Interpretation of the kinetic mechanism and the structural sensitivity of the catalytic CO–NO reaction

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The experimental results for the superficial reduction reaction of NO by CO over a number of different particle size rhodium catalysts supported on silica have been analysed quantitatively by the kinetic mechanism of Peden and Permana. The increased activity with increasing particle size can be interpreted by considering that the sites located near the edges of supported particles would have a lower dissociation capacity.

Keywords: CO–NO reaction, rhodium catalysts

The reduction of NO by CO (CO–NO reaction) over Rh supported on silica, an important reaction of the catalytic control of motor vehicle exhaust emissions,[1] has been shown to be highly complex. A series of mechanisms have been proposed over the last 20 years, [2–5] and the following has been largely accepted in the current literature:[4,5]

$$CO(g) + S \xrightarrow{k_1} CO(a) \quad (1)$$

$$CO(a) \xrightarrow{k_2} CO(g) + S \quad (2)$$

$$NO(g) + S \xrightarrow{k_3} NO(a) \quad (3)$$

$$NO(a) \xrightarrow{k_4} NO(g) + S \quad (4)$$

$$NO(a) + S \xrightarrow{k_5} N(a) + O(a) \quad (5)$$

$$2N(a) \xrightarrow{k_6} N_2(g) + 2S \quad (6)$$

$$CO(a) + O(a) \xrightarrow{k_7} CO_2(g) + 2S \quad (7)$$

$$NO(a) + N(a) \xrightarrow{k_8} N_2O(g) + 2S \quad (8)$$

One aspect of great interest whose study was pioneered by Oh *et al.* [6] and which we have considered[7] is the structural sensitivity shown by the CO–NO reaction. This, together with the fact that kinetic models, in general, have been little used for the quantitative interpretation of the experimental information in heterogeneous catalysis, has led us to consider the way in which the analytic solution of the reaction mechanism[1–8] can interpret the changes in the kinetic behaviour of the CO–NO reaction with particle size for a series of Rh catalysts supported on silica in experiments carried out in our laboratory.

A number of catalysts with 0.4% (w/w) Rh supported on Aerosil 130 (Degussa) were prepared as reported previously[7] by the dry impregnation method, using $RhCl_3$ (Merck) dissolved in a pH = 2 aqueous solution as precursor, and subjecting them to various calcination treatments followed by reduction in a stream of 5% H_2 in argon flowing at 15 cm^3/min at the temperatures and times shown in Table 1. The particle diameters given in Table 1 were calculated from the dispersion values of the catalysts determined by chemisorption of H_2 at 298 K using a dynamic pulse method. The order of magnitude of these values were confirmed approximately for some of the samples by using a JEOL model 1200 EX II transmission electron microscope (TEM) at 120 KV and 4 Å resolution. The activity of the catalysts in the CO–NO reaction at 523 K was determined in a plug flow reactor with 5.0 % CO and NO at a flow rate of 100 cm^3/min balanced with helium measured on the inflow of the gas streams, which in this case is approximately equal to that of the outflow due to the low conversion. The products of the reaction were determined by analysing in a gas chromatograph using a Hayasep D column for CO_2 and N_2O, an MSSA column for N_2, and a thermal conductivity detector. Selectivity toward N_2O was calculated from the expression $S_{N_2O} = TON_{N_2O}/(TON_{N_2O}+TON_{N_2})$, with the turn over number, TON, in molecules per site and per second.

The mechanism[1–8] was solved analytically for the superficial coverage θ_i of the i species (CO, NO, N, O) assuming that the CO(a) and NO(a) adsorbates are in equilibrium with the gas phase, which was confirmed by the complete numerical solution of certain cases using the ode45 routine of the MATLAB software. With the equilibrium constants $K_{CO} = \dfrac{\theta_{CO}}{\theta_S p_{CO}}$ and $K_{NO} = \dfrac{\theta_{NO}}{\theta_S p_{NO}}$, if p_{CO} and p_{NO} are the partial pressures of the gas phase and considering the steady state conservation equations for the superficial species N(a) and O(a), the following relations are obtained:

$$A = \frac{p_{NO}K_{NO}}{p_{CO}K_{CO}} \quad (9)$$

$$B = \frac{1}{K_{CO}p_{CO}} \quad (10)$$

$$C = \left(\frac{-k_8 A \pm \left((k_8 A)^2 + 8k_5 k_6 AB\right)^{1/2}}{4k_6} \right) \quad (11)$$

$$D = \frac{k_5 AB}{k_7} \quad (12)$$

$$\theta_{CO} = 1/(1 + A + B + C + D) \quad (13)$$

$$\theta_{NO} = A\theta_{CO} \quad \theta_S = B\theta_{CO} \quad \theta_N = C\theta_{CO} \quad \theta_O = D\theta_{CO} \quad (14)$$

Therefore, the r_i productions are the following:

$$r_{CO} = k_7\theta_{CO}\theta_O \quad r_{N_2} = k_6\theta_N^2 \quad r_{N_2O} = k_8\theta_{NO}\theta_N \quad (15)$$

The above development assumes that the rate constants are independent of the θ_i fractions. However, since some k_i constants are functions of θ_i, it is necessary to make the calculation as an iteration, starting from initial values of the k_i constants assumed to be independent of θ_i, until the calculated values stop changing.

