Development of a Quality Control Procedure for Characterizing Supported Nickel Catalysts

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 <u>Altamira Note</u> discusses how a quality control procedure was developed for a supported nickel catalyst used in hydrogenation reactions.

<u>EXPERIMENTAL</u>

A known supported nickel catalyst was used as the reference material for this series of experiments... metal loading by weight: 17.7% ... metal surface area: 30 m^2/g ... metal dispersion: 26%. Hydrogen pulse chemisorption and temperature-programmed desorption (TPD) were performed using an AMI-1 Catalyst Characterization System (Altamira Instruments). For the purpose of these experiments, the following definitions of dispersion, metal surface area and crystallite size were used:

Dispersion of Nickel: D

$$D = \frac{A \cdot U}{B \cdot W} \times 100\%$$

$$= 0.5242 \times \frac{Vg\%}{W}$$

Metal Surface Area: S_M

$$S_M = \frac{U \times N \times \sigma}{\beta} \quad (m^2/g_{cat})$$

$$3.3175 \times Vg \ (m^{2/}g_{cat})$$

Ni (0) Crystallite Size

Spherical crystals:	Cubic Crystals:

diameter = $\frac{6xV}{S}$ Cube Length = Sphere diameter x $\frac{1}{1.24}$

$$= \frac{10.0061}{D} \ (\text{Å})$$

Where:

U = amount gas chemisorbed (mole/g cat)

P = stoichiometry (mole gas/mole metal) (=0.5 for Ni-H_2)

A = atomic weight metal (58.71 g/mole)

W = weight fraction of metal in catalyst

Vg = volume gas chemisorbed at STP (1 mole = 22400 ml)

σ = area of surface metal atom (Geus, Schwarz)σ = 6.17 A^2
$$= 6.17 \cdot 10^{-20} m_2$$

