Chemical Reactivity of Supported Gold

IV. Reduction of NO by H_2

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Received January 26, 1978; revised June 30, 1978

The rates of reduction of NO by H_2 and of H_2–D_2 equilibration were measured in a flow system on Au supported on SiO_2, Al_2O_3, and MgO. For the NO reduction the temperature was 350°C, partial pressures were $1.52 \leqslant p_{NO} \leqslant 12.16$ Torr, $6.08 \leqslant p_{H_2} \leqslant 9.12$ Torr, $0.5 \leqslant p_{NO}/p_{H_2} \leqslant 5$, and total pressure was 1 atm. For the H_2–D_2 equilibration the temperature was 150 to 300°C, $10 \leqslant p_{H_2} \leqslant 100$ Torr, and $p_{D_2}/p_{H_2} = 1$. The Au preparations were characterized by wide-angle X-ray scattering and transmission electron microscopy. No characteristic effect on the rate of reaction was observed by varying the Au precursor salt or the preparative method. There was an effect of the support on the reaction selectivity to N_2, SiO_2-supported preparations showing the lowest and Al_2O_3-supported preparations the highest value of the selectivity. The rate of the H_2–D_2 equilibration was fastest on Au supported on SiO_2. It is argued that the different tendency of the supports employed to act as electron donor–acceptor with supported Au influences the electron density at the surface Au site. The interpretation is consistent with the relative acid–base ranking of the supports and of the precursor Au salt. An increased electron density at the Au site increases electron back donation from metal to adsorbed NO, weakening the N–O bond and facilitating the formation of N_2 over that of NH_3. This interpretation of the role of the support in modifying the electronic conditions at the Au site is employed to suggest that the higher H_2–D_2 equilibration rate on Au–SiO_2 results from a more ionic hydrogen chemisorption bond. Suggestions on the morphological and chemical nature of the Au which interacts with the support are advanced in the context of the highly heterogeneous morphology of the supported Au, as revealed by the characterization methods employed. The meaning of these findings in the framework of present ideas for high N_2 selectivity in the NO reduction as well as the impact of the conclusions from the present study on other important reactions ($CO + H_2$, $N_2 + H_2$) are pointed out.

Previous studies in this series have demonstrated that hydrogen and oxygen transfer reactions may be catalyzed by supported Au preparations under relatively mild conditions. Oxygen transfer between CO and CO_2 was readily observed at 350°C; its rate, however, varied between wide limits with the material employed as a support and with the amount of Au present in

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the sample (1). Similarly, the hydrogen transfer between cyclohexane and benzene was found to be catalyzed by supported Au at temperatures in the range 200 to 250°C (2). Subsequent studies by extended X-ray absorption fine structure spectroscopy (EXAFS) (3) brought out the discovery that in some of the Au preparations up to 60% of the metal present was "dissolved" in the support and interacting with the latter as evidenced by the formation of Au–O bonds. It was felt that this complex

reactive, structural, and morphological pattern required further effort to elucidate the basic question on the role of support and Au dispersion, thus leading to the most intriguing aspect of this system: the presence of considerable chemical interaction between combinations of materials which are among the most inert known. There was further interest in pursuing this study for the possibility of ramifications of the effects discovered in supported Au to other supported metal systems and reactions. In fact, recent publications report additional findings on the catalytic activity of supported Au in hydrocarbon hydrogenation reactions (4).

It was felt that further progress could be made by extending the investigations to cover a wider range of the experimental conditions, the nature of the support and the Au precursor salt, the preparation method, and Au particle size. To obtain a more accurate kinetic analysis of the reactivity of supported Au it was decided to record catalytic selectivity instead of catalytic activity. To this end the reaction chosen was the reduction of NO by H$_2$, namely,

$$2NO + 5H_2 \rightarrow 2H_2O + 2NH_3, \quad (1a)$$

$$2NO + 2H_2 \rightarrow 2H_2O + N_2. \quad (1b)$$
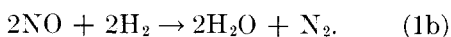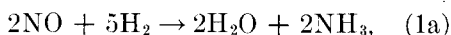
Preliminary studies showed that supported Au did indeed catalyze the formation of N$_2$ and NH$_3$ from NO and H$_2$ under relatively mild conditions without the formation of side products. In addition, there is the possibility that a study of reactions (1a) and (1b) will contribute to the understanding of the elementary steps of the reaction itself, the kinetic sequence of which is not yet unambiguously resolved (5). To provide additional insight into the reactivity of supported Au we have also conducted measurements on the equilibration reaction of isotopic hydrogen,

$$H_2 + D_2 \rightarrow 2HD. \quad (2)$$

The results obtained from reactions (1a), (1b), and (2) are summarized in the present communication.

EXPERIMENTAL

A. Catalyst

Supported Au was prepared according to the following methods:

(a) Appropriate amounts of an aqueous solution of Au(en)$_2$Cl$_3$ (6) were slurried with the support, which had been previously treated with aqueous NH$_3$; the resulting paste was dried and reduced in flowing H$_2$ for 2 hr at 420°C.

(b) The support was impregnated with an aqueous solution of KAu(CN)$_2$ (Fluka), dried, and decomposed at 350°C and 0.1 Torr for 2 hr.

