

APPLICATION OF TEMPERATURE-JUMP ADSORPTION MEASUREMENT FOR THE DETERMINATION OF NICKEL SURFACES OF SUPPORTED NICKEL CATALYSTS*

By

G. RÁCZ, G. SZÉKELY, K. HUSZÁR and K. OLÁH

Department of Physical Chemistry Technical University Budapest

Received June 19, 1970

Presented by Prof. G. VARSÁNYI

Nickel surface determination by hydrogen adsorption

There are several possibilities for the unambiguous determination of monolayer capacity in the case of physical adsorption. In the case of chemisorption the situation is far less favourable. In general it is difficult to obtain true equilibrium value in chemisorption at the expected temperature of com-

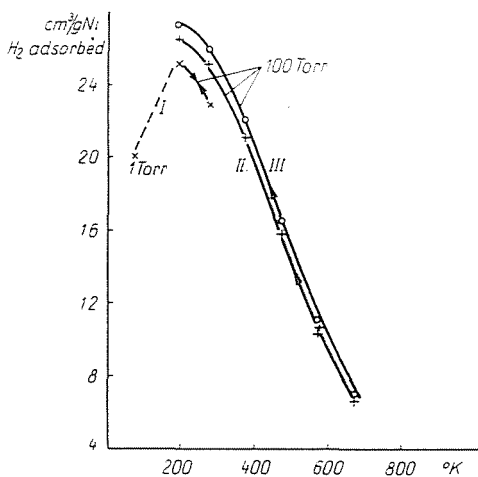


Fig. 1. Sorption isobars on nickel catalyst measured by SCHUIT and VAN REIJEN [1]. (I) 1 Torr 80 K followed by 100 Torr 273 K; (II) 100 Torr temperature decreasing from 673 K in 3 hrs., (III) in 6 days

plete coverage. For determinations with chemisorptive surfaces the conditions of adsorption measurement (temperature, pressure, etc.) have been more or less arbitrarily fixed by the authors.

Fig. 1 shows the adsorption isobar of hydrogen on a nickel-on-silica catalyst measured by SCHUIT and VAN REIJEN [1]. The adsorbed quantity is

* Dedicated to Prof. Z. Csűrös on the occasion of his 70th birthday.

seen not only to depend on temperature and pressure but also on history. The authors determined the nickel surface from the hydrogen amount adsorbed after an adsorption time of 3 h at -78°C and 100 torr pressure. The measurements of MAXTED and HASSID [2] show that the most reasonable temperature for the determination of complete coverage is approximately 0°C , because at

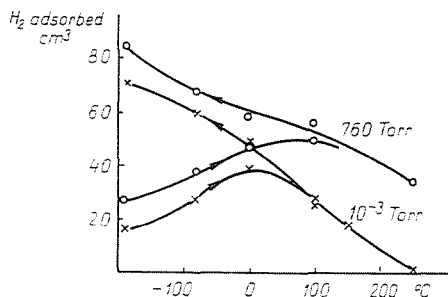


Fig. 2. Sorption isobars on nickel catalyst plotted from the data of MAXTED and HASSID [2]

lower temperature adsorption is greatly dependent on history and at higher temperature the pressure-dependence prevails. The inflexion point at room temperature on the isobars for (Fig. 2) decreasing temperature seems to give the approximate quantity of hydrogen for complete coverage, because the area occupied by one hydrogen atom on the surface (measured by standard BET procedure) is equal to the area of one nickel atom on the surface of a plane with low crystallographic indices (Table 1).

Table 1

Author	Occupied surface of H atom Å^2	Surface belonging to Ni atom Å^2	Crystallographic index
O. Beeck (2)	6.1	5.87	110
G. C. A. Schuit (1)	6.4	6.8	111
		6.1	100

The measurement of adsorption

In catalyst investigations often preference is given to chromatographic methods rather than to static methods. The advantages of the chromatographic adsorption method are velocity and the simple way of preparing the adsorbent. If the adsorption is accompanied by another type of process (e. g. the reduction of catalyst, displacement of impurities from the surface of the adsorbent, or the process of disproportioning of the adsorbate), the chromatographic method can only be applied [3, 4].