N = Avogadro number 6.02245 10^{23}

V = Volume crystal

S = Surface

D = dispersion (not in %)
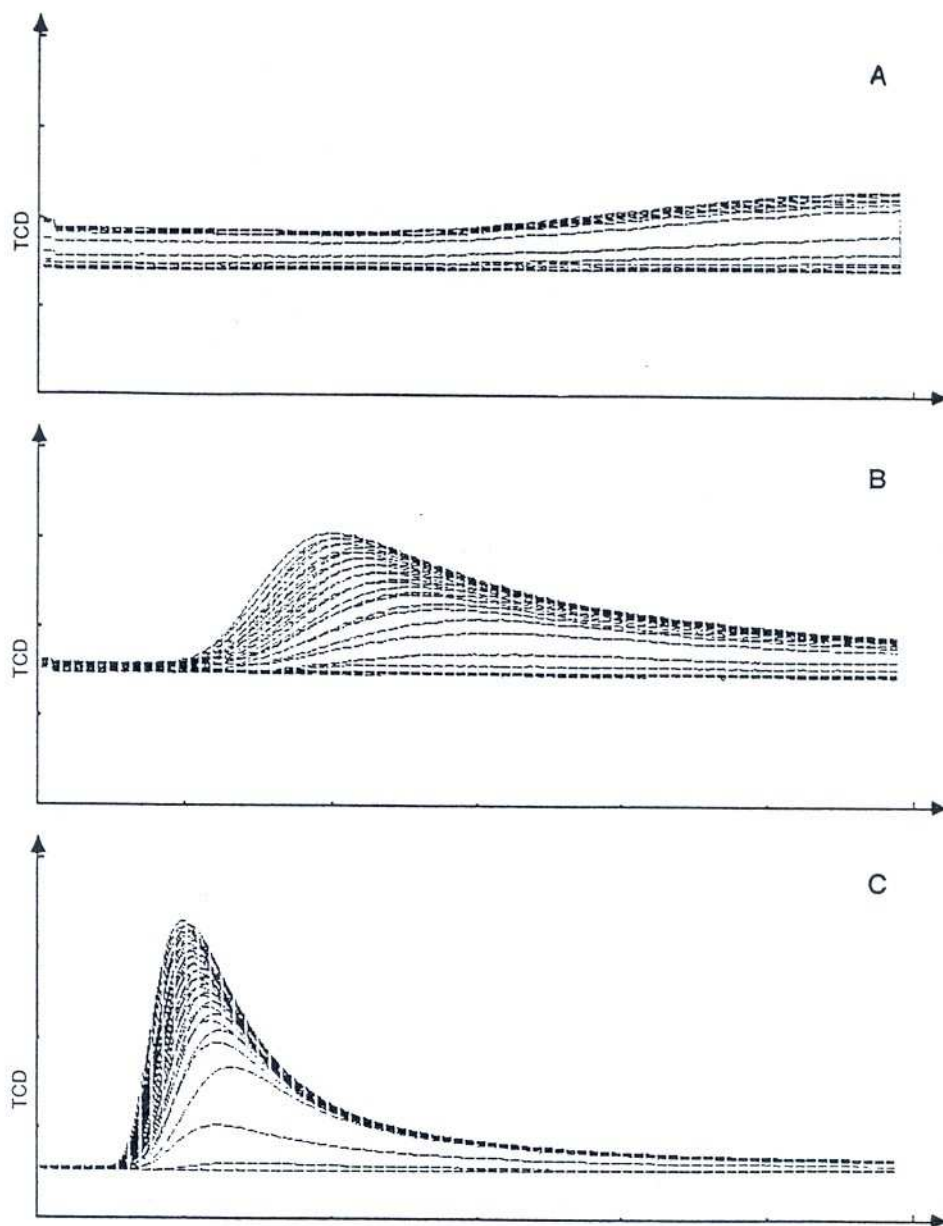

PULSE CHEMISORPTION

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 this group of 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.

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 1.C, gave the best results in terms of the sharpest peaks and least amount of base line drift. Figure 2 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.

Figure 1.   Pulse Chemisorption: Influence of Catalyst Weight

Pulse chemisorption curves for a catalyst weight of 0.3205 (A), 0.1788 (B) and 0.1014 g(C)

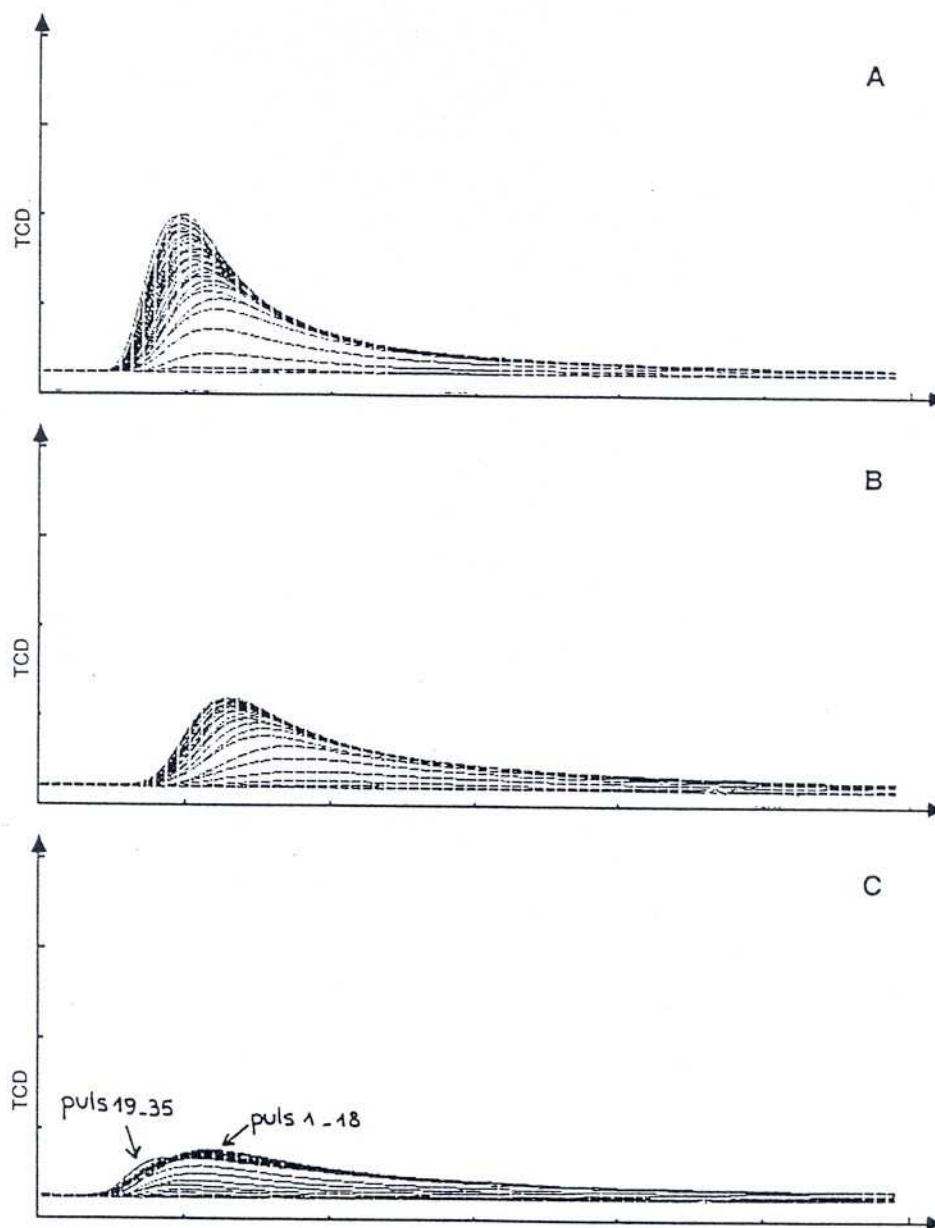Figure 2.   Pulse Chemisorption: Influence of Catalyst Weight

