Surface Areas of Pt–Rh Catalyst Gauzes Used for Ammonia Oxidation

Edvard Bergene,* Olav Tronstad,† and Anders Holmen†,[1]

*SINTEF Applied Chemistry, N-7034 Trondheim, Norway; and †Department of Industrial Chemistry, The Norwegian Institute of Technology,
The University of Trondheim, N-7034 Trondheim, Norway

The changes in structure and surface composition of new and used Pt–Rh catalyst gauzes have been studied by gas adsorption methods. The total surface area was measured by physical adsorption of Kr (Kr-BET). The surface area of used samples varied between 0.01 and 0.06 m^2/g representing an increase in surface area of 2 to 20 times compared with the surface area of new catalysts. A gauze with Rh_2O_3 whiskers exhibited the largest increase in surface area. Except for this abnormal sample, the top gauze in the catalyst pack exhibited the largest surface area. The active surface area of the Pt–Rh gauze catalysts was measured by H_2-titration/adsorption. It was assumed that Pt represents the active part of the catalyst. When exposing a spent gauze to H_2 at 298 K, only platinum oxide on the catalyst surface was titrated. During operation the catalyst deactivates partly by the formation of Rh_2O_3, which was found to be inert against H_2 at 298 K. However, reduction of used catalyst gauze in H_2 at 623 K and reoxidation at 623 K made all the Rh_2O_3 reactive toward H_2 at 298 K, indicating the presence of two forms of Rh_2O_3. It was observed that only the first gauze in a gauze pack from a NH_3-oxidation reactor comprised a noteworthy active area. All the other gauzes investigated were more or less blocked by Rh_2O_3.

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INTRODUCTION

HNO_3 is produced by oxidation of NH_3 to NO which is further oxidized to NO_2. The NO_2 is then absorbed in H_2O to form HNO_3. In the first step an ammonia/air mixture is passed through a Pt–Rh gauze catalyst layer and near total conversion to nitric oxide is achieved:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$\Delta H^{\circ}_{1200 \text{ K}} = -227 \text{ kJ/mol } NH_3. \qquad [1]$$
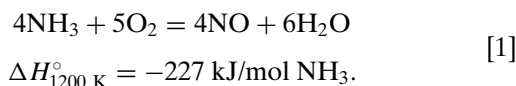
The early development of the ammonia oxidation process has been reviewed by Connor (1). The ability of Pt to catalyze the ammonia oxidation reaction was first discovered by Kohlman. The catalyst system was improved by Ostwald and others and in 1909 Kaiser (2) patented the catalyst in the state of a woven gauze. Gauzes woven from 0.060 mm wires with 1024 mesh/cm^2 are still widely used. Recently,

knitted gauzes have also been introduced (3). These gauzes are reported to have a number of advantages compared to woven gauzes. Today the process is commonly operated at temperatures from 700 to 950°C and from atmospheric pressure up to 10 bar in different commercial designs (4). The effective lifetime of the catalyst is from 60 to 360 days (5). The mechanical and catalytic properties of the gauze can be improved by alloying with 5–10 wt% Rh. Other platinum group metals are also used (4, 6).

During the first hours of operation the smooth surface of the catalyst gauzes is heavily restructured. Starting from the grain boundaries large crystals develop (7–10). The most extensive restructuring occurs on the top two or three gauzes because these convert most of the ammonia. Pretreatment to increase the initial surface area have been suggested (11, 12). This will shorten the time for the catalyst to gain full activity, but the effects over the total lifetime of the catalyst are more uncertain. Transportation of PtO_2 in the vapor phase has been assumed to be responsible for the restructuring (7, 13). Other mechanisms involving unstable volatile gas phase species (radicals) have also been suggested (14). Figure 1 shows a typical restructured surface of a Pt–Rh catalyst gauze. In addition to restructuring, some loss of Pt-metals occurs. Catchment gauzes are commonly installed downstream of the catalyst pack to recover lost Pt-metals. Recent catchment systems utilize alloys with a very high Pd content (15, 16).

The activity and selectivity depend on the surface composition and on the structure of the catalyst. The state of the catalytic surface which develops is determined by the initial bulk composition of the catalyst and by the operating parameters. Deactivation by formation of large amounts of Rh_2O_3 may for instance occur if the temperature is too low (5, 17). In addition to deactivation by Rh_2O_3, the catalyst may also lose activity due to the accumulation of impurities (18, 19). When the catalyst is exhausted by deactivation or by lack of mechanical strength, it is replaced.