(c) The support was impregnated with an aqueous solution of HAuCl$_4 \cdot$3H$_2$O (C. Erba), reduced with 3% oxalic acid solution, 40°C, filtered, washed, dried, and heated at 350°C and 0.1 Torr (1 Torr = 133.3 N m^{-2}) for 2 hr.

The supports were: SiO$_2$ (surface area, 400 m^2/g), Al$_2$O$_3$ (surface area, 180 m^2/g), and MgO (surface area, 12 m^2/g). Details on the preparation of samples A1141 and A1241 may be found elsewhere (1). The Au content of the preparations was determined by atomic absorption and neutron activation analysis. Information on metal particle size was obtained by wide-angle X-ray scattering (WAXS) using Cu$K\alpha$ radiation and transmission electron microscopy (TEM) employing an extractive replica technique. A summary of the Au preparations studied, their particle sizes, and preparative methods is collected in Table 1. The discrepancy between the values of metal particle size determined by WAXS and TEM, especially in the higher range of particle sizes, should be noted. The fact that the TEM values are consistently lower than the WAXS values is a consequence of the fact that TEM observations weigh

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TABLE 1

Preparation and Characterization of Supported Au

Code	Support	Au (wt% ± 0.01)	Particle size (Å) (WAXS)	Particle size (Å) (TEM)	Preparation method
2411	SiO₂ (C. Erba)	0.19	<30	—	b
4433	SiO₂ (C. Erba)	2.21	40	60	a
4433b	SiO₂ (C. Erba)	2.21	n.d.*	85	a
4443	SiO₂ (C. Erba)	1.30	50	90	a
2441	SiO₂ (C. Erba)	2.86	300	—	b
2431	SiO₂ (C. Erba)	1.66	450	—	b
2441b	SiO₂ (C. Erba)	3.21	500	—	b
2421	SiO₂ (C. Erba)	0.81	516	165	b
1442	SiO₂ (C. Erba)	4.75	600	—	c
1432	SiO₂ (C. Erba)	1.46	>1000	—	c
4633	SiO₂ (Degussa)	1.16	430	91	a
1631	SiO₂ (Degussa)	2.04	1000	—	c
4133	Al₂O₃ (Alcoa)	0.06	<30	—	a
2131	Al₂O₃ (Alcoa)	1.68	<30	—	b
2111	Al₂O₃ (Alcoa)	0.31	<30	—	b
2121	Al₂O₃ (Alcoa)	0.67	<30	—	b
2141	Al₂O₃ (Alcoa)	4.25	150	—	b
2141b	Al₂O₃ (Alcoa)	5.40	205	—	b
1142	Al₂O₃ (Alcoa)	5.24	>1000	—	c
1132	Al₂O₃ (Alcoa)	1.62	>1000	—	c
A1141	Al₂O₃ (Davison)	6.87	1200	—	c
2321	MgO (C. Erba)	0.67	<30	—	b
2311	MgO (C. Erba)	0.26	<30	—	b
1332	MgO (C. Erba)	2.16	290	165	c
2341	MgO (C. Erba)	3.29	470	75	b
4343	MgO (C. Erba)	1.00	630	—	a
1342	MgO (C. Erba)	4.39	630	220	c
A1241	MgO (Fisher)	5.00	100	—	c

ᵃ Cationic exchange with $Au(CN)_2Cl_3$; 2 hr; 400°C in H_2.
ᵇ Impregnation with $KAu(CN)_2$; 2 hr; 350°C; 0.1 Torr.
ᶜ Impregnation with $HAuCl_4$, reduction with oxalic acid; 2 hr; 350°C; 0.1 Torr.
* n.d., not determined.

smaller particles more than WAXS. High purity H_2, He, and NO were employed. The oxygen content in NO was <10 ppm.

Procedure

The rate of reactions (1a), (1b), and (2) was followed in a flow system employing a tubular reactor at atmospheric pressure. The reactor was a 10-mm-o.d. glass tube, filled with 0.5 to 2.0 g of 40- to 60-mesh catalyst. Metered amounts of reactants were purified by passage through a deoxo unit (H_2) and a molecular sieve trap at dry ice temperature. NO and N_2 were analyzed by gas chromatography employing a column (o.d. 6 mm) filled with Poropak Q, which permitted the separation of NO and N_2 at 30°C. The NH_3 formed was absorbed in a standardized H_2SO_4 solution and back-titrated with NaOH. Catalyst pretreatment included *in situ* heating in a stream of H_2 at 120°C for 0.5 hr and, subsequently, at 350°C for 1 hr. In the study of reactions (1a) and (1b) the partial pressure of NO ranged between 0.002 and 0.016 atm (1 atm = 101.3 kN m⁻²) and that of H_2
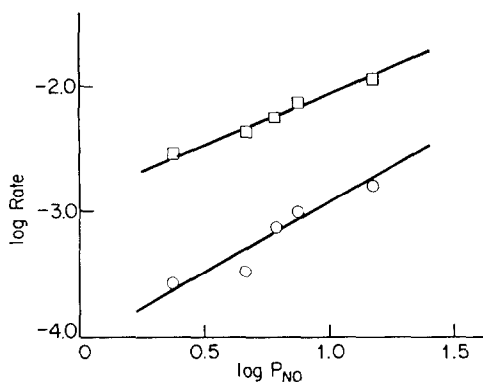
FIG. 1. Rate of formation of N$_2$ (O) and NH$_3$ (□) through reactions (1a) and (1b) vs the partial pressure of NO, p_{NO}. Catalyst 4443; 350°C; H$_2$, 0.90 vol%.

between 0.008 and 0.012 atm. All runs were made at 350°C.

