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Hydroxylamine Production via Hydrogenation of Nitric Oxide in Aqueous Sulfuric Acid Catalyzed by Carbon-Supported Platinum

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This paper reports a study of the hydrogenation of nitric oxide to hydroxylamine in aqueous sulfuric acid in the presence of platinum supported on high-surface-area active carbon as catalyst. Industrially relevant catalysts (low Pt content and finely divided carbon particles) were used. In particular, conditions for the kinetic regime have been investigated. Measurements in the range 15–55°C and on catalysts with platinum contents approximately from 1 to 11 wt% have been carried out. An activation energy of 11.8 Kcal/mol has been calculated.

1. INTRODUCTION

The catalytic hydrogenation of nitric oxide is an important industrial process for the production of hydroxylamine, an intermediate in the manufacture of ε-caprolactam. The reaction

$$2NO + 3H_2 \rightarrow 2NH_2OH$$

is usually carried out with platinum as a catalyst, supported on fine carbon particles stirred in a sulfuric acid solution (*1*).

The problem of the role played by mass transport phenomena, as well as that of the mechanism involved (a purely kinetic model, an electrochemical process, or a combination of both), has not yet been solved (*2*).

From a kinetic point of view, the most systematic studies of the reaction are those by Temkin and co-workers (*3–5*). They reported a complete study (*3*) of catalysts with high platinum content (≅10 wt%) and large particle size (≅0.1 mm); the reactions took place at low temperatures (15 and 25°C). These catalysts may not be the most convenient ones from an industrial point of view and they were obviously chosen in order to avoid, as far as possible, diffusion problems to make the catalytic activity more stable.

The most significant experimental aspects of the reaction are that (i) the formation of hydroxylamine is accompanied by the formation of side products such as ammonia and nitrous oxide; (ii) the rates of formation of hydroxylamine and ammonia as a function of P_{NO}, for a constant P_{H_2}, pass through a maximum at $(P_{NO})_{max}$ and then decrease to negligible values; (iii) $(P_{NO})_{max}$, which is relatively low (0.11 atm), is not temperature dependent; (iv) the rate of hydroxylamine formation is independent of the acidity for H_2SO_4 concentrations in the range 1–20%; (v) the ratio $NH_2OH : NH_3$ does not depend on P_{NO} and

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P_{H_2}, nor on the concentrations of the acid and of the reaction products.

On the basis of these data a kinetic model was proposed (*4*) which calls for two different active sites on the catalyst surface; one responsible for the formation of hydroxylamine and ammonia and the other for the formation of nitrous oxide. The latter hypothesis was also supported by the fact that oxygen or copper ions poison the catalyst surface relative to the formation of NH_2OH and NH_3, while the effect on N_2O formation is weak (*5*). The role of small amounts of other various modifiers (or poisons) on the selectivity of platinum catalysts has been studied by Jockers (*6*) and van de Moesdijk (*1*). In particular, this latter author has stressed the importance with respect to industrial applications of selenium as a modifier in order to increase the hydroxylamine activity and to decrease the formation of ammonia. Similar behavior is reported by van de Moesdijk for the activation by S and Te. The addition of small amounts of GeO_2 also increases the selectivity to hydroxylamine, with a simultaneous decrease of NH_4^+ and N_2O selectivities (*1*).

The kinetic equations of Temkin *et al.* (*4*) for the rate of reaction to hydroxylamine, r_1, ammonia, r_2, and nitrous oxide, r_3, are

$$r_1 = k_1 P_{H_2} P_{NO}(1 - AP_{NO}) \quad (1)$$

$$r_2 = k_2 P_{H_2} P_{NO}(1 - AP_{NO}) \quad (2)$$

$$r_3 = k_3 P_{NO}^2 \quad (3)$$

where k_i are the relevant rate constants, P_x is the pressure of gas x, and $A = 1/[2(P_{NO})_{max}]$. In a later work (*5*), Temkin and co-workers claim, unfortunately reporting little data, to have obtained the same results with industrial catalysts with low platinum content ($\cong$0.5 wt%) and particle size not exceeding 40 μm.

With regard to the temperature effect, Temkin (*7*), on the basis of theoretical calculations and of experimental data, claims that the kinetic regime is maintained below 25°C, while no statement is made concerning the region above this temperature.

In the present work, we report a kinetic study of the hydrogenation of nitric oxide in the temperature range 15–55°C promoted by industrial catalysts with a platinum content in the range 1–11 wt%, supported on charcoal particles a few microns in size and with surface areas of several hundred m^2/g. The catalytic activities are correlated with the free metal surface areas, measured by chemisorption. This study has been carried out in order to investigate better the upper limit of the kinetic regime and to check systematically the catalytic behavior using catalysts with different structures and which were progressively richer in platinum. The latter purpose is very important from an industrial point of view in order to optimize the amount of platinum to be used. Moreover, to understand better the mechanisms involved in the catalytic process, a complete microstructural characterization of the catalysts has been carried out, using small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), and transmission electron microscopy (TEM). Results of this characterization are reported in the preceding paper (*8*).