Nr	Number of Pulses	Weight (g)	H_2- uptake (mol/g)$*10^6$	Dispersion (%)	Crystallite $(m)*10^{10}$	Metal Surface (m^2/g cat)
1	25	0.3205	a	a	a	a
2	35	0.3205	a	a	a	a
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

a, no calculations done

Influence of Temperature

In the second series of chemisorption experiments, 25, 30 and 35 pulse runs were performed at three different temperatures, 303 K, 333 K and 363 K. Figure 3 shows that the temperature at which chemisorption is performed can also affect chemisorption results. Figure 4 details the calculated results for the eight runs. Reviewing the information in Figures 3 and 4, the results of the 35 pulse run at 333 K gave the best results in comparison to the reference data.

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Figure 3.   Pulse Chemisorption: Influence of temperature

Chemisorption at 303 K (A), 333 K (B) and 363 K (C

Figure 4.   Pulse Chemisorption: Influence of Temperature

| Nr	T (K)	Number of pulses	Dispersion (%)	Crystallite Size $* 10^{10}$	Metal Surface (m^2/g cat)
1	303	25	9.6	104	12.28
2	303	30	9.8	102	12.54
3	303	35	9.8	102	12.57
4	333	25	22.2	45	24.88
5	333	30	24.0	42	26.92
6	333	35	25.4	39	28.48
7	363	25	25.6	39	28.80
8	363	35	32.2	31	36.19
Reference Data			26.0	38	30.00

TEMPERATURE-PROGRAMMED DESORPTION

TPD was selected because it too is 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 this series of 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. For TPD, the time and temperature of the adsorption step must be optimized in order to achieve full coverage of the surface.

Influence of Adsorption Time and Temperature

Three TPD experiments were performed, one in which hydrogen was adsorbed at 303 K for 60 minutes, the second in which hydrogen was adsorbed at 333 K for 60 minutes and the third in which hydrogen was adsorbed at 303 K for 180 minutes. From the previous chemisorption experiments, it was known that higher temperatures should be avoided, therefore TPD was not performed at 363 K. Comparing the TPD curves in Figure 5 and the calculations in Figure 6, the second and third runs gave the best results in terms of peak deconvolution and matching the reference data.