The main objective of the present work was to investigate the possibility of using adsorption methods for measuring the total surface area and the remaining active surface area of gauze catalysts used in the oxidation of NH_3. The total surface area was measured by physical adsorption

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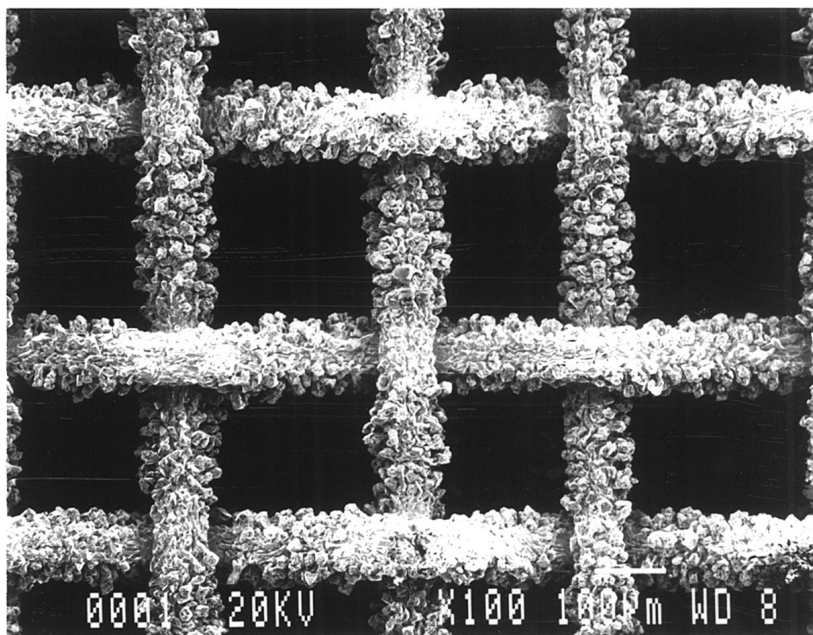[1] To whom correspondence should be addressed.

FIG. 1. SEM image of a Pt–Rh gauze catalyst from a commercial nitric oxide plant. The white bar on the micrograph equals 0.1 mm.

of Kr whereas the active surface area of spent catalysts was measured by H_2 titration/adsorption. To our knowledge the use of chemisorption to characterize Pt–Rh catalyst gauzes has not been reported previously. By cyclic voltammetry Anderson was able to measure the increase in total surface area of individual gauzes (20). The surface area of the first gauze was 0.025 m^2/g corresponding to about 10 times the area of a new gauze. The surface area of the last gauze in the pack was 0.0035 m^2/g which is comparable to a new gauze.

Chemisorption of H_2 is the standard method for characterization of the active surface area of supported Pt catalysts (21). For Pt–Rh gauze catalysts, however, there are some serious problems which can be summarized as follows:

(i) Very low surface area. The total surface area of a gauze catalyst is in the range 0.005–0.06 m^2/g whereas the Pt-surface area of a supported Pt catalyst can be about 1 m^2/g. This means that the experimental apparatus must have high sensitivity and accuracy.

(ii) Interpretation of the results. Assuming that significant adsorption can be measured there is no established adsorption stoichiometry, but measurements on reduced samples can probably be interpreted according to similar measurements on supported samples or Pt black. If the surface is completely reduced such measurements would yield the total surface area.

EXPERIMENTAL

Gauze Catalysts

The catalyst samples were Pt–Rh gauzes from a commercial nitric acid plant. From one gauze pack, we have studied gauzes 1, 4, 7, and 8 numbered from the inlet. A simplified sketch of the ammonia oxidation reactor showing the positions of the gauzes in the gauze pack is given in Fig. 2. The gauzes were woven from a Pt–Rh wire of 0.060 mm diameter. This particular gauze pack was chosen because it contained some very different surface structures. The restructuring varied considerably through the catalyst pack as can be seen on the SEM images (Figs. 3a– 3d).

