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To cite this version:

K. Fujimoto, M. Boudart. PREPARATION OF SUPPORTED IRON CLUSTERS AND THEIR MÖSSBAUER EFFECT SPECTRA. Journal de Physique Colloques, 1979, 40 (C2), pp.C2-81-C2-83. <10.1051/jphyscol:1979228>. <jpa-00218626>

HAL Id: jpa-00218626
https://hal.archives-ouvertes.fr/jpa-00218626
Submitted on 1 Jan 1979
PREPARATION OF SUPPORTED IRON CLUSTERS AND THEIR MÖSSBAUER EFFECT SPECTRA

K. Fujimoto and M. Boudart

Department of Chemical Engineering, Stanford University, Stanford, CA. 94305, U.S.A.

Résumé.- Une nouvelle méthode est proposée pour préparer de petites particules de fer supportées par un matériau poreux. Une solution aqueuse de Fe(NO₃)₃ contenue dans les pores d'une almôna est hydrolisée par NH₄OH. Il en résulte une précipitation d'hydroxyde ferrique sur les parois des pores. Ce précére est ensuite réduit par H₂. La moitié du fer est ainsi réduit en particule de fer métallique. Leur taille moyenne est environ 1 nm d'après les mesures de chimisorption du CO. La spectroscopie d'effet Mössbauer montre les six raies du fer métallique, une raie due au fer superparamagnétique et un doublet due à Fe⁺⁺. La fraction de fer réduit, déterminée par ces spectres, est en accord avec celle déterminée par adsorption de O₂. La fraction de fer superparamagnétique est 30% de la quantité totale de fer métallique. Ceci confirme la petite taille des particules de ce dernier.

Abstract.- A new method for the preparation of iron clusters on porous materials was developed. An aqueous ferric nitrate solution in the micropores of alumina was hydrolized with ammonium hydroxide to depose ferric hydroxide on the wall of micropores. Then the precursor was reduced at 450 - 500°C with hydrogen to convert about half of the iron complex into metallic iron. The average size of the metallic iron clusters was determined from the amount of chemisorbed CO to be about 1 nm. Mössbauer effect spectra of reduced samples were composed of the six magnetically split peaks of metallic iron, a single peak of superparamagnetic iron metal and a ferrous doublet. The fractions of metallic iron in the reduced samples were determined from the spectra were and with that determined by dioxygen adsorption. The fraction of superparamagnetic iron metal in the total metallic iron was about 30% at room temperature, confirming that metallic particles were quite small.

1. Introduction.- Supported metal samples are important objects of catalytic research in both theory and practice. In particular, small metal particles have recently attracted much attention as reactions have been found with turnover numbers which may or may not depend on the particle size of the metal. For example, the rate of ammonia synthesis on iron depends on the particle size whereas that of cyclohexene hydrogenation on nickel doesn't. Unfortunately, little is known about the preparation of iron clusters on porous materials.

A new method of the preparation of iron clusters relies on the precipitation of ferric hydroxide on the surface of magnesium hydroxy-carbonate followed by the reduction of it with hydrogen /1/. The method gave iron particles with an average diameter of 1.5 nm with Mössbauer effect spectrum composed of the six magnetically split peaks of metallic iron, a single peak of superparamagnetic iron metal (the peak area of the latter being about 20% of the former) and a ferrous doublet.

In this study a new method for the preparation of very small iron clusters (ca. 1.0 nm) on porous materials was developed and their Mössbauer spectra were measured.

2. Experimental.- 2.1. The "In-pore" precipitation method.- In-pore precipitation method means a procedure which includes an operation of insolubilizing metal salts or metal complexes while keeping the solvent in the pores only. As the mother solution is separated in each pore, molecules which form a cluster are only those in each pores, because the molecules in a pore are not able to come out of it to go into another pore. Insolubilized metal complexes in the pore aggregate to form clusters. If the pore size is small enough a cluster may stick on the wall of the pore before it grows larger.

Consider for instance a pore with a diameter and a height of 5 nm (the average pore size of an alumina) and containing 1 molal solution of metal salt, then the number of the metal atoms in the pore is 59. Therefore, if one cluster is formed in each of the pore the cluster is composed of 59 atoms. The dispersion, i.e. the ratio of the number of surface atom to the total number of atoms which compose a cluster is about 0.9.

2.2. Sample preparation.- Into 50 ml of 1 molal ferric nitrate solution 20 g of alumina (Merck, for chromatography, acidic) which had been dried at 125°C in vacuo for 5 hours, was added at room temperature and stirred for 0.5 h. The slurry was filtered to remove the excess ferric nitrate solution. The alumina which contained the solution was partial-
ly dried to remove water on the outer surface of the granules, which still contained the solution in the pores. Then, it was poured into a 2 normal ammonium hydroxide solution to hydrolyze ferric nitrate in the pore, washed with distilled water and dried in an air oven at 360 K, for 16 h. The catalyst precursor was reduced in flowing hydrogen purified by passing through a column of Deoxo catalyst (from Engelhard U.S.A.) at 520 K for 1–2 h and then at 720 K for 15–17 h.

2.3. Carbon monoxide and dioxygen chemisorption. Carbon monoxide chemisorption and dioxygen chemisorption were performed at 193 K and 673 K, respectively. The details of the chemisorption measurements have been described elsewhere /1/. 2.4. Mössbauer effect spectroscopy. Mössbauer effect spectra were taken using the spectrometer shown elsewhere /1/. The source was 100 mCi $^{57}$Co diffused into Cu. Absolute velocities were determined by means of a helium laser interferometer.

