Development of a Quality Control Procedure for Characterizing Supported Nickel Catalysts

1. Background

Quality control and instrument maintenance are important functions in all laboratories. Periodically running a QC procedure like the one described in this Note can provide early detection of instrument contamination, failing instrument components, or gas contamination, factors that can negatively affect experimental results. This *AMI Note* discusses how a quality control procedure was developed for a supported nickel catalyst used in hydrogenation reactions.

2. Experiment

A known supported Ni catalyst was used as the reference material for this series of experiments.[1-3] Hydrogen pulse chemisorption and temperature-programmed desorption (TPD) were performed using an **AMI** catalyst characterization system. For the purpose of these experiments, the following definitions of dispersion, metal surface area and crystallite size were used. The equations were then condensed after accounting for unit conversions and assuming H_2-TPD on Ni catalyst.

Dispersion of Nickel:

$$Dispersion\ (\%) = \frac{U \times M_w}{w_i \times SF} \times 100\% = 0.5242 \times \frac{V_g\%}{w_i} \quad (1)$$

Metal Surface Area:

$$S_M = \frac{U \times N \times \sigma}{SF}\left(\frac{m^2}{g_{cat}}\right) = 3.3175\, V_g \left(\frac{m^2}{g_{cat}}\right) \quad (2)$$

Ni (0) Crystallite Size:

Spherical crystals

$$d = \frac{6 \times V_{sphere}}{SA_{sphere}} = \frac{10.0061}{D} \quad (3)$$

Cubic crystals

$$cube\ length = sphere\ diameter \times \frac{1}{1.24} \quad (4)$$

Where:
U = amount gas chemisorbed (mole/g cat)
SF = stoichiometric factor (mole gas/mole metal, SF =0.5 for Ni-H_2)
M_w = atomic weight of metal (58.71 g/mol for Ni)
w_i = weight fraction of metal in catalyst
V_g = volume gas chemisorbed at STP (1 mole = 22400 ml)
σ= area of surface metal atom = 6.17 A^2 or 6.17×10^{-20} m^2
N = Avogadro's number 6.02245×10^{23} mol^{-1}
V = volume
SA = surface area
D = dispersion (from 0 - 1)

Pulse chemisorption and temperature programmed desorption techniques were conducted using an **AMI** catalyst characterization system. Pulse chemisorption was initially selected because it is a simple technique, it distinguishes between physisorption and chemisorption, and it provides direct information about accessible, catalytically active sites.

In the pulse chemisorption experiments, the nickel sites were titrated with hydrogen. Physisorbed hydrogen was continuously purged from the surface of the catalyst. The number of pulses per experiment ranged from 25 to 35, and the time between pulses was four minutes. The pulse volume was 50 microliters and the gas flow rate of both hydrogen and argon was 40 ml/min.

TPD was selected because it is also a fast technique that quantifies percent dispersion, metal surface area, and crystallite size. TPD has the added advantage of providing information about the thermodynamics of the catalyst system.

For TPD experiments, hydrogen was adsorbed at a flow rate of 30 ml/min. The time and temperature of adsorption was varied for each run. Physisorbed hydrogen was purged from the surface of the catalyst and the chemisorbed hydrogen was then desorbed by ramping up to a maximum temperature.

