolite based catalyst is required for this reaction and is shaped as ~80 µm spheres. Propose and describe a shaping technique suitable for obtaining this catalyst body. (3-4 sentences) *[10 points]*

Question 4 – Ion adsorption – Pt/Al_2O_3 [max. 30 points]

To prepare Pt/Al_2O_3 catalyst, an aqueous Pt-containing solution is brought in contact with alumina cylindrical extrudates (2 mm diameter).

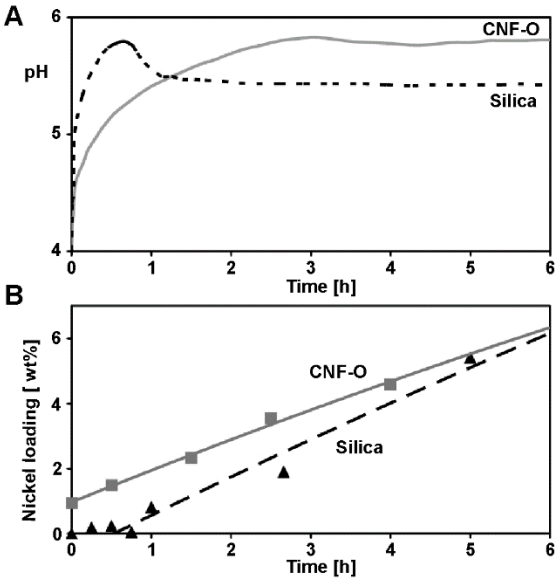
a) Based on the PZC of alumina (PZC=8.5), which Pt precursor do you propose to use and explain why? *[10 points]*
b) It is known that in the preparation of the above Al_2O_3-supported Pt catalyst, the platinum complex will form a so-called "inner-sphere complex" with the alumina support. Provide a drawing of such interaction and discuss the difference between "inner-sphere" and "outer-sphere" complex. *[10 points]*
c) Considering that adsorption is performed on the millimeter sized support bodies, different metal distributions can be obtained at the millimeter scale. Sketch three possible distributions and explain why they may occur. Also point out which of the Pt distribution you expect for the above catalyst and why. *[10 points]*

Question 5 – Deposition precipitation Ni/CNF-O and Ni/SiO_2 [max 40 points]

Deposition precipitation of Ni^{2+}(aq) on surface-oxidized carbon nanofibers (CNF-O) and silica, with urea as a precipitating agent, has been studied by van der Lee et al. through monitoring pH changes over time (Figure A). The authors also measured Ni content on CNF-O and silica as a function of deposition time (Figure B).

a) What would be the rationale behind using urea instead of e.g. NaOH as a precipitating agent? *[10 points]*
b) What do the following 3 key differences between Ni/CNF-O and Ni/SiO2 pH-time curves (Figure A) tell you about the Ni deposition precipitation mechanism on silica and on CNF-O:
   - pH increase slows down for Ni/CNF-O already at 4.5.
   - pH overshoot is present at 0.5-1.0 h for Ni/SiO_2.
   - the final pH for Ni/SiO2 is lower than pH for Ni/CNF-O

   [20 points]



c) The increase in Ni loading over time for silica seems to be faster than for CNF-O (see differences in slope, Figure B). What do you propose to be the cause of this? *[10 points]*

Question 6 – Impregnation and drying [max 30 points]

Impregnation and drying is the most commonly used method for preparing the catalysts in industry. Understanding the underlying mechanisms of each step in this process has motivated a number of fundamental studies – including the provided paper by T.M. Eggenhuisen et al.

a) In your opinion, what are the 2 key advantages for this technique to be industrially most attractive and what are the 2 disadvantages compared to co-precipitation? *[10 points]*
b) In the paper of T.M. Eggenhuisen et al. the authors opted to use cryo-electron tomography to study impregnation of Co and Ni precursor solutions into SBA-15 support. Discuss in 5-6 sentences the reasons behind the choice of the technique and support material. *[10 points]*
c) After the impregnation, drying has been recognized as crucial step to arrive to well disperse metal phase. Based on the Figure 2 of the provided paper, describe the adverse effects of drying under conventional conditions, and how does freeze-drying compare to it. *[10 points]*