The frontal method can be used excellently when the adsorbed quantity compared to the gas capacity of the chromatographic device is big. The adsorbed quantity is equal to the difference between the gas volumes flown in and flown out up to the saturation of the chromatographic column [5].

The elution method is fit for the measurement of little adsorbed quantities in case of irreversible adsorption. The adsorbed quantity is equal to the difference between the quantity fed in and the material content of the elution peak.

The elution peak is deformed by reversible adsorption, but the area of the peak remains unchanged. The determination of the adsorption isotherm on the basis of the shape of the peak seems to be hopeless owing to many other factors.

For the determination of physical adsorption Nelson and Eggensen's temperature-jump method [7] has been applied since more than ten years. We applied this method for the determination of hydrogen chemisorption.

Adsorption measurement by temperature-jump method

The procedure is the following:

There is a continuous gas flow of constant composition produced from indifferent gas and adsorptive through the adsorbent. At a certain temperature equilibrium is attained between the adsorbent and the flowing gas mixture. Then the adsorbent is put into another thermostat different in temperature from the previous one. At the new temperature an adsorption equilibrium will be reached again, but during the time of the adsorption (or desorption) the composition of the gas stream changes. The difference between the input and output gas composition yields the total adsorption or desorption.

The method is used mainly for measuring the physical adsorption of nitrogen or for a rapid surface determination.

In surface measurements with nitrogen, helium (or hydrogen) is used as a carrier gas, using thermostates at room temperature and liquid nitrogen. At room temperature the physical adsorption of the nitrogen is negligible. The quantity adsorbed during cooling is equal to the total of nitrogen adsorbed on the surface. For the determination of a complete isotherm the measurement should be repeated at different nitrogen partial pressures. For rapid, comparative measurements it is enough to determine a properly chosen isotherm point [8, 9].

In the region of little relative pressures the equilibrium position of the physical adsorption is independent of the history, so it is all the same to approach the equilibrium at constant temperature from higher pressure (as it is usual with volumetric instruments), or to approach it at a certain pressure from higher temperature.

The situation is not so unambiguous in chemisorption. This is reversible only in a certain temperature region, and besides even in this region quick and slow parallel processes are possible. The temperature region used for adsorption measurements with carrier gas should remain within the only reversible region of chemisorption.

Experimental

The argon and hydrogen gases were taken from gascylinders. The uniform flow was assured by a manostat set before a differential manometer. The gas mixture was led through a combusting reactor for removing the traces

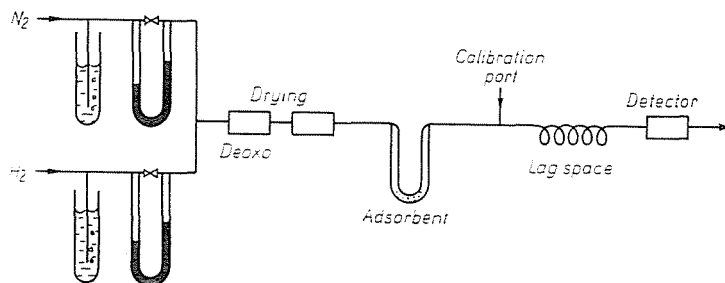


Fig. 3. The apparatus

of oxygen. Then the mixture was dried. The dry mixture of constant composition was led to the detector through the U-tube, containing the adsorbent, the sample injection port for calibration and the time lag volume (Fig. 3).

The role of the time lag volume is to separate the concentration wave appearing with the changing of the temperature from the shock wave caused by the volume change, by assuring the concentration wave to reach the detector only when the speed of flow had become constant.

The detector was made with platinum resistance wires. The detector signs were proportional to the concentration in wide concentration interval. The reference cell was filled with air.