Results and discussion

Table 1 shows the experimental results obtained with the CO–NO reaction at 523K and an equal CO and NO gas phase partial pressure of 38 torr, corresponding to what was indicated in the previous section for a set of Rh catalysts supported on silica at different calcination and reduction temperatures and times, to obtain the sequence of dispersion values shown in the table. It is seen that, in reasonable agreement with what was found by Oh *et al.*,[6] the selectivity to N_2O appears to be only slightly dependent on the catalyst's particle size.

To interpret the experimental data of Table 1 with the solution of the mechanism[1–8] from the previous section, we have used the values of the ki constants published by Oh *et al.*[3] for steps[1–3] and (7), and those of Belton *et al.*[8] for steps (4) and (6), adjusting the model to the experimental data, optimising the dissociation constant k_5 and the N_2O formation constant k_8 by minimising the following function *F*:

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Table 1 Specific rate TON (molec./site seg) of the CO–NO reaction at 523 K and p_{CO}=p_{NO}=38 torr for CO_2, N_2O and N_2 formation (in parentheses the model's prediction) and selectivity of N_2O, dispersion (%) for different temperatures and times of calcination and reduction and optimum parameters k_{disNO} and k_{rN2O} for different average particle sizes *D*

				Optimum parameters					
Calcination /°C/h	Reduction /°C/h	Dispersion /%	Diameter /nm	k_{disNO} 1/s	kr_{N2O} 1/s	TON CO_2 molec/Rh*s	TON N_2O molec/Rh*s	TON N_2 molec/Rh*s	Selectivity /%
425/5	425/5	38.3	3.0	11723	0.323	0.15 (0.15)	0.04 (0.04)	0.05 (0.05)	44.4
550/4	550/4	25.5	4.5	17024	0.441	0.24 (0.22)	0.07 (0.06)	0.09 (0.08)	43.8
600/4	600/4	15.2	7.6	21663	0.491	0.28 (0.28)	0.07 (0.07)	0.105 (0.11)	40.0
675/5	600/4	6.8	17.0	51636	0.981	0.67 (0.68)	0.17 (0.16)	0.25 (0.24)	40.5
800/4	600/4	4.9	23.5	76565	1.407	1.02 (0.98)	0.25 (0.26)	0.38 (0.36)	39.7

$$F=\left(\frac{r_{N_2}(\text{exp})-r_{N_2}}{r_{N_2}(\text{exp})}\right)^2+\left(\frac{r_{N_2O}(\text{exp})-r_{N_2O}}{r_{N_2O}(\text{exp})}\right)^2+\left(\frac{r_{CO_2}(\text{exp})-r_{CO_2}}{r_{CO_2}(\text{exp})}\right)^2 \quad (16)$$

In choosing the constants k_5 and k_8 to be optimised, we have considered the observation of Permana *et al.*[4] that the values of these two constants reported in the literature have a high degree of uncertainty.

Fig. 1a shows a linear variation of the dissociation constant with the mean diameter of the supported particle. A nice explanation of this phenomenon is given in Fig. 1b, which shows a clear linearity of the dissociation constant with the inverse of the fraction *f* of sites located on the edges of the particle in relation to the total. Fraction *f* has been calculated making the simple approximation that the particle sites are forming a sphere or a circle, as shown in the insert of Fig. 1b. In the case of the circle this leads to the following equation, with D expressed as number of atoms of Rh.

$$f=1-\left(\frac{D-2}{D}\right)^2 \quad (17)$$

This is in agreement with the observation of Oh *et al.*,[3] who argue that the requirement of vacant nearest-neighbor sites for the dissociation step explains why catalysts made up of supported metallic particles have lower capacity than single crystal catalysts, because the sites located near the edges of supported particles would have a lower dissociation capacity. If the 1/*f* expression is developed in series we get $\frac{1}{f}=\frac{36}{25}+\frac{12D}{25}+\frac{(D-12)^2}{500}+\cdots$, which is approximately linear with the diameter *D* of the particle if the higher terms are considered to be negligible. This indicates that the linearity seen in Fig. 1a is an approximate consequence of what is seen in Fig. 1b, where *f* has been calculated assuming a Rh atom with a diameter of 3 Å. In the figure it is also seen that the linearity is retained if a spherical particle is assumed.

In general, a specific