3. Results and discussion. 3.1. Reduction of supported ferric oxide. It is generally found that more highly dispersed ferric salt is deposited the more difficult it is to reduce /2/. For example, on a Fe$_2$O$_3$-MgO (Fe 1 wt%) sample which gives iron particles of 1.5 nm upon reduction 40% of iron is reduced to the metallic state in the 700 K hydrogen, whereas 70% of iron can be reduced at the same condition on another Fe$_2$O$_3$-MgO sample (Fe:40 wt%) giving particles of 30 nm.

As can be seen in figure 1 about 50% of iron oxide in Cat A is reduced to the metallic state in the 673 K hydrogen to form fine particles. The reduction to the zero valence state begins at 570 K and progresses with the rise in temperature. However above 673 K the increase in the reduction rate is small. It is suggested that the unreduced iron oxide is strongly bound to the support. The fraction of metallic iron which is calculated from volumetric oxidation agrees well with that from the room temperature Mössbauer effect spectrum at each reduction temperature. Sample B which has been prepared by an impregnation method using the same support is far easier in being reduced because of poor dispersion.

3.2. Particle size of iron metal. The dispersion of metallic iron of the samples (the fraction of surface metallic iron atoms) determined from carbon monoxide chemisorption assuming the stoichiometry of Fe : Co = 2 : 1 lies between 0.83 and 1.0 independently of the reduction temperature.

Fig. 1: Reduction of sample A with hydrogen. Sample A is reduced in flowing hydrogen for about 16 h. The particle size, $d$, is then obtained using the relation, $d$ (nm) = 0.85/D /1/. Data in table I shows that the particle size is around 1 nm. The facts that particle size and reduction rate are actually independent of the reduction temperature above 673 K indicate that metallic particles are very stable and hard to sinter on this support.

Fig. 2: Mössbauer effect spectra of supported iron catalysts. Concentration of $^{57}$Fe was about 10% and the measurements were conducted in hydrogen at room temperature for 6 h.
Table I: Adsorption and Mössbauer effect data of alumina supported iron catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduction temp. (K)</th>
<th>Total iron loading (umol/g)</th>
<th>CO uptake (pmol/g)</th>
<th>O₂ uptake (pmol/g)</th>
<th>Metallic Fe (pmol/g)</th>
<th>Fe⁸⁺/(Fe⁸⁺Fe⁺⁺) from O₂ uptake</th>
<th>Dispersion from CO uptake</th>
<th>Particle size (nm)</th>
<th>Fe⁺/Fe⁺⁺</th>
<th>Asp/(NeoNeAsp)</th>
<th>Metallic isomer shift (δ: mm/s)</th>
<th>Fe⁺⁺ isomer shift (δ: mm/s)</th>
<th>Fe⁺⁺ quadrupole splitting (μm/s)</th>
<th>Central peak isomer shift (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>593</td>
<td>337</td>
<td>23</td>
<td>107</td>
<td>46</td>
<td>0.14</td>
<td>1.00</td>
<td>0.9</td>
<td>0.20</td>
<td>0.25</td>
<td>0.00</td>
<td>0.875</td>
<td>0.663</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample B</td>
<td>673</td>
<td>337</td>
<td>67</td>
<td>165</td>
<td>162</td>
<td>0.48</td>
<td>0.83</td>
<td>1.0</td>
<td>0.35</td>
<td>0.26</td>
<td>0.00</td>
<td>0.864</td>
<td>0.644</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample C</td>
<td>723</td>
<td>337</td>
<td>85</td>
<td>176</td>
<td>183</td>
<td>0.54</td>
<td>0.93</td>
<td>0.9</td>
<td>0.44</td>
<td>0.30</td>
<td>0.30</td>
<td>0.864</td>
<td>0.644</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample D</td>
<td>773</td>
<td>337</td>
<td>85</td>
<td>179</td>
<td>190</td>
<td>0.56</td>
<td>0.89</td>
<td>1.0</td>
<td>0.49</td>
<td>0.17</td>
<td>0.17</td>
<td>1.043</td>
<td>0.802</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample E</td>
<td>723</td>
<td>341</td>
<td>31</td>
<td>202</td>
<td>253</td>
<td>0.85</td>
<td>0.12</td>
<td>7.1</td>
<td>0.54</td>
<td>0.39</td>
<td>1.5</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sample F</td>
<td>700</td>
<td>170</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- Prepared by the method reported in this paper.
- Prepared by the impregnation method using HNO₃ and Fe(NO₃)₃·H₂O.
- Iron magnesium oxide catalyst reported in reference /1/.
- With respect to metallic iron at 298K.

On the other hand, the particle size of metallic iron on sample B is about 7 times larger than that of sample A. This illustrates the superiority of our new method to prepare clusters of iron.

The fraction of the superparamagnetic peak in the Mössbauer effect spectrum of a reduced sample which can be attributed to small particles /3/ is about 30% of the total metallic peak. The value is 50% larger than that of the Fe-MgO catalyst (sample C) on which the particle size is 1.5 nm.

References

/1/ Boudart, M., Bömmel, M., Constabaris, G. and Lindquist, R.M., J. Catalysis 37 (1975) 486.
/2/ Gager, H.M. and Hobson, M.C., Catalysis Rev. 11 (1975) 117.