Gauze no. 1, closest to the inlet of the reactor, was heavily restructured with the development of large cauliflower structures (Fig. 3a). This is the normal restructuring which is necessary to gain full activity of the catalyst (10).
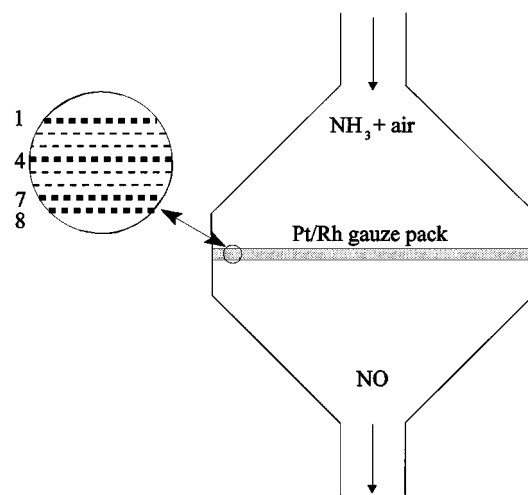

FIG. 2. Simplified sketch of an ammonia oxidation reactor showing the positions of the Pt–Rh gauzes (nos. 1, 4, 7, and 8) in the gauze pack.
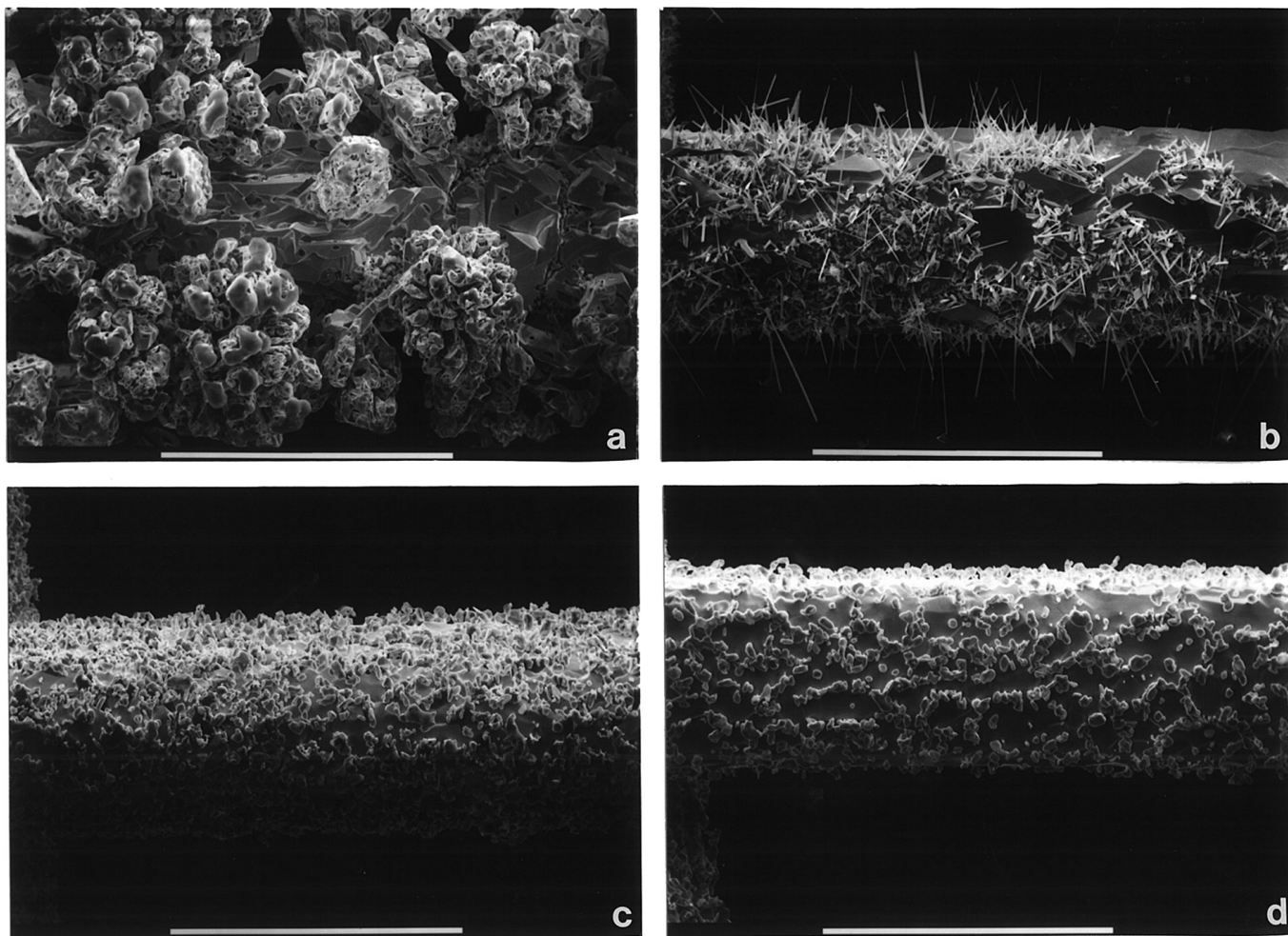
FIG. 3. SEM images of the Pt–Rh gauzes examined in this investigation. The gauzes are from a commercial nitric oxide plant and the following gauzes in one particular gauze pack have been studied: Gauze no. 1 (a), gauze no. 4 (b), gauze no. 7 (c), gauze no. 8 (d). The gauze numbers correspond to the numbers in Fig. 2. The white bar in the micrograph equals 0.1 mm.