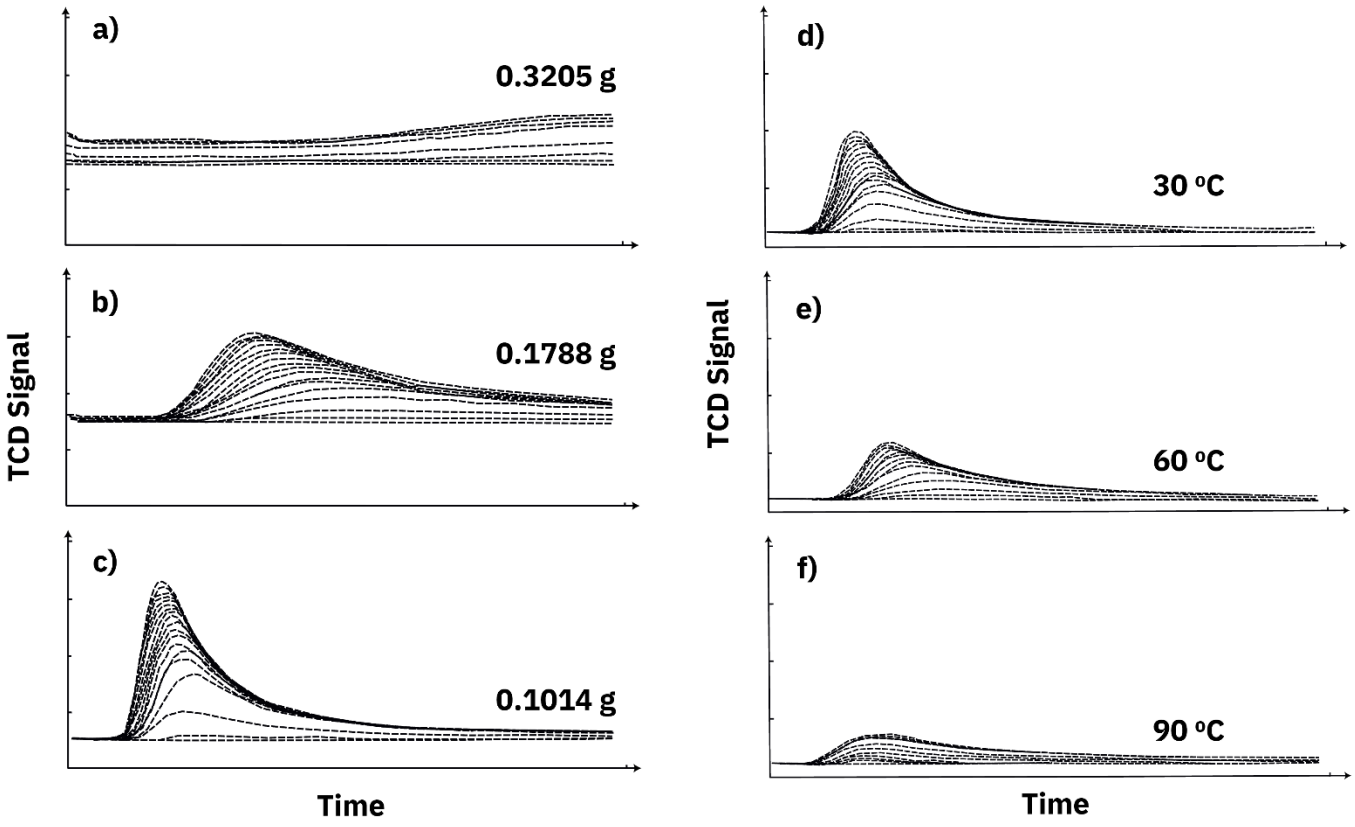

Figure 1: Pulse chemisorption curves measured at RT with a catalyst weight of a) 0.3205 g, b) 0.1788 g, and c) 0.1014 g; a second pulse chemisorption experiment conducted with the same weight of catalyst at d) 30 °C, e) 60 °C, and f) 90 °C

3. Pulse Chemisorption Results

Run #	Number of Pulses	Weight (g)	H_2 Uptake *10^6 (mol/g cat.)	Dispersion (%)	Crystallite Diameter *10^{10} (m)	Metal Surface Area (m^2/g cat)
1	25	0.3205	*	*	*	*
2	35	0.3205	*	*	*	*
3	25	0.1788	243.6	14.3	70	18.10
4	35	0.1788	304.0	17.0	56	22.59
5	25	0.1014	157.4	9.2	100	11.69
6	35	0.1014	160.6	9.4	106	11.93
Ref.	-	-	-	26	38	30

*no calculations done

Table 1: Results calculated from pulse chemisorption experiments with varying catalyst weights

3.1 Influence of Catalyst Weight

For the first series of chemisorption experiments, two runs, one with 25 pulses and one with 35 pulses, were performed on each of three sample weights. Figure 1 shows that the sample weight has a significant effect on chemisorption curves with larger samples causing a significant broadening of the signal. From these three curves it is apparent that the 0.1014 g sample weight, represented in Figure 1c, gave the best results in terms of the sharpest peaks and least amount of base line drift. Table 1 gives the calculated dispersion, crystallite size and metal surface area for the six runs. Unfortunately, neither the results of the 0.1788 g nor the 0.1014 g samples match the reference data thus indicating that either 35 pulses were not enough to obtain full coverage or other parameters needed to be optimized.