2. EXPERIMENTAL

Catalysts with 1.2, 3.0, 5.6, and 11.3 wt% of platinum dispersed on a Lurgi KE active carbon were prepared by reduction with formic acid of K_2PtCl_4 in an aqueous acid slurry of carbon at 70–100°C, at pH 2–4, under vigorous stirring. The platinum surface areas[1] were 118, 49, and 25 m^2/g of Pt, respectively (the value for the last sample is not available), while that of carbon was about 1000 m^2/g. The particle size of the active carbon was within the range 1–15 μm.

Nitric oxide was purified by passing the

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[1] Results for the Pt areas, obtained by chemisorption and hydrogen titration of preadsorbed oxygen, were kindly supplied by Dr. G. R. Tauszik (*2*).

gas by a NaOH trap and a 1-m-long tube filled with a molecular sieve. The reaction vessel was a thermostated glass cylinder of 250 cm^3 volume, fitted with a coaxial vibromixer. The vessel was charged with 100 ml of a 20% aqueous sulfuric acid solution. Various types of "chemically pure" sulfuric acids have been tested in order to avoid poisoning effects: a very pure type from Carlo Erba (RSE) was finally utilized.

The inlet and outlet gas mixtures were analyzed by gas chromatography. The outlet NO concentration was also continuously controlled by a NO_x chemiluminescence analyzer.

A rather strong influence of the position and shape of the stirrer and of the intensity of agitation on the reaction rates was noticed.

3. RESULTS AND DISCUSSION

In order to find optimal running conditions for the kinetic regime various experimental parameters were tested (*8*).

The quantity of catalyst to be placed in the vessel in order to remain in the kinetic region was investigated. In Fig. 1 the rates of NO conversion to hydroxylamine and ammonia, r_1 and r_2, are reported as a function of the amount of catalyst at 40°C, $P_{NO} = 0.06$ atm, and $P_{H_2} = 0.56$ atm for the catalyst with 1.2 wt% platinum. The plateau indicates the region where the mass transfer problems at the gas–liquid interface are important. These data show that, in order to work in the kinetic region, experiments at 40°C have to be carried out with an amount of catalyst less than 4 g/liter.

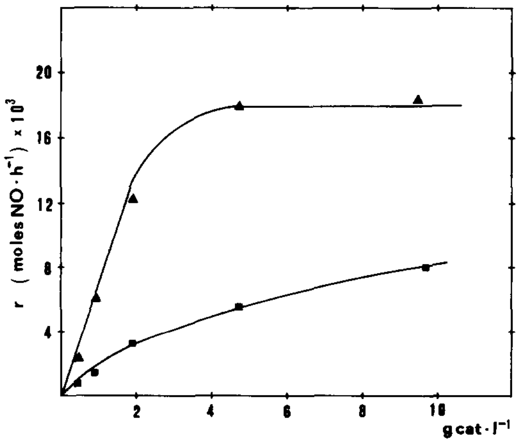

FIG. 1. Rates of NO conversion to hydroxylamine (▲), r_1, and ammonia (■), r_2, as a function of the amount of catalyst at 40°C.

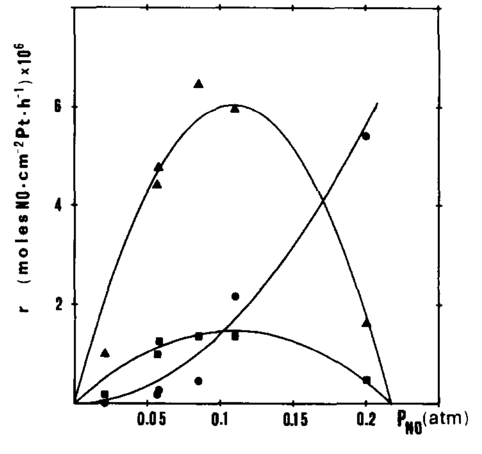

FIG. 2. Rates of NO conversion to hydroxylamine (▲), ammonia (■), and nitrous oxide (●) as a function of P_{NO}. $P_{H_2} = 0.6$ atm, $T = 40$°C; sample with 1.2 wt% of platinum.

The effect of P_{NO} on the rates of NO conversion to hydroxylamine, ammonia, and nitrous oxide is shown in Fig. 2 for a 1.2 wt% Pt sample at 40°C and $P_{H_2} = 0.6$ atm, obtained with 1.9 g/liter of catalyst. The value of $(P_{NO})_{max}$ is 0.11 atm [$A = 1/[2(P_{NO})_{max}] = 4.6$ atm^{-1}]; at about 0.22 atm the activity of the catalyst practically ceases as far as the formation of hydroxylamine and ammonia is concerned, whereas the rate of nitrous oxide formation increases with P_{NO}.