Gauze no. 4 (Fig. 3b) showed no cauliflower structures. However, whiskers of Rh_2O_3 were visible in addition to grainlike structures (Rh_2O_3) at the core of the wire. Extensive formation of Rh_2O_3 is a highly unwanted situation because it may lead to complete deactivation of the catalyst (22). In addition to the whisker and the grain forms of Rh_2O_3, large surface-facets, probably of PtRh, were exposed. Gauzes nos. 7 and 8 share a rather similar appearance. The surface was more or less covered with grainlike structures, probably of Rh_2O_3.

Surface Area by the BET Isotherm

The determination of the total surface area is based on the BET isotherm (multipoint). For very low surface areas Kr is the preferred adsorption gas instead of N_2 due to its very low vapor pressure at 77 K compared to N_2. The p_o values for Kr can be calculated theoretically and at 77 K the values are $p_{o\,solid} = 300$ Pa (2.25 Torr) and extrapolated

$p_{o\,liquid} = 487$ Pa (3.65 Torr). Our own measurements of the saturated vapor pressure have given $p_o = 360$ Pa (2.7 Torr). Based on this value the same surface areas have been obtained for some other samples using both N_2 and Kr as the adsorbate. The Kr isotherm was measured in the range $p/p_o = 0.1$–0.4. The surface area was calculated assuming that each Kr atom occupies 19.5 Å^2 of adsorbent surface. The measurements of the total surface area were performed using a commercial apparatus (Carlo Erba Sorptomatic with Kr-unit). Due to the very low surface areas of the gauzes, large samples (10 g) were necessary.

Chemisorption Apparatus and Procedure

The chemisorption measurements were performed in a conventional glass apparatus. The design corresponded closely to ASTM Standard D-3908-82 (23). The apparatus was optimized to give high sensitivity by minimizing the dead-volume. All the gases were purified with oxygen traps

and moisture traps before entering the chemisorption apparatus.

The Pt–Rh catalyst gauzes were first studied in the "as received" condition. The sample was inserted into the sample cell and the cell was evacuated. With a background pressure below 1.33×10^{-3} Pa (10^{-5} Torr), H_2 was admitted and the pressure monitored by an electronic pressure gauge. Calibration of this gauge was performed by a quartz spiral gauge (Mensor). The equilibrium pressure was recorded after 10–30 min. The stepwise increase in pressure was continued until the equilibrium pressure reached about 46.6×10^3 Pa (350 Torr). After the first isotherm, the sample cell was evacuated for 20 min and a second isotherm was measured. Both isotherms were extrapolated to zero pressure and the amount of "irreversible" adsorbed hydrogen was calculated as the difference between the first and the second isotherm. The amount of adsorbed hydrogen removed by evacuation before measurement of the second isotherm is strongly dependent on experimental parameters (24). Although the procedure with two isotherms was used with the gauze catalysts, the calculations were based on the total amount adsorbed. In some cases the "reversible" fraction may give further information especially with the titration experiments. A small reversible fraction with hydrogen titration on oxidized samples indicates reaction with more than a monolayer of oxide.

After the initial measurements, the gauzes were reduced *in situ* using flowing H_2 at 623 K for 1 h and subsequently cooled to 298 K under vacuum. The chemisorption measurements described above were then repeated. Finally, the samples were preoxidized in air at 623 K for 1 h and cooled to 298 K in vacuum before titration/chemisorption with H_2 as described above.