Figure 5.   Temperature-Programmed Desorption: Influence of Adsorption Time and
             Temperature
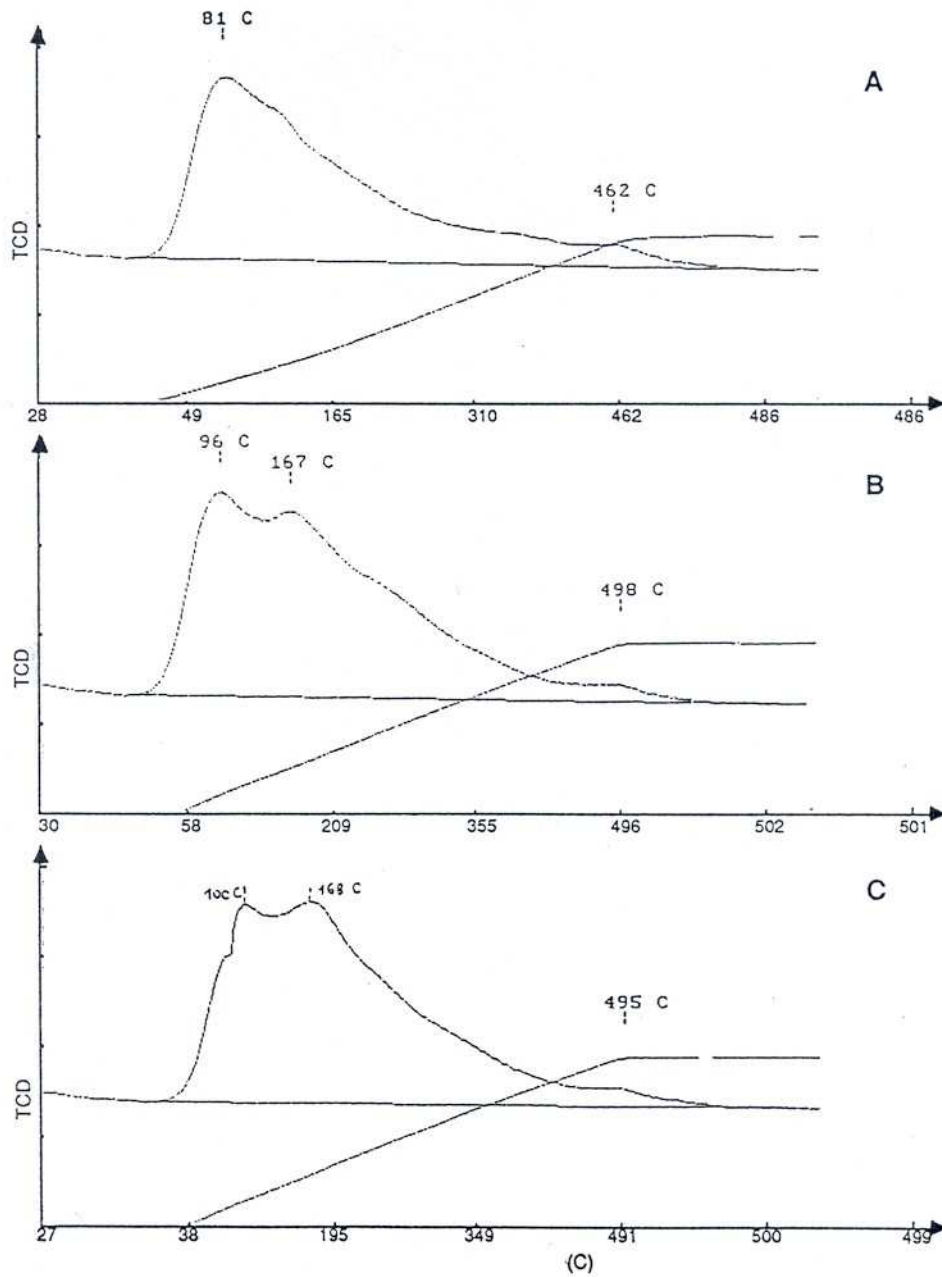
TPD Curves, adsorption temperature and time: 303 K and 60 min (A),
333 K and 60 min (B) and 303 K and 180 min (C)