The rate trends as a function of P_{H_2} are shown in Fig. 3 for $P_{NO} = 0.067$ atm and $T = 15$°C: as predicted by the kinetic equations of Temkin *et al.* (*4*), r_1 and r_2 steadily increase with P_{H_2}, while r_3 is nearly constant.

The behavior shown in Figs. 2 and 3 is similar to that of the catalyst tested by Temkin and co-workers (*3*), even though our rates are a little lower, as can be seen in

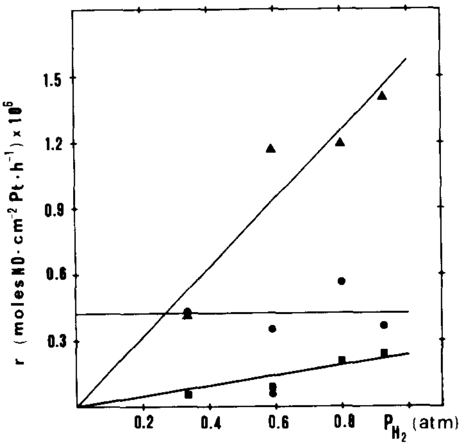

FIG. 3. Rates of NO conversion to hydroxylamine (▲), ammonia (■), and nitrous oxide (●) as a function of P_{H_2}. P_{NO} = 0.067 atm, T = 15°C; sample with 1.2 wt% of platinum.

Table 1 where different rate constants k_1, k_2 and k_3 are reported for comparison. Since Temkin and co-workers gave only qualitative results for their measurements with catalysts of about 0.5 wt% of Pt (5), we do not know whether they found a similar lowering in rates.

Selectivities toward the three products at 40°C, together with those calculated from the data of Temkin *et al.* at 25°C, expressed as the ratio between r_i at $(P_{NO})_{max}$ and the relevant total rate of NO consumption, are reported in Table 2. As can be seen, our selectivity toward hydroxylamine is slightly lower than that of Temkin *et al.*, while the one toward nitrous oxide is higher; perhaps this can be ascribed to the temperature difference.

TABLE 1

Rate Constants[a] for Hydrogenation of Nitric Oxide

Rate constant	Previous work[b] 15°C	25°C	This work 40°C
k_1	1.5	3.4	1.85
k_2	0.22	0.65	0.45
k_3	—	0.75	1.41

[a] Moles NO 10^4 cm^{-2} Pt h^{-1} atm^{-2}.
[b] From Ref. (3).

TABLE 2

Selectivities in Hydrogenation of Nitric Oxide

Selectivity (%)	Previous work[a] 25°C	This work[b] 40°C
S_1	75	67
S_2	15	15
S_3	10	18

[a] P_{H_2} = 0.35 atm, P_{NO} = 0.11 atm, from Ref. (3).
[b] P_{H_2} = 0.56 atm, P_{NO} = 0.11 atm.

As expected from the kinetic equations, the ratio $NH_2OH:(NH_2OH + NH_3)$ was found to be independent of P_{NO} and P_{H_2}; the value of 0.81 we obtained at 40°C is in line with those found by Temkin *et al.* (0.84 at 25°C and 0.87 at 15°C), this parameter being influenced little by temperature.

In order to investigate the effect of temperature on the kinetics, experiments were carried out in the temperature range 15–55°C using the sample with 1.2 wt% of platinum. Experimental results and P_{NO} and P_{H_2} running conditions are reported in Table 3. These pressures were chosen in order to maintain, at all temperatures, constant concentrations of dissolved NO and H_2 corresponding to the equilibrium values at 15°C, P_{NO} = 0.067 atm and P_{H_2} = 0.59 atm, which is equivalent to $(C_{NO})_{eq} = 1.10 \times 10^{-4}$ mol/liter, $(C_{H_2})_{eq} = 3.25 \times 10^{-4}$ mol/liter.

The Arrhenius plot is shown in Fig. 4: excellent linearity is found and an activation energy of 11.8 kcal/mol is calculated. This value is near to 13.5 kcal/mol which

TABLE 3

Rates of NO Conversion to Hydroxylamine

T (°C)	P_{NO} (atm)	P_{H_2} (atm)	r_1[a]
15	0.067	0.590	1.35
25	0.086	0.668	2.67
40	0.122	0.679	7.01
55	0.157	0.708	17.63

[a] Moles NO × 10^6 cm^{-2} Pt h^{-1}.

