

Effect of the high pressure of hydrogen on the reduction temperature of oxides as observed by the mean of a Mass Spectrometer used as a detection device

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Introduction:

It is well known that reduction of oxides at a high pressure of H₂ reduces notably the reduction temperature and hence, reduces or minimizes the sintering of the active species dispersed on the surface of solids. 2,3,4,5 It is well understood that sintering of active species means growing of particles and therefore reducing the active surface area where reaction typically takes place. Less active area translates to less activity of the catalyst. Several reduction experiments on the Micromeritics reference material of silver oxide (Ag₂O) were carried out on the EFFI Microreactor PID connected to a MKS Cirrus II mass spectrometer to follow the depletion of H₂ during reduction. It has been observed that while high pressure of the reducible mixture was used, the response of the mass spectrometer was delayed, showing the opposite of the expected result. This meant that one would expect a lower reduction temperature as the reducible gas pressure increases. It is logical to think that a high pressure inside the reactor will delay the effluent molecules to get out and reach the mass spectrometer, so the reduction temperature shown by the MS was an artefact. In order to overcome this problem, several tests were carried out to calibrate the MS signal and bring the signal down to normal and expected value.

A flow rate of 50 ml/min of the reducible mixture was used as a reference for all our tests. The mass spectrometer was set to follow a mass of 28 that corresponds to CO or carbon monoxide. The first test was to inject a pulse of about 0.5 ml of CO and follow the MS response. This lasted about 630 seconds. The next step was to increase the pressure to 5 bars with the same flowrate of the gas (50 ml/min). Again, a pulse of CO was made and the mass of 28 was followed. The response this time was 750 seconds. To synchronize the time of the response, the flow was increased to 250 ml/min to give the same response time of 630 seconds. This procedure was repeated for 10 and 20 bars and the corresponding flow rates are shown on table 1. A shift of the reduction temperature was observed as the pressure increased. It is logical to think that

both high pressure as well as the higher flow rate of the mixture had a direct influence on the reduction of the oxide. Hence, it must be concluded from this work that reducing the reduction temperature of the material would positively impact the reduction of the active species with a minimum sintering effect.

Flow ml/min	Pressure (bar)	Reduction Temp. (C)	Response Time(S)
50	1	130	630
50	5	145	750
250	5	125	600
50	10	160	810
480	10	120	570
50	20	170	870
925	20	120	570

Table 1: This table shows the resulting reduction temperature before and after the adjustment made to the flow at each considered pressure.



Experimental:

All the tests were carried out on the EFFI Microreactor PID using a 9 mm id SS straight tube reactor. A double headed thermocouple was used for these experiments (fig.1), one head was used to heat and control the oven where the reactor is placed, and the other head of the thermocouple was connected to the mass spectrometer to pick up both required reduction temperatures. An initial detected temperature that showed on the temperature curve graph

Figure 1: This figure shows the device used for these experiments well as the double headed thermocouple

APPLICATION NOTE 031

of the mass spectrometer was taken at the zone of the curve where the liberated heat from the exothermic reaction was detected (blue graphs). This temperature was considered to be the actual reduction temperature since the thermocouple was inserted in the catalyst bed and therefore is capable to detect any change in the temperature. The second reduction temperature was taken at the maximum of the peak detected by following mass 2 at the mass spectrometer (red graphs). This latest show the observed shift on the temperature as it is detected once the hydrogen depletion signal reaches the analysis chamber of the instrument. The liquid gas separator of the EFFI, that can cool down to about 3°C to 4°C, was used as a trap for the produced water during reduction. The final reduction temperature was achieved by ramping the oven temperature with a rate of 10°C/min. The Cirrus II MKS mass spectrometer was connected at the exhaust of the reactor after the cold trap. This was set to follow mass 2 for the H₂ during all reduction experiments and mass 28 for the calibration purpose.

All data was reduced using the Micromeritics MicroActive program that enables the integration of peaks as well as the detection of the max temperature of each peak.