Figure 6.   Temperature-Programmed Desorption: Influence of Adsorption
Time and Temperature

	Gas	T (K)	Flow (ml/min)	Time (min)	Dispersion (%)	Metal Surface (m^2/g cat)	Crystallite Size $*10^{10}$ (m)
1	Adsorption: H2	303	30	60			
	Purge: Ar	303	30	20			
	Desorption: Ar	773	30	10	21.9	24.62	46
2	Adsorption: H2	333	30	60			
	Purge: Ar	303	30	20			
	Desorption: Ar	773	30	10	25.0	28.09	40
3	Adsorption: H2	303	30	180			
	Purge: Ar	303	30	20			
	Desorption: Ar	773	30	10	27.0	30.29	37
	Reference Data				26	30	38

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.

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 7 shows the data logged from 14 QC runs. The researcher notes that run 13, which shows a percent dispersion well outside the acceptable range, was actually due to a leaking flow controller.

Figure 7.   TPD Confidence Interval
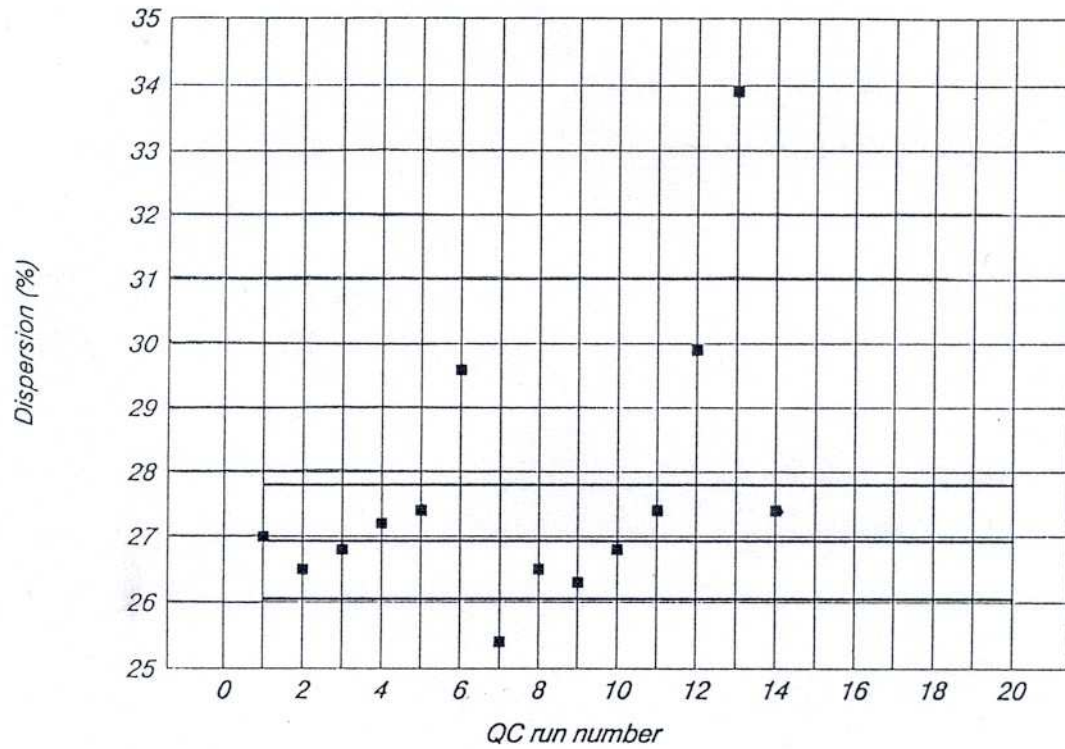
Experimental data was provided by Dr. Ir. Luc Martens at Exxon Chemical International, Inc. in Machelen, Belgium.