Run #	T (°C)	Number of Pulses	Dispersion (%)	Crystallite Diameter *10^{10} (m)	Metal Surface Area (m^2/g cat)
1	30	25	9.6	104	12.28
2	30	30	9.8	102	12.54
3	30	35	9.8	102	12.57
4	60	25	22.2	45	24.88
5	60	30	24.0	42	26.92
6	60	35	25.4	39	28.48
7	90	25	25.6	39	28.80
8	90	35	32.2	31	36.19
Ref.			26.0	38	30.00

Table 2: Results calculated from pulse chemisorption experiments at varying catalyst temperatures

3.2 Influence of Temperature

In the second series of chemisorption experiments, 25, 30 and 35 pulse runs were performed at three different temperatures, 30 °C, 60 °C, and 90 °C. Figure 1d-f shows that the temperature at which chemisorption is performed can also affect chemisorption results. Table 2 details the calculated results for the eight runs. Reviewing the information in Figure 1e and Table 2, the results of the 35-pulse run at 60 °C gave the best results in comparison to the reference data.

4. Temperature Programmed Desorption Results

4.1 Influence of Adsorption Time and Temperature

For TPD, the time and temperature of the adsorption step must be optimized in order to achieve full coverage of the surface. Three TPD experiments were performed, one in which hydrogen was adsorbed at 30 °C for 60 minutes, the second in which hydrogen was adsorbed at 60 °C for 60 minutes and the third in which hydrogen was adsorbed at 30 °C for 180 minutes. From the previous chemisorption experiments, it was known that higher temperatures should be avoided (Fig. 1f), therefore TPD was not performed at 90 °C. Comparing the TPD curves in Figure 2 and the calculations in Table 3, the second and third runs gave the best results in terms of peak deconvolution and matching the reference data.

Run #	Gas	T (°C)	Flow (mL/min)	Time (min)	Dispersion (%)	Metal Surface Area (m^2/g cat)	Crystallite Diameter *10^{10} (m)
1	Adsorption: H_2	30	30	60	21.9	24.62	46
	Purge: Ar	30		20			
	Desorption: Ar	500		10			
2	Adsorption: H_2	30		60	25.0	28.09	40
	Purge: Ar	30		20			
	Desorption: Ar	500		10			
3	Adsorption: H_2	30		180	27.0	30.29	37
	Purge: Ar	30		20			
	Desorption: Ar	500		10			
Ref.					26	30	38

Table 3: Results calculated from TPD experiments varying adsorption time and temperature

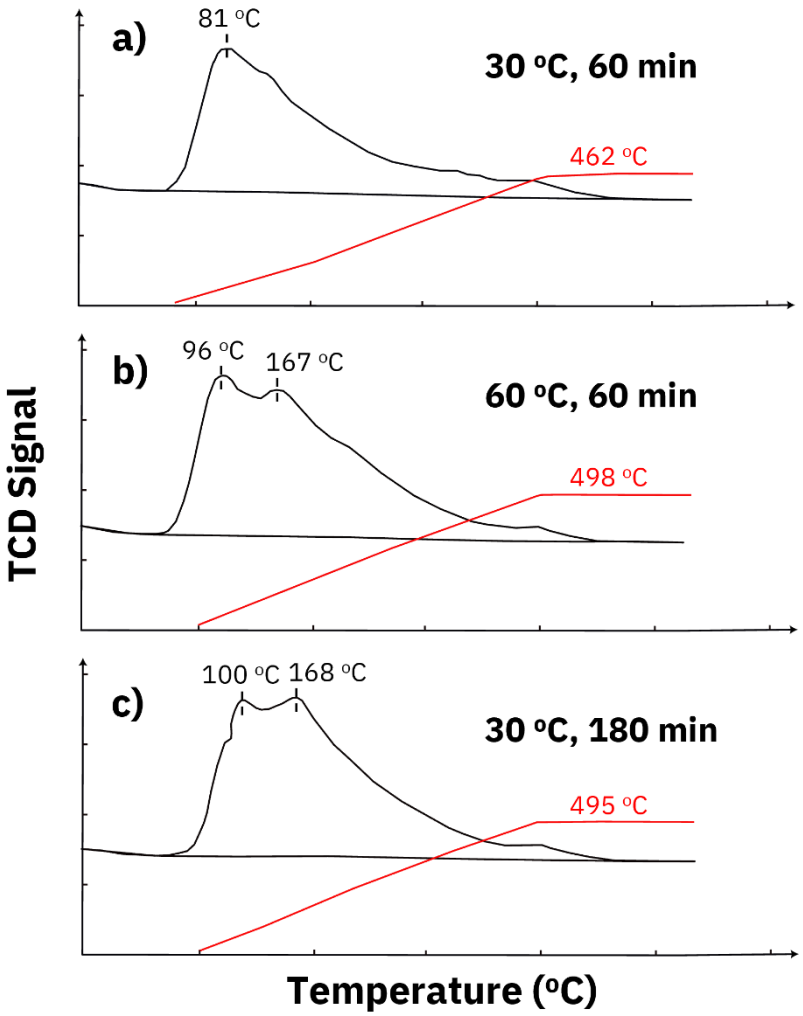

Figure 2: TPD curves varying adsorption time and temperature a) 30 °C at 60 min, b) 60 °C for 60 min, and c) 30 °C for 180 min

5. Conclusions

In conclusion, these experiments show that both pulse chemisorption and temperature-programmed desorption are easy and powerful techniques that quantify dispersion, metal surface area, and crystallite size.