RESULTS AND DISCUSSION

Total Surface Area of Gauze Catalysts

The total area (m^2/g) of the gauzes, measured by Kr-BET is given in Fig. 4. The surface area of a new gauze, as shown in Fig. 4, was measured to be 0.005 m^2/g.

The theoretical surface area of completely smooth wires of 0.060 mm diameter has been calculated to be 0.0031 m^2/g. However, there are several good reasons why the measured value should be higher than the calculated. Some roughness from the processing of the wires and the gauzes is expected. Scratches in the surface of the new wires were easily observable by optical microscopy. However, the macroscopic roughness observed by optical microscopy was estimated to be somewhat too small to account for the difference between the measured and the calculated surface area. Another explanation for the difference between the calculated and the measured surface area is microroughness. The cleaning procedure (heating in an inert gas) applied by the manufacturer may have induced initial restructuring of
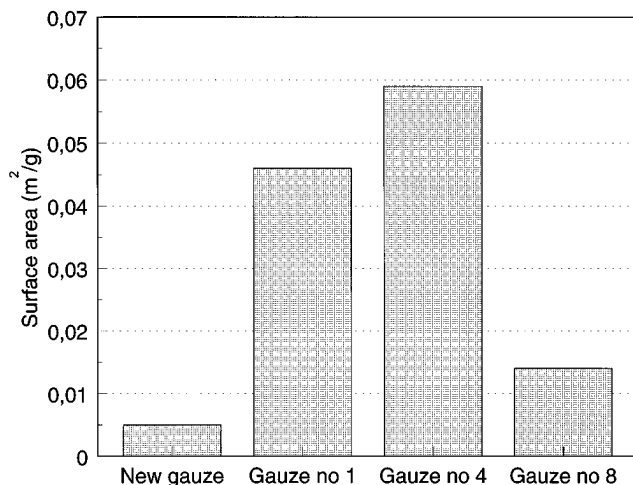

FIG. 4. Total surface areas of Pt–Rh gauzes measured by physical adsorption of Kr at 77 K. Gauze numbers correspond to the numbers in Fig. 2.

the surface with an increase in available surface area as a result (25).

Figure 4 shows that the increase in the total surface area for gauze no. 1 was approximately 10 times compared to a new gauze. From the SEM image in Fig. 2a it is likely that the increase in surface area is due to the facetted cauliflower structures which were formed.

Gauze no. 4 shows formation of Rh_2O_3 whiskers. This gives an even larger increase in surface area than the cauliflower structures on gauze no. 1. Gauze no. 8 (Fig. 2d) shows less restructuring with approximately a 3 times increase in surface area.

Measurements of surface areas of spent Pt–Rh gauzes were not published until the work by Anderson (20). It has previously been assumed that the increase in total surface area of the catalyst could be as high as 100 times (15). Anderson (20) used cyclic voltammetry for the measurements of surface areas of gauzes. Cyclic voltammetry is based on measurements in solution. The principle of the method is that hydrogen can be adsorbed and desorbed from a platinum surface in an acidic solution. The main advantage of the method is the ability to measure small samples ($\sim$1 cm^2 gauze). However, the possibility of restructuring of the surface during the measurements could exist because material is dissolved from the sample. Quantification and interpretation also seem to be more complicated than for the chemisorption technique.

Anderson's results show the same overall tendency of decreasing area through the catalyst pack as the present work. The main difference between his results and the present work is the high surface area measured on our gauze no. 4. The obvious reason for the large surface area is the formation of Rh_2O_3 whiskers. Formation of this type of Rh_2O_3 is highly undesirable and can deactivate the catalyst
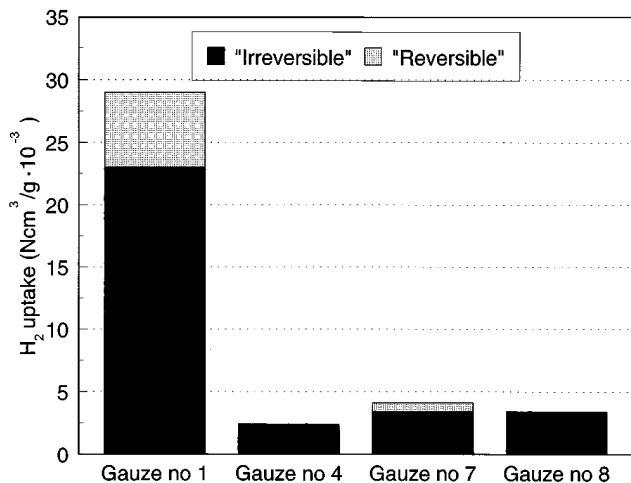
FIG. 5. H_2 uptake at 298 K of Pt–Rh gauzes in the as received state. Gauze numbers correspond to the numbers in Fig. 2.