N$_2$ was used as a diluent in reaction (2). Prepurified H$_2$ and D$_2$ were passed through Pd asbestos (400°C) and a molecular sieve trap at liquid N$_2$ temperature. N$_2$ was passed through Cu turnings (400°C), followed by a molecular sieve trap at liquid N$_2$ temperature. Effluent analysis was carried out by mass spectroscopy. A constant p_{H_2}/p_{D_2} ratio of 1 was employed throughout. The experimental error in the rate of reactions (1a), (1b), and (2) and that in the selectivity to N$_2$ is estimated at ±20%.

RESULTS

NO Reduction

Rates were calculated from the relation:

$$V = (F/A_s)\alpha[\text{molecules}/A_s \times \text{sec}], \quad (3)$$

where F represents the feed rate of NO in molecules per second, A_s is the number of surface Au atoms (by WAXS), and α represents the fraction of NO that disappeared or was converted to a particular product. Percentage selectivity to N$_2$, S_N, and reaction conversion, α_{NO}, were calculated by means of the expressions:

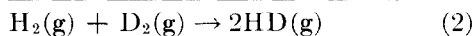$$S_N = \frac{2V_N}{2V_N + V_{NH_3}} \quad (4)$$

and

$$\alpha_{NO} = \frac{(p_{NO})_{in} - (p_{NO})_{out}}{(p_{NO})_{in}}, \quad (5)$$

where V_N and V_{NH_3} are the rate of N$_2$ and NH$_3$ formation, respectively, and $(p_{NO})_{in}$ and $(p_{NO})_{out}$ are the NO partial pressure at the reactor inlet and outlet, respectively. Within the range of flow rates investigated the reaction conversion was found to be independent of the gas flow rate. Thin (~10 mm) catalyst beds and low reaction conversions (~10%) were employed throughout. No reaction was found to take place on the catalyst supports or on the empty reactor walls (Pyrex glass). In the range of conditions used, no N$_2$O formation could be detected. Typical results on the influence of p_{NO} on the rate of reactions (1a) and (1b) are reported in Fig. 1, while in Table 2 the values of α_{NO}, V_{NO}, and S_N are collected.

H$_2$–D$_2$ Equilibration

The rate of the H$_2$–D$_2$ equilibration was derived on the assumption of the following reaction scheme:

$$H_2(g) + D(s) \rightarrow HD(g) + H(s) \quad (2a)$$

$$D_2(g) + H(s) \rightarrow HD(g) + D(s) \quad (2b)$$

$$\overline{H_2(g) + D_2(g) \rightarrow 2HD(g)} \quad (2)$$

Consider the rate of reaction step (2a)

$$\frac{V}{wRT}\frac{dp_{HD}}{dt} = k'_D p_{H_2} - k_D{}^b p_{HD}, \quad (6)$$

where V, w, R, T, k'_D, and $k_D{}^b$ are the volume of the catalyst bed, the weight of the catalyst, the gas constant, the reactor temperature, and the forward and backward rate coefficients of reaction step (2a), respectively. Introducing the reaction conversion and the subscripts t, 0, and ∞ referring to time t, zero, and infinity, respectively,

$$\alpha = \frac{\beta_t - \beta_0}{\beta_\infty - \beta_0},$$

TABLE 2

Reaction Conversion α_{NO}, Rate of NO Reduction, v_{NO}, Selectivity to N_2, S_N, for
Reactions (1a) and (1b) Catalyzed by Supported Au, $3 \leqslant p_{H_2}/p_{NO} \leqslant 5$, 350°C