In the case of pulse chemisorption, one must optimize sample weight and temperature. The disadvantage of this technique is that the end-point is sometimes difficult to determine. Also, optimization depends on the catalyst type.

For TPD, adsorption time and temperature must be optimized. TPD is advantageous because results are very reproducible and test parameters need not be changed when analyzing different types of nickel catalysts.

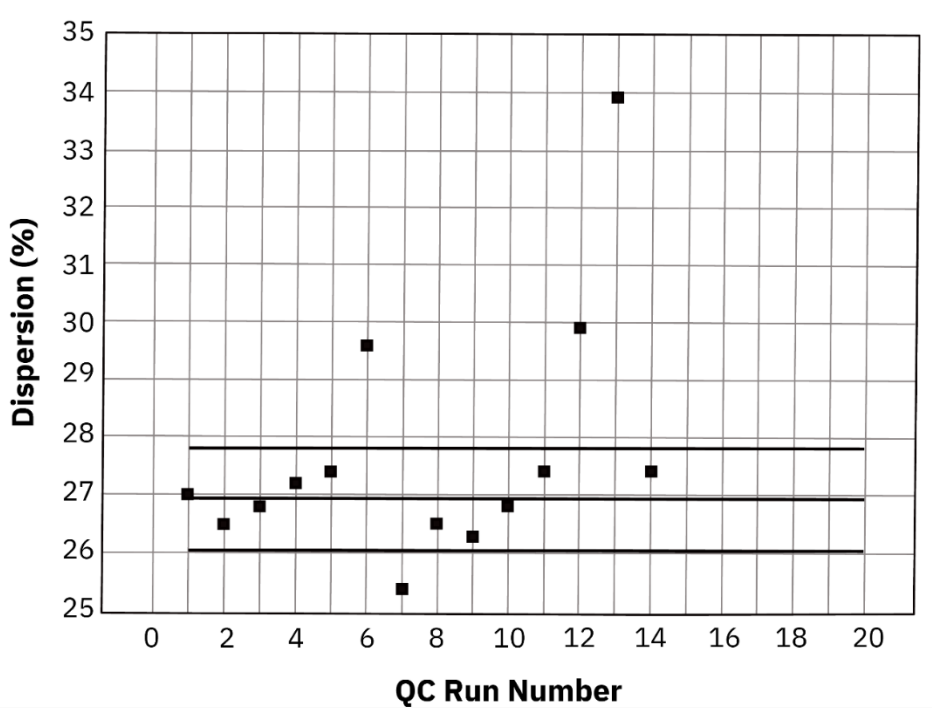

Figure 3: TPD confidence interval plotted vs experimental dispersion values from QC runs

In the case of this QC method for nickel hydrogenation catalysts, it was determined that hydrogen TPD was a preferable procedure to hydrogen pulse chemisorption. After running a number of hydrogen TPD experiments, a 95% confidence interval of 26.0 - 27.8% dispersion was determined. The researcher now runs this TPD procedure at least once per week for quality control purposes. Any results which fall outside the confidence interval are investigated. Figure 3 shows the data logged from 14 QC runs. The researcher notes that run 13, which shows a dispersion well outside the acceptable range, was actually due to a leaking flow controller.

Experimental data was provided by Dr. Ir. Luc Martens at Exxon Chemical International, Inc. in Machelen, Belgium.

6. References

(1) Smeds, S.; Salmi, T.; Lindfors, L. P.; Krause, O. Chemisorption and TPD studies of hydrogen on Ni/Al2O3. *Appl. Catal. A*, **1996**, *144*, 177-194.
(2) Velu, S. and Gangwal, S. K. Synthesis of alumina supported nickel nanoparticle catalysts and evaluation of nickel metal dispersions by temperature programmed desorption. *Solid State Ionics*, **2006**, *177*, 803-811.
(3) Konvalinka, J. A.; Van Oeffelt, P. H.; Scholten, J. J. F. Temperature programmed desorption of hydrogen from nickel catalysts. *Appl. Catal.* **1981**, *1*, 141-158.