FIG. 6. H_2 uptake at 298 K of spent Pt–Rh gauzes. The samples were reduced at 623 K in flowing H_2 at atmospheric pressure for 60 min. Gauze numbers correspond to the numbers in Fig. 2.

completely. Anderson reports no such features except as a reason for the slight increase in surface area toward the end of one of the catalyst packs. Anderson's measurements were performed on gauzes made from heavier (0.076 mm diameter) wires with lower geometric surface area (0.0025 m^2/g).

Chemisorption Measurements

The experiments confirmed that it was possible to measure the adsorption of H_2 on these Pt–Rh gauze catalysts. The H_2-adsorption results for gauze nos. 1, 4, 7, and 8 in the as received state are shown in Fig. 5.

On the unreduced samples (as received), H_2 may be consumed by reduction of the oxides and then by adsorption as H atoms:

$$PtO_x + \left(\tfrac{1}{2} + x\right)H_2 = PtH + xH_2O \qquad [2]$$

$$\tfrac{1}{2}Rh_2O_3 + 2H_2 = RhH + \tfrac{3}{2}H_2O. \qquad [3]$$

Our starting hypothesis was that oxygen on Pt could be completely titrated according to Eq. [2] whereas Rh_2O_3 was inert, which means that no reaction occurred according to Eq. [3]. The hypothesis was applied only for the current experimental conditions: 298 K, $\leq 101 \times 10^3$ Pa (760 Torr) H_2.

Gauze no. 1 adsorbed much more hydrogen compared to the other gauzes in the as received state. Following the hypothesis outlined above, this implies that more Pt was accessible on this gauze than on the others. For gauze nos. 7 and 8 which have a low total area, the low adsorption seems reasonable. Gauze no. 4 behaves differently by adsorbing very little hydrogen in spite of the high surface area. This is an indication that the Rh_2O_3 whiskers were not reduced in H_2 at 298 K.

After the initial adsorption the samples were reduced in flowing H_2 at 623 K and atmospheric pressure for 60 min.
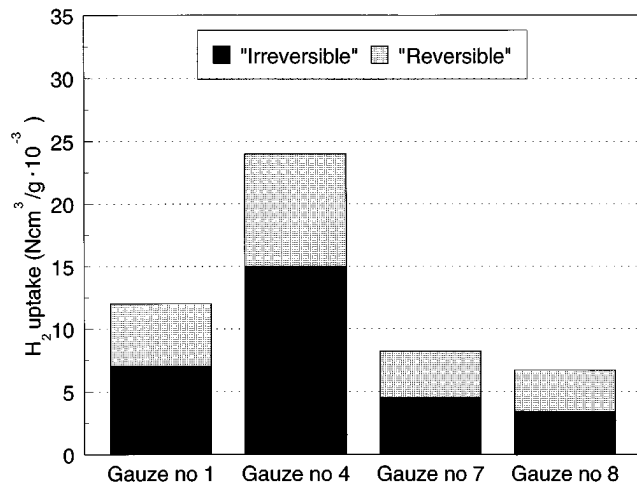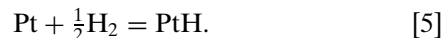
The results from the measurements of the reduced gauzes are shown in Fig. 6.

After reduction gauze no. 4 adsorbs more hydrogen than the other samples. The Rh_2O_3 whiskers are probably reduced to metallic Rh which adsorbs hydrogen together with reduced Pt:

$$Rh + \tfrac{1}{2}H_2 = RhH \qquad [4]$$

$$Pt + \tfrac{1}{2}H_2 = PtH. \qquad [5]$$

Figures 5 and 6 show that the fraction reversibly adsorbed is larger on the reduced samples. On these samples H_2 is consumed only by adsorption, whereas the total consumption of H_2 on oxidized samples is the sum of both the reduction of oxides and of adsorption of H_2. The observed differences in the fraction reversibly adsorbed are therefore expected. The fraction reversibly adsorbed is larger on gauze no. 4 compared to the other samples. This may be due to differences in desorption energies between Pt and Rh which may lead to a larger fraction of reversible adsorption when the surface is dominated by Rh.