Catalyst code	Support	Particle size (Å) (WAXS)	α_{NO} (%)	V_{NO} [molecules/sec × A_s] × 10^3	S_N (%)
2411	SiO_2 (C. Erba)	<30	12.60	<5.5	8.40
4433	SiO_2 (C. Erba)	40	15.42	1.3	14.33
4433b[a]	SiO_2 (C. Erba)	n.d.	10.63	2.5[b]	4.12
4443	SiO_2 (C. Erba)	50	15.80	3.4	17.24
2441	SiO_2 (C. Erba)	300	10.13	1.6	26.20
2431	SiO_2 (C. Erba)	450	7.43	1.8	25.10
2441b	SiO_2 (C. Erba)	500	5.92	6.3	21.83
2421	SiO_2 (C. Erba)	516	11.36	8.6	19.27
1442	SiO_2 (C. Erba)	600	14.12	6.2	15.04
1432	SiO_2 (C. Erba)	>1000	11.38	>8.2	8.71
4633	SiO_2 (Degussa)	430	35.57	31.35 (6.6[b])	11.52
1631	SiO_2 (Degussa)	1000	7.18	8.0	19.99
4133	Al_2O_3 (Alcoa)	<30	12.32	<8.4	69.45
2131	Al_2O_3 (Alcoa)	<30	11.32	<3.3	72.99
2111	Al_2O_3 (Alcoa)	<30	38.30	<6.5	87.43
2121	Al_2O_3 (Alcoa)	<30	11.13	<4.1	84.29
2141	Al_2O_3 (Alcoa)	150	29.21	4.2	65.79
2141b	Al_2O_3 (Alcoa)	205	25.20	7.4	54.53
1142	Al_2O_3 (Alcoa)	>1000	5.76	>0.4	66.67
1132	Al_2O_3 (Alcoa)	>1000	7.84	>1.6	50.25
A1141	Al_2O_3 (Davison)	1200	3.59	3.0	67.12
2321	MgO (C. Erba)	<30	23.91	<6.2	88.83
2311	MgO (C. Erba)	<30	10.49	<7.2	77.44
1332	MgO (C. Erba)	290	13.03	9.4	55.56
4343	MgO (C. Erba)	630	4.38	3.1	34.13
1342	MgO (C. Erba)	630	3.19	2.1	31.25
A1241	MgO (Fisher)	100	22.42	3.5	62.92

[a] 3 hr; 700°C in air.
[b] Employing TEM results for calculation of average particle size.

where $\beta = p_{HD}/(p_{H_2})_0$. Eliminating $k_D{}^b$ and integrating, Eq. (6) yields

$$k'_D = \frac{V}{wRT\tau}\beta_\infty \ln \frac{1}{1-\alpha}$$

$$[\text{moles/g} \times \text{atm} \times \text{sec}], \quad (7)$$

where τ is the contact time. Since the rate of reaction (2) is similar to that of reaction step (2a), we may write for the rate of reaction (2)

$$V_D = \frac{k'_D}{A_s} N_A((p_{H_2})_{total})$$

$$[\text{molecules}/A_s \times \text{sec}]. \quad (8)$$

The validity of Eq. (7) was tested at various τ's and the calculated values of k'_D were found to be within ±20%. Typical values of k'_D for catalyst 4443 at 200°C are plotted versus $(p_{H_2})_{total}$ in Fig. 2, and the values of k'_D are summarized in Table 3. The influence of temperature on k'_D in the range $10 \leqslant p_{H_2} \leqslant 100$ Torr and $150 \leqslant T \leqslant 300$°C is reported in Fig. 3 for various preparations. The calculated activation energies (Table 3) were in the range of 9 to 13 kcal/mole (1 kcal = 4.18 10^3 kJ); this is to be compared with the values of 10 to 14 kcal/mole previously found on Au wires and foils (7). When the total H_2
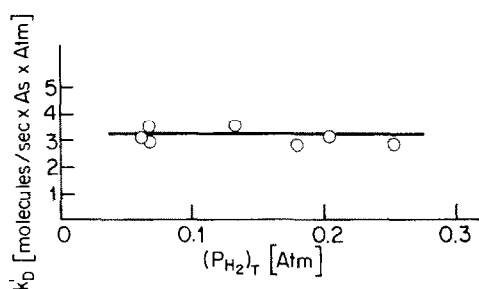
FIG. 2. Rate coefficient of reaction (2), k_D, Eq. (7) versus $(p_{H_2})_{total}$. Catalyst 4443; 200°C; $p_{H_2}/p_{D_2} = 1$.

pressure was changed, the rate V_D was found to be first order in the H$_2$ pressure for the catalysts tested. In a few runs NO was added to the feed. This produced a strong depressing effect on the rate of the H$_2$–D$_2$ reaction. At 200°C, $p_{NO} = 0.007$ atm, $(p_{H_2})_t = 0.02$ atm, a decrease of about 50% in the reaction rate was observed. Under the experimental conditions employed in this study, reaction (2) was found to take place on the Al$_2$O$_3$ and MgO supports to a measurable extent while SiO$_2$ was found to be inert.

DISCUSSION

An inspection of Tables 1 and 2 shows that no substantial influence of the precursor Au salt or of the preparative method upon V_{NO} and S_N is apparent. Also, it is

not possible to reach a definitive conclusion on the role of metal particle size on V_{NO}. The experimental results on Au–SiO$_2$ show a tendency for V_{NO} to increase with particle size, while this is not evident from the results on Au–MgO and Au–Al$_2$O$_3$. A detailed morphological characterization of the Au particles is necessary for the correct interpretation of any potential effect on V_{NO} in the particle size range investigated. While the particle size question must be left open, two points may be of interest for future work. In earlier studies by WAXS on catalyst A1141 (3) it was found that in the direction perpendicular to the (111) plane the particle dimension was 2200 Å, while in the direction perpendicular to the (200) plane the particle dimension was 1300 Å, indicating a "faster" particle growth in the direction perpendicular to the octahedral plane. The role of surface morphology has been found to be an important factor in the surface chemistry and reactivity of polycrystalline alloys (8). In comparative studies on reactivity variations at surface irregularities of metals, it was pointed out the large variation in charge density at low coordination sites of Pt, 2.1 [electrons/V × atom], contrasted by a relatively minor change in Au, 0.3 [electrons/V × atom] (9), leading to the conclusion that Au surfaces should show a