On one hand the sign of the detector was registered with compensograph, on the other it was integrated after proper amplification. At the time of the measurements reported below, the characteristics of the device were as follows:

Speed of hydrogen flow:	10 ml/min
Speed of argon flow:	30 ml/min
Retardation time: cca	1,5 min

Temperature dependence of hydrogen sorption

A catalyst sample (containing 67 mg nickel/g carrier) was used for the series of experiments following (the catalyst preparation was described in [10]). The temperature of desorption of the catalyst sample varied in the range of 200 to 800°C. For cooling down liquid thermostates of 25°C or -78°C were applied. The effect of the cooling rate and of the heating time on the sorbed quantity were investigated in a given temperature range. The results are summarized in Table 2. Only that quantity of hydrogen figures in the table which

Table 2

Measurement of hydrogen adsorption on D Mg [10] catalysts

a) Change in the cooling procedure

Temperature °C	Time of desorption min	Temperature of cooling °C	Adsorbed H ₂ ml/g in cooling	Notice
600	30	25	0.22	
600	30	-78	0.25	quick cooling slow cooling
600	30	-78	0.24 ₅	
600	10	-78	0.25 ₅	
600	30	25	0.25	
600	30	25	0.22	

b) Investigation of the temperature-dependence of hydrogen adsorption

Temperature of 15' desorption °C	Adsorbed H ₂ ml/g in cooling to 25°C
800	0.22
700	0.20 ₅
600	0.20 ₅
400	0.15
300	0.15 ₅
500	0.16 ₅
550	0.18
325	0.09 ₅
200	0.03 ₅

was adsorbed during cooling. Desorbed hydrogen peaks at heating could be perceived but these were much more smeared than the adsorption peaks and on account of the uncertainties of the base-line the integration was far less exact than in the case of adsorption. Namely, for cooling, the sample was taken out from the air thermostat and put into a liquid thermostat, therefore it cooled rapidly (the width of the adsorption peak at half height is about 15 s),

but in heating, the adsorbent was warmed in the air thermostat slowly, the peak was asymmetrical, the desorption was protracted.

When investigating the effect of the time of heating, the sample was cooled in air for a minute, then the cooling was continued and finished in liquid. Thus we had got a double adsorption peak with one minute postpone-

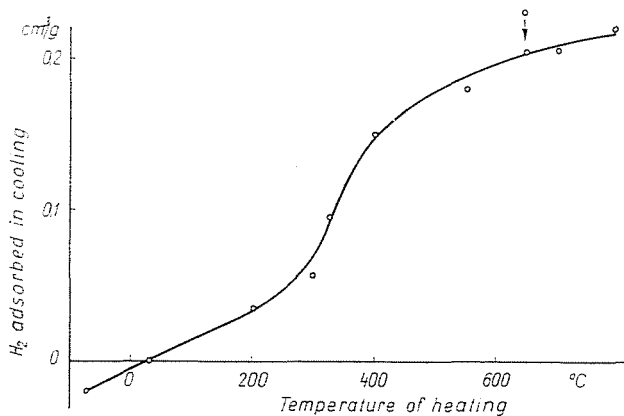


Fig. 4

ment and a well defined end. The changes in the cooling rate did not cause any observable difference in the quantity sorbed.

Over ten minutes of heating even the time of desorption did not influence the result.

The quantities sorbed in cooling to 25°C are plotted against the temperature of desorption (Fig. 4). In the figure the sorbed quantities obtained after heating to 800°C are less than the results of the first cooling from 600°C, and it may be concluded that the surface is already sintered to a certain extent

Table 3

Sintering at 900°C of nickel catalyst supported on mullite. The surface of the catalyst support measured with nitrogen adsorption is 1.3/m²/g
The nickel content of the catalyst is 55 mg/g support