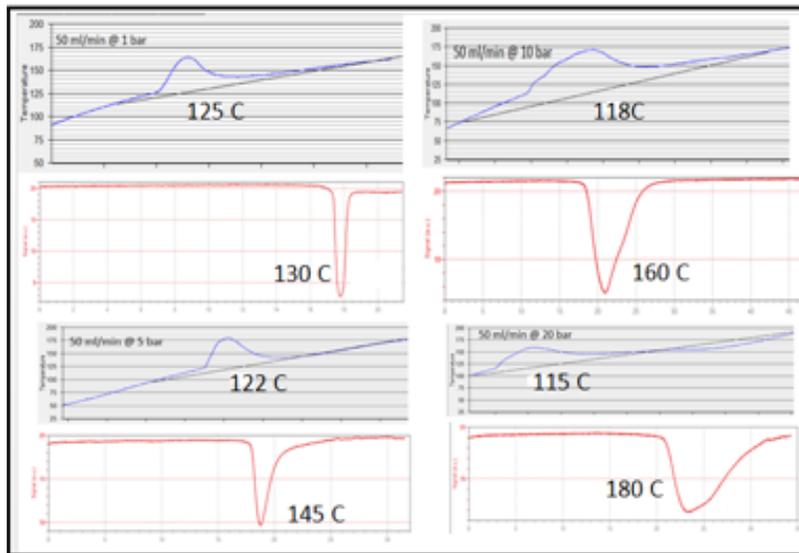


Figure 2: This figure shows the apparent shift on the reduction temperature detected by the Mass Spectrometer as the pressure increases compared to the basic reduction temperature of 130C for Silver Oxide

Results:

The results obtained in this study confirm what it has been suspected from the beginning, and that is the high pressure causes a shift in the reduction temperature that has to be corrected in order to obtain the exact reduction temperature. Table 1 shows the behavior of the reduction temperature of the silver oxide before the adjustment made to the flow. All reduction temperatures increased as the pressure increased as is observed from experiments on figure 2. However, the expected reduction temperatures obtained after the adjustment of the flow according to calibration can be seen on figure 3.

All obtained results shown in these figures showed that an increase in the pressure inside the reactor where the sample to be studied is placed, causes a shift on the reduction temperature due to the delay on the response of the mass spectrometer.

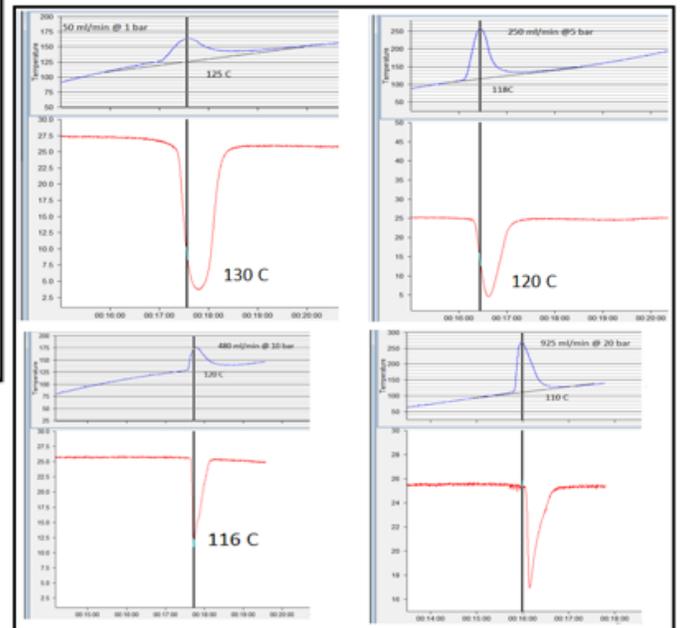


Figure 3: This figure shows shows the reduction temperature as detected by the Mass Spectrometer after adjusting the flow according to the calibration mentioned in the text

Conclusion:

It can be concluded from this application note that, on one hand, the high pressure of H₂ has a direct impact on the reduction temperature of any oxide sample. Since oxides will reduce at lower temperature, therefore the active particles encountered on the surface will not suffer major transformation, hence, the activity of the solid will remain in optimum conditions. On the other hand, carrying experiments at higher pressure of hydrogen, will delay the response of the depleting hydrogen at the detection device, therefore, wrong reduction data can be obtained. Raising and calibrating the flow of the H₂ mixture will yield to the expected results and that is a lower reduction temperature as function of increasing pressure over the oxide sample bed.

References:

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