After oxidation in air at 623 K and atmospheric pressure for 60 min the adsorption behavior is very similar to the reduced samples as shown in Fig. 7. The main difference is that the oxidized samples adsorb more hydrogen due to reactions with the surface oxides. If the reaction followed Eqs. [2]–[5], the maximum attainable ratio of H_2 adsorbed on oxidized and reduced samples would be 5. This corresponds to a surface composition of only Pt with x in Eq. [2] being equal to 2. $x = 1$ or 0.5 yields a ratio of 3 and 2, respectively. x has commonly been assumed to be equal to 1 when adsorbed oxygen on supported Pt is titrated with hydrogen (13).

If the surface consists of 100% Rh_2O_3, the ratio of hydrogen adsorbed on oxidized and reduced samples should be 4
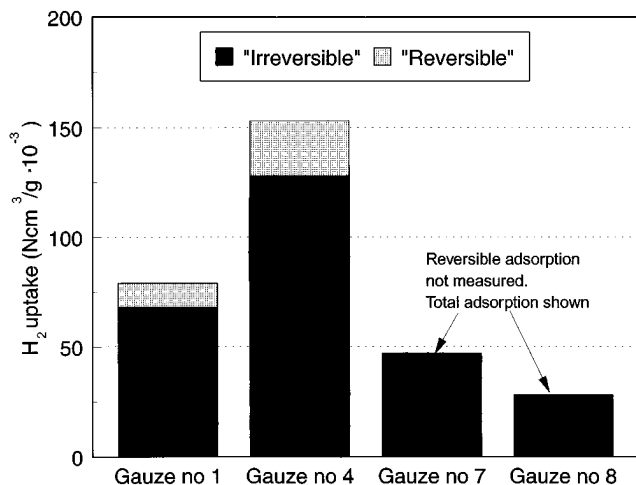
FIG. 7. H_2 uptake at 298 K. The samples were oxidized at 623 K in flowing air at atmospheric pressure for 60 min after having been reduced at 623 K in flowing H_2 at atmospheric pressure for 60 min. Gauze numbers correspond to the numbers in Fig. 2.

according to Eqs. [3] and [4]. This includes the assumption that Rh_2O_3 reacts with H_2 at 298 K. In contrast to the initial Rh_2O_3 present on the catalyst in the as received state, the Rh_2O_3 formed by reoxidation at 623 K seems to react with H_2 at 298 K. The Rh oxide formed under ammonia oxidation conditions may be of a different texture which is more resistant to reduction. The Rh oxide formed after reduction and reoxidation is also probably more uniformly distributed on the surface. This may render the oxide less stable than an oxide in the form of "large" islands. A reduction mechanism which may explain this behavior is that the reduction proceeds via dissociation of H_2 on Pt^0 and Rh^0 (if present).

The observed values for the ratio of H_2 adsorbed on oxidized and reduced samples are given in Table 1. The ratio is 6.6 for gauze no. 1, decreasing to 4.2 for gauze no. 8. These values are higher than the maximum values as explained above. A reduction mechanism which may explain this could be that titration of more than one monolayer of Rh_2O_3 by H_2 occurs. The titration may be catalyzed by Pt. In contradiction to Pt, passivation of Rh does not stop with a monolayer or less of oxygen. The oxidation does not stop until a solid layer of Rh_2O_3 is formed at the surface (26). When Rh is alloyed with other metals such as Pt the passivation behavior could change. One possibility is that the alloy behaves like a linear combination of the two components. In this case one would expect that the alloy would form an oxide thinner than with pure Rh but more extensive than the monolayer of oxygen adsorbed on pure Pt. The alloy is a solid solution and there is no strong surface segregation.

The total surface area of the gauzes can also be calculated from the H_2-adsorption data. This requires some assumptions regarding the adsorption stoichiometry and the surface area per metal atom. The stoichiometry from

TABLE 1

The Ratio between Amount H_2 Adsorbed on Oxidized and Reduced Gauzes

Gauze no.[a]	1	4	7	8
H_2^{ox}/H_2^{red}	6.6	6.4	5.9	4.2

[a] Gauze numbers show position from top of the reactor (Fig. 2).