Pretreatment	N ₂		H ₂	
	adsorption ml/g	surface m ² /g	adsorption ml/g	surface ml/g
New catalyst reduced at 600°C	0.70	2.8	0.42	1.35
Sintered for 1 h at 900°C	0.50	2.0	0.16	0.51
Sintered for 3 h at 900°C	0.35	1.4	0.09	0.29
Sintered for 1 h at 1100°C	0.35	1.4	<0.01	<0.03

at 800°C. The degree of sintering is marked by arrows in the figure. In the figure the point belonging to -78°C was obtained from the difference of the results between cooling to 25°C and -78°C. On the basis of the informatory experiments the method was thought fit for the characterization of nickel catalysts. In the chemisorption measurements the catalyst was heated to 600°C for 15 minutes and was cooled to 25°C. The hydrogen quantities sorbed in cooling can be directly compared. For the sake of illustration we computed the nickel surface too, supposing that 1 ml of hydrogen gas at 25°C and 1 atm pressure covers 2.3 m² surface (6.4 Å²/atom) (Table 3).

Observation of the sintering of catalysts containing nickel

In gas industry nickel catalyst supported on ceramic material is used for the conversion of methane-air mixture into hydrogen and carbon monoxide [11]. The working temperature of the catalyst is 800 to 900°C. The change of the nickel surface of a catalyst sample supported on mullite (used in gas industry as well) was determined in dependence of the time of heating.

The experiments were carried out with the adsorption device described above. The catalyst sample was heated in the same gas flow in which the adsorption measurements were done. When the prescribed time for heating was over, the adsorbent was kept at 600°C for 15 minutes, then it was cooled to room temperature quickly and the hydrogen chemisorption was determined (column 4, Table 3). Later the nitrogen adsorption in nitrogen-hydrogen mixture was determined at -183°C. The nitrogen adsorption was not influenced by the presence of hydrogen, the adsorption peak did not show any irregularity or deformation.

The nickel surface of nickel catalyst supported on ceramic material quickly decreases in the region of the working temperature. The change of the surface could be well observed by means of hydrogen adsorption.

The relation between the activity in methane partial oxydation and the area of the nickel surface of the catalysts will be discussed in a subsequent paper.

Summary

A sorptometer method was applied to measure the chemisorption of hydrogen on supported nickel catalysts. The temperature-jump between adsorption and desorption process was 25 to 600°C, time of heating at 600°C was 15 minutes. Sintering processes of the support and of the metal were followed by the method described.

References

1. SCHUIT, G. C. A., VAN REIJE, L. L.: Adv. Catalysis Vol. X. 242—318. Academic Press 1958.
2. MAXTED, E. B., HASSID, N. J.: Chem. Soc. 1532 (1932).
3. SCHAY, G., RÁCZ, G., SZÉKELY, G.: Budapesti Műszaki Egyetem 1960. évi Tudományos Évkönyve, 277—282.
4. SZÉKELY, G., PARLAGH, G., RÁCZ, G., TRAPLY, G.: Period. Polytechnica (Ch) **10**, 21—25 (1966).
5. SCHAY, G., SZÉKELY, G., SZIGETVÁRI, G.: Acta Chim. Hung. **12**, 309 (1957).
6. DE MORGUES, L.: Method. Phys. Anal. 1966. 178—80. Ref. ČA. 66: 108571 p.
7. NELSEN, F. M., EGGERTSEN, F. T.: Anal. Chem. **30**, 1387—90 (1958).
8. GAVRILOVA, T. B., KISELEV, A. V.: Zh. Fiz. Khim. **39**, 2582—5 (1965).
9. VAJTA, Z.: Diploma Thesis, BME Fizikai Kémia Tanszék, 1969.
10. HUSZÁR, K.: Doctor's Thesis, BME Fizikai Kémiai Tanszék 1969.
11. BARSÍ, L., BUNYITAI, J., HORVÁTH, J.: Energia és Atomtechnika **4**, 145 (1967).

Dr. György RÁCZ Dr. György SZÉKELY Dr. Klára HUSZÁR Dr. Károly OLÁH	}	Budapest XI, Műegyetem rkp. 3. Hungary
--	---	--