TABLE 3

Rate Constant k'_D for the H$_2$–D$_2$ Equilibration, Eq. (7), 200°C, and Activation Energy, E, Catalyzed by Supported Au

Catalyst	Support	Au (wt%)	Particle size (Å)	k'_D (molecules/ sec × A_s × atm)	E [kcal/mole]
4433	SiO$_2$	2.21	40	2.83	12.4
4443	SiO$_2$	1.30	50	3.90	13.7
2441b	SiO$_2$	3.21	500	4.31	9.2
2341	MgO	3.29	470	5.96 (0.89)[a]	9.4
1332	MgO	2.16	290	<0.42	9.9
1342	MgO	4.39	630	<0.30	13.5
A1141	Al$_2$O$_3$	6.87	1200	—	9.8

[a] Metal dispersion calculated from TEM measurements.

similar chemical behavior regardless of
atomic structure (10).

The nature of the support has been
known to influence the activity of the sup-
ported metal. Variations in product distri-
bution in the dehydrogenation of cyclo-
hexane on supported Pt were found as a
function of the support (11). At 500°C the
amount of C_6H_6 decreased and that of non-
condensed products increased as Pt was
supported on TiO_2, Al_2O_3, MgO, SiO_2, and
carbon. In the present study, while no
clear-cut influence of the support on V_{NO}
is evident (Table 2), there is a decisive
influence of the former upon S_N (Fig. 4).
In all ranges investigated, Au samples with
similar particle size but supported on
different materials show a large variation
in the selectivity to N_2. In view of the
various kinetic tests made, neither im-
purities present in the support, nor type of
precursor salt, nor preparative procedure
employed may have influenced the reported
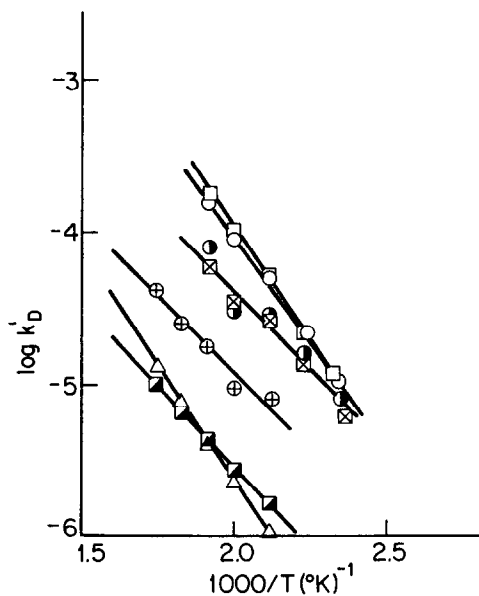distribution of S_N among the Au prepara-

FIG. 4. Selectivity to N_2, S_N, for reactions (1a)
and (1b) and Au support. 350°C; $3 \leqslant p_{H_2}/p_{NO} \leqslant 5$;
total pressure, 1 atm.

tions. The conclusion that the selectivity
effect was due to support interaction is
compelling. Furthermore, Au–Al_2O_3 and
Au–MgO preparations show (Table 2) a
decrease in the selectivity to N_2 with an
increase in the particle size, while this is
not evident for Au–SiO_2 samples. Since the
effect occurs in a particle size range largely
outside that considered important for
optimizing special surface coordination
sites (12), we believe that in the case of
smaller Au particles a stronger interaction
between metal and support is responsible
for higher values of S_N. After testing the
selectivity in reactions (1a) and (1b),
sample 4433 was given a thermal treatment
at 700°C for 3 hr in air, and the selectivity
to N_2 was subsequently measured. From
an initial S_N value of 14.30% a decrease
to 4.12% upon heat treatment was found
(Table 2).

To assess the underlying mechanism of
the support effect let us consider the chemi-
sorption of NO at metal sites. Taking the
(111) plane the most exposed one on f.c.c.
Au and assuming that promotion of d-
electrons takes place in Au, then its surface
atoms may be considered to possess par-
tially occupied hybrid d-orbitals, "dan-
gling" at an angle of 30 to 36° from the
surface (13). There are several conceivable
ways in which the NO may be bonded to
such a surface (14). The important point is
that, in addition to the formation of σ

FIG. 3. Log k'_D (Eq. (7)) vs temperature for
supported Au. $10 \leqslant p_{H_2} \leqslant 100$ Torr; ○, 4433;
□, 4443; ◑, 2341; ◪, 1332; △, 1342; ⊗, 2441b;
⊠, A1141.

bonding which utilizes a lone pair of σ electrons from NO and the partly filled d metal orbitals, there is also the possibility of back donation from the metal to the highest partially filled π^*_x antibonding orbital of the $^2\pi$ ground state of NO. In the absence of information on work function and on ir frequency changes upon NO chemisorption on Au, we shall assume that electron back-donation into π^*_x antibonding orbitals is a contributing bonding mode to the NO chemisorption on Au. It is conceivable that the extent of electron back donation is dependent, *inter alia*, upon the electron density at the Au site, the back donation increasing with the electron density. Consequently, increasing the electron density at the metal site will induce a destabilization and bond weakening in the NO adsorbate. Since this condition is most probably the precursor of the fission of the N–O bond, the former reflects the requirements for a dissociative chemisorption of NO at the metal site. Conversely, a decreased electron density at the metal site will decrease electron back donation and the result will be the associative chemisorption of NO.

Now, considering reactions (1a) and (1b), it is likely that reaction (1b) is favored by NO chemisorption with a destabilized N–O bond, and therefore, occurring at metal sites with higher electron density than that of metal sites at which reaction (1a) is favored. In fact, a weakened N–O adsorbate is more likely to be the reaction path leading to N₂, since N and O separation at the surface may be followed by surface migration (at the appropriate temperature) and recombination to molecular N₂ and O₂ (15). In the presence of a large excess of H₂, dissociatively adsorbed NO may also lead to the formation of NH₃, as in the case of Pt (16). However, this may never become a preponderant route to NH₃ at Au surfaces. In fact, it requires the co-adsorption of NO and H₂, the latter either in atomic or molecular form. As the subsequent experi-

ments on the H₂–D₂ equilibration have demonstrated, this is an unlikely possibility, due to the stronger chemisorption of NO, which effectively poisons the Au surface for H₂. Large amounts of NH₃, as it was found to occur at Au–SiO₂ surfaces, may only be formed through a reaction of H₂ with adsorbed NO. These considerations on NO chemisorption, electron density at the metal site and S_N lead to the conclusion that on SiO₂, Au was in a more "oxidized" state than Au on Al₂O₃ and MgO.

These conclusions raise two questions: What is the nature of this interaction and of the Au which undergo this interaction?

Metal–support interaction has been discussed and invoked in several studies for the interpretation of specific behavior of supported metal particles. An excellently documented case is that of Pd supported on Y zeolite. By means of ir spectra of chemisorbed CO, the Pd particles were found to be electron deficient. This had been interpreted as resulting from their interaction with the Lewis acid sites of Y zeolite (17). Earlier it was discovered that similar electronic interactions may be induced at the metal site by preferential adsorption of Lewis bases (18). As a rough approximation the relative acid–base values derived from solution chemistry may be employed to indicate the conditions prevailing between the Au precursor salt and the support. The relative acidity of the hypothetical substances SiO₂·2H₂O, Au₂O₃·3H₂O, and Al₂O₃·3H₂O, as given by their first acidity constants, is 2×10^{-10}, 1.8×10^{-12}, and 6.3×10^{-13}, respectively (19), indicating that the acidity of H₃AuO₃ falls between that of H₄SiO₄ and H₃AlO₃. The value for MgO·H₂O is not available, but its basic properties are well known, placing this hydroxide with a dissociation constant lower than that of Al₂O₃·3H₂O. According to this ranking, the Au salt has basic properties, i.e., the tendency to donate electrons to SiO₂·2H₂O, the same salt has acid properties, i.e., the tendency to accept

electrons relatively to $Al_2O_3 \cdot 3H_2O$ and $MgO \cdot H_2O$. A simple visualization of these conditions is to assume that the formation of an Au silicate complex between the Au precursor salt and SiO_2 Au atoms in this complex will be in a more "oxidized" condition, as when undergoing compound formation with substances with a lower acidity constant like Al_2O_3 and MgO. In this case we may picture the corresponding surface compounds as aurates (20). Supporting evidence for this interpretation on the nature of the metal–support interaction and its consequences for the stability of the NO adsorbate may be found in recent ir studies on the adsorption of CO on supported Au (21). Indeed, the stretching frequency of adsorbed CO was found to be in the range 2084 to 2106 cm^{-1} for Au supported on MgO, and in the region 2120 to 2115 cm^{-1} for Au supported on SiO_2. The lowest unfilled molecular orbital in CO is a π^* orbital. Thus, the previous considerations on bond formation and destabilization of the adsorbate as a result of chemisorption involving back donation from the metal apply in a similar manner to CO chemisorption and the ir results show the correct sequence. In earlier investigations (22), the stretching frequency of CO chemisorbed on Pd particles deposited on supports of increasing acidity was found to vary as follows: NaX zeolite, 2035 cm^{-1}; MgO, 2056 cm^{-1}; Al_2O_3, 2075 cm^{-1}; SiO_2–$Al_2O_3K_{13}$, 2100 cm^{-1}; HY zeolite, 2105 cm^{-1}; CaY zeolite, 2115 cm^{-1}. These results again point out the relation between support acidity and reactivity with Pd and CO adsorption mode. Clearly, the correlation seems to be general and independent of the nature of the metal. Finally, it is worth emphasizing a point made previously (2), that the effects here discussed took place between groups of substances which are among the most chemically inert known.

We shall now discuss the second question: What is the nature of the Au which interacts with the support? On three of the Au preparations examined in this study, A1141, 4433, and 2441b, an extensive SAXS (small-angle X-ray spectroscopy), and EXAFS (extended X-ray absorption fine structure spectroscopy) analysis has been carried out (3, 23). These studies have shown that on Al_2O_3 a large amount of Au was not in the metallic state. Catalyst A1141 was found to contain, in addition to the large particles detected by WAXS, a fraction of particles in the 10 to 100 Å range (SAXS) and a fraction of two-dimensional "rafts" or "dissolved" single Au atome (EXAFS). In a recent study of the same catalyst by ESCA, only metallic Au was detected (Catalyst C4) (24). The binding energy of the Au $4f_{7/2}$ line was found to be 84.8 or 0.8 eV above that of Au foil, pointing to the existence of electron-deficient Au in the Al_2O_3 matrix. The EXAFS work on this Au sample (3) indeed indicated the presence of Au–O bonding and from the observed shift in the L_{III} electronic transition it was suggested that this corresponded to a reduced form of Au, most probably Au$^+$. Because of the complexity of the state of aggregation and morphology of the supported Au definitive statements on the nature of the Au interacting with the support cannot be made, since ways must be found to control the fraction of the various Au morphologies during sample preparation (3).

An indication of the electronic mechanism underlying the interaction between the support and Au atoms and/or metal particles may be suggested in analogy with similar interactions in dilute Au alloys. There is considerable theoretical and experimental (26) support for partial overlap between the 5d band and the 6s conduction band and d–s hybridization in Au alloys (AuAl$_2$, AuGa$_2$) (25). From Mossbauer spectra of Au alloys, substantial 5d–6s mixing was found to occur with nearly matching charge compensation between 5d and 6s bands; some additional depletion of 5d levels took place through interaction with

host orbitals of proper symmetry (*27*). Assuming that hybridization between the $5d$ and $6s$ levels of Au has taken place, the direction of charge flow between Au and X in a dilute AuX alloy depends upon the details of the hybridization: (a) if the $5d$–$6s$ mixing involves a fully matching charge compensation between the levels, there is no net flow of charge between Au and X; (b) if in the mixing a full charge compensation between the Au levels does not take place, there will be a net charge flow between Au and X in either direction, according to the relative position of the electron levels in Au and X.

Support for the presence of an electronic interaction with the Au $5d$ electronic levels is derived from observation on the color of

the Au catalysts employed in the present study. It had been previously established that optical transitions in binary alloys AuX_2 (X = Ga, In, Al) involve the $5d$ band of Au (*28*). Results from ESCA studies of $AuAl_2$ are also suggestive of the role of Au d bands in the purple color of the alloy (*29*). The color of the supported Au catalysts ranged from blue to purple, pink, mauve, black, gray, and creamy yellow. There are several factors which contribute to the color of these preparations: support interaction and texture, Au particle size, size distribution, morphology, and amount of Au. It was qualitatively established that the source of the support did not have influence on the color but within the same support the color varied, following the sequence:
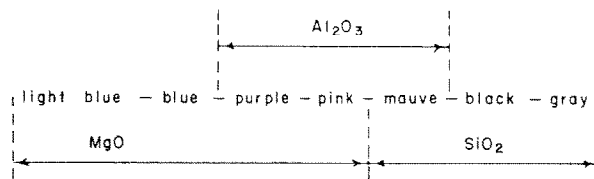
In addition, at high Au content the creamy yellow color characteristic of massive Au appeared. It is interesting to note the trend, evident in the above sequence, that separates the optical response of Au on MgO from that on SiO_2, with that of Au supported on Al_2O_3 playing an intermediate role. Within the same support, samples with various Au particle sizes were present, and there was a tendency for the color to vary from left to right in the above sequence as the Au particle size increased. A quantitative analysis of this particle size effect is difficult for the complexity of these systems, which do not lend themselves easily to optical absorption or reflection experiments. Light scattering effects may have played a role with larger particle sizes. Considering a wavelength of 4000 to 5000 Å, Au particle size was in most cases $> \lambda/20$, which is the condition for multiple scattering. The
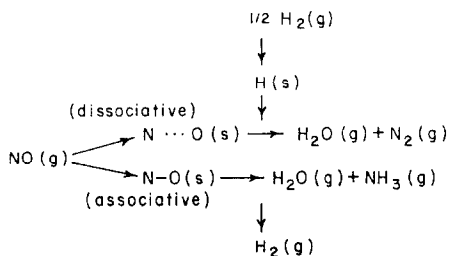
situation is less complex in samples with particle size < 30 Å, since complicating factors due to broader or multimodal particle size distribution were absent. In this particle size range, the color of the Au samples was as follows:

light blue (MgO)—

purple (Al_2O_3)—mauve (SiO_2).

Thus, in going from Au supported on MgO to that supported on SiO_2 the frequency of the optical transition responsible for the color of the sample increased. It is tempting to assign to the chemical interaction with the support the responsibility for this trend. Quantitative estimates of the interaction energy from the energy of the optical transition cannot be made, but it is possible to rank in terms of decreasing energy $Au–SiO_2 > Au–Al_2O_3 > Au–MgO$.

Let us now turn to reactions (1a) and

(1b). The results reported in Table 2 show that, within the range of reaction conversion investigated, S_N was practically independent of the former. This is taken as an indication that a parallel instead of a consecutive reaction sequence is more likely for reactions (1a) and (1b), as represented by the following scheme:

$$
\begin{array}{c}
\text{1/2 H}_2\text{(g)} \\
\downarrow \\
\text{H (s)} \\
\text{(dissociative)} \quad \downarrow \\
\nearrow \text{N}\cdots\text{O (s)} \longrightarrow \text{H}_2\text{O (g)} + \text{N}_2\text{(g)} \\
\text{NO (g)} \\
\searrow \text{N–O (s)} \longrightarrow \text{H}_2\text{O (g)} + \text{NH}_3\text{(g)} \\
\text{(associative)} \quad \downarrow \\
\text{H}_2\text{(g)}
\end{array}
$$

Whether H_2 adsorption in the presence of NO took place on separate sites or on sites occupied by NO was not investigated in detail. The poisoning experiments of NO on the H_2–D_2 reaction showed that NO did indeed block the adsorption sites for H_2; this, however, does not rule out for reactions (1a) and (1b) H_2 adsorption on an NO occupied site. The presence of an intermediate complex HNO in the adsorbed phase has been postulated by several authors (30), but rejected by others (16). According to the correlation between support and S_N and its interpretation, as presented here, higher amounts of N_2 from reactions (1a) and (1b) are the consequence of a more reduced Au site, that is, more electron rich than the site yielding NH_3. At constant p_{H_2}, V_N, V_{NH_3} were found to be represented by $V_N = k_N p_{NO}$, $V_{NH_3} = k_{NH_3} p_{NO}^{0.76}$ (Fig. 1), indicating that S_N increased with p_{NO}. This pattern is consistent with previous observations (31). As previously mentioned, in the range of reaction conversion investigated, S_N was found to be independent of reaction conversion, indicating that the rates of the two NO adsorption steps in the above reaction scheme are similar. Although the coverage of the reacting Au surface is not known, the observation that the rates

V_{N_2}, V_{NH_3} were first order or in close to first order p_{NO} is an indication of lack of surface saturation, a condition considered important for observing the influence structural pecularities of the surface have on the reaction rate.

H_2–D_2 Equilibration

The results showed that the rate V_D increased with $(p_{H_2})_{\text{total}}$ following a first-order relation. In terms of a Langmuir formulation, this observation may be explained by setting the rate of reaction step (2a) (or 2b).

$$V_D = k''_D \theta_H p_{H_2},$$

where

$$k''_D \theta_H = \frac{k''_D p_{H_2}^{\frac{1}{2}}}{1 + b p_{H_2}^{\frac{1}{2}}} = k'_D.$$

If $b p_{H_2}^{\frac{1}{2}} \gg 1$, k'_D becomes independent of p_{H_2}, as was found (Fig. 2). The rate of reaction (2) at 350°C was about one order of magnitude faster than that of reactions (1a) and (1b). In view of the recognized difficulty of accounting for the ready activation of molecular hydrogen at Au surfaces (32), this result is of interest. In the presence of NO, however, the rate of reaction (2) decreased sharply, indicating successful competition on the part of NO for surface adsorption sites. Au supported on SiO_2 was found to be at least one order of magnitude more active than that supported on MgO. In the light of the previous discussion on the influence of support interaction on the electron density at the Au site, a decreased density, as suggested for SiO_2-supported Au, will facilitate the activation of the H–H bond whenever the latter process entails a decrease of the bond electron density. This is the trend generally associated with H_2 chemisorption on metals.

CONCLUSION

The observed influence of the supporting material on the product selectivity in the

reduction of NO by H_2 catalyzed by Au is a vivid demonstration of subtle physico-chemical interactions between a most chemically inert metal and similarly inert metal oxides. The effect of this interaction in changing the electronic conditions at the Au surface site is reflected in various degrees of destabilization of the N–O bond upon chemisorption, a weakened bond in the adsorbate being more likely to lead to N_2 instead of NH_3. It is suggested that an increased electron density at the Au site leads to an increase in the N_2 selectivity. In this context the role of the support in modifying the reactivity and selectivity of the Au may be related to that of other agents which are known to play a role in the product selectivity of heterogeneous catalytic reactions (promoters, poisons). The fundamental nature of these effects is electronic; this, however, must be viewed in the context of the widely different morphology and size of the Au aggregates.

Although the actual nature of the catalytic active Au and that of the Au–support interaction have not been resolved, the study has defined the direction for future investigations.

It will be possible to examine further cases, in which the support tendency to donate or accept electrons is controlled by various effects: cation interchange between metal and support, by high surface Madelung potential of the support, by the use of mixed oxide supports with mismatching cation coordination numbers, by control of surface acidity through selective temperature dehydration conditions. It is also likely that the considerations suggested for Au are valid for other catalytic metals, notably Pt and Pd. Similarly, it is conceivable that the interpretation of the N_2 selectivity in reactions (1a) and (1b) may be applicable to other reactions where product distribution plays a determinant role, notably the $CO + H_2$ reaction. Finally, and more generally, the reactive chemisorption of molecules involving elec-

tron back donation from surface metal sites may be influenced by the details of the electron density at the sites themselves. Although this is a well-known effect in homogeneous catalysis, this study has provided additional evidence of its operation in heterogeneous catalysis and the qualitative ideas expressed may, in principle, be applied to other important catalytic systems ($N_2 + H_2$).

ACKNOWLEDGMENTS

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