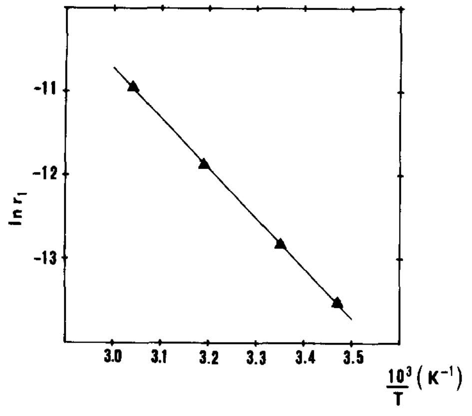

FIG. 4. The effect of temperature on the rate of conversion to hydroxylamine. $C_{NO} = 1.10 \times 10^{-4}$ mol/liter, $C_{H_2} = 3.25 \times 10^{-4}$ mol/liter, sample with 1.2 wt% of platinum.

follows from the two k_1 values found by Temkin and co-workers in the absence of diffusion limitations (3). This suggests that the kinetic regime is maintained in the whole temperature region explored by us.

We also performed a set of measurements on samples with different platinum contents, in order to investigate the problem of mass transfer limitations at the liquid–solid interface.

Following the two-film model (9) of mass transfer in a slurry reactor, for a first-order reaction, $r = k \cdot C$ (C is the reactant concentration) and, if gas–liquid transfer limitations are negligible, the equilibrium mass transfer equation can be written in the form

$$C/r = 1/(S_{\mathrm{met}}\eta k) + 1/(K_s S_{\mathrm{sup}}), \quad (4)$$

where S_{met} and S_{sup} are the metal and support surface areas, η is the efficiency of the support (related to the pore penetration of the liquid), and K_s is the mass transfer coefficient of the liquid–solid interface (liquid film around the catalyst particle). If one carries out experiments with the same amount of the same support but with increasing S_{met}, the reaction rate expressed in moles per gram of catalyst and per hour should be linear, with S_{met} expressed as square centimeters of metal per gram of catalyst, only if the mass transfer at the liquid–solid interface is not the slowest step of the process.

In order to fit the equations outlined above to the present case of the rate of NO conversion to hydroxylamine, we have to operate under experimental conditions where the kinetic Eq. (1) reduces to a pseudo-first-order relation, i.e., constant P_{H_2} and low P_{NO}.

Results of our measurements at 40°C, $P_{H_2} = 0.57$ atm, $P_{NO} = 0.029$ atm, and 0.46 g of catalyst per liter, are reported in Table 4. The reaction rate appears to be independent of the platinum content; if the platinum content were proportional to the platinum surface area, this would suggest a strong mass transfer limitation. As widely discussed by Temkin (7) and as reported in Table 4 this is not the case, as the metal surface area per gram of catalyst is similar for all of the catalysts investigated, so that the present test is unfortunately not conclusive in terms of understanding the role played by liquid–solid mass transfer.

In Table 4 the turnover number, N^{CHEM}, i.e., the number of NO molecules reacted per exposed platinum atom and per second (calculated from the total rate of NO consumption and from the exposed surface areas obtained by chemisorption), is also reported. It can be seen that this value does not notably vary with the degree of metal dispersion D^{CHEM} (ratio of surface atoms to bulk atoms, from chemisorption data); this

TABLE 4

Rates of NO Conversion to Hydroxylamine, Surface Areas, Turnover Numbers, and Dispersions for Samples with Different Platinum Contents

Pt (wt%)	r_1[a]	S^{CHEM}[b]	N^{CHEM}	D^{CHEM}
1.2	2.7	1.24	0.35	0.54
3.0	2.7	1.26	0.29	0.26
5.6	2.6	1.20	0.27	0.14
11.3	2.9	—	—	—

[a] Moles NO g^{-1} cat h^{-1}.
[b] m^2 g^{-1} cat.

rules out a structure sensitivity of the reaction. More detail on this point is reported in the preceding paper (*8*).

4. CONCLUSIONS

A kinetic study of the production of hydroxylamine by hydrogenation of nitric oxide, using industrial Pt/C catalysts (1.2 wt% of platinum, catalyst particle size of a few μm), has been reported.

The kinetics show trends similar to those reported by Temkin and co-workers (*3*) for catalysts having high platinum content (10 wt%) and large particle size ($\cong$0.1 mm), though the observed rates are a little lower.

The investigation of experimental parameters such as stirring efficiency, amount of catalyst, and sulfuric acid purity, has shown that the kinetic regime is a rather delicate condition and great care has to be taken with these parameters in order to avoid diffusion limitation.

No negative effect of temperature on the kinetic regime has been observed in the range 15–55°C; this extends the upper limit of the kinetic region from the value of 25°C, indicated by Temkin (*7*), to 55°C.

Finally, a set of measurements on samples with different platinum content (up to 11 wt%) have shown that an amount of platinum exceeding about 1.5 wt% is completely ineffective for the production of hydroxylamine and thus economically unprofitable, as already indicated in a similar case by Renouprez *et al.* (*10*).

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