Eq. [4] and [5] and a coverage area of 9×10^{-20} m^2 are commonly used for H_2 adsorption on supported Pt catalysts (27). This value represents the mean value between the Pt (111), (110), and (100) crystal faces. The results from this calculation are summarized in Table 2.

The precision of the measurements is estimated to be better than ± 0.005 m^2/g. The surface area of one H atom on Pt was also used for Rh. The two metals have very similar atomic radii ($r_{met, Pt} = 1.39$ Å, $r_{met, Rh} = 1.34$ Å) (28) and identical crystal structure (face centered cubic). For gauze no. 1 the H_2-adsorption data on reduced samples yields a lower surface area than the corresponding measurement by Kr-BET. For the other gauzes the situation is reversed with Kr-BET giving higher areas. The reason for this is not obvious. The main difference between gauze no. 4 and the others is the low surface concentration of Pt on this gauze. When the assumed error limits are taken into account the difference may not be as large as indicated, but the surface titration on oxidized samples show the same tendency.

It is, however, more difficult to interpret titration measurements on oxidized samples due to the uncertainties in the stoichiometry and the possible effects of water formation. The vapor pressure of water would partly compensate for the pressure drop due to adsorption and give a lower amount adsorbed than the correct value. The effect of water formation was investigated by placing a small amount (~ 1 mg) of water adsorbing zeolite together with the sample. The zeolite had no effect on the results indicating that evolved water was probably adsorbed on the internal surfaces of the apparatus. An additional indication that the present results from surface titration on oxidized samples was probably not affected by water formation was that the observed values were higher than expected.

The surface areas calculated from the H_2-adsorption measurements with the samples in the as received state were considered to be the Pt area only, according to our starting hypothesis. If Pt is the active catalyst and if Rh is always blocked by inactive Rh_2O_3, the measured area would be the active surface area of the catalyst. For gauze no. 4 this seems reasonable. For this gauze a small Pt area is consistent with the high surface area Rh_2O_3 whiskers. For gauze no. 1 the same idea of Rh_2O_3 being inert was applied. For this gauze the active area was about half of the total area.

TABLE 2

Surface Area Measured by Kr Adsorption and H$_2$ Adsorption

Method	Assumptions	Surface area × 10^3 (m^2/g) Gauze no.			
		1	4	7	8
Kr adsorption BET isotherm	1.9×10^{-19} m^2/Kr-atom	46	59	—	14
H$_2$ adsorption, reduced gauzes	Eqs. [4] and [5], 9×10^{-20} m^2/H atom	58 (34)	116 (73)	40 (22)	32 (16)
H$_2$ adsorption, oxidized gauzes	Eq. [2] with $x = 1$, 9×10^{-20} m^2/H atom	76 (66)	148 (124)	45 (—)	27 (—)
H$_2$ adsorption as received	Eq. [2] with $x = 1$, Rh$_2$O$_3$ inert, only Pt measured, 9×10^{-20} m^2/H atom	28 (22)	2.3 (—)	4.0 (3.2)	3.3 (—)

Note. Calculated areas based on the "irreversible" amount of adsorbed hydrogen are shown in parentheses. Gauze numbers show position from top of the reactor (Fig. 2).

CONCLUSIONS

Physical adsorption of Kr (Kr-BET) was found to be a suitable method for measuring the total surface area of Pt–Rh catalyst gauzes. The increase in the total surface area of gauzes from a commercial nitric acid plant was from 2 to 20 times compared to the measured area of a new gauze. A gauze with Rh$_2$O$_3$ whiskers exhibited the largest increase in the surface area.

The active surface area of the catalyst was measured by chemisorption of hydrogen. Assuming that the active part of the catalyst is Pt, a working hypothesis was formulated. The hypothesis states that adsorbed oxygen could be titrated by the first exposure to H$_2$, representing the active surface area of the catalyst. The results indicate that oxygen, which was present on Pt after the catalytic reaction was stopped, reacted selectively with H$_2$ at 298 K. Rh$_2$O$_3$ was assumed to be inert. After reduction and reoxidation the properties of the surface oxide changed. In this case, Rh$_2$O$_3$ could also be titrated by H$_2$ at 298 K.

Comparison of the active surface area with the total area revealed that only the first gauze comprised a noteworthy active surface area. All the other gauzes were more or less blocked by Rh$_2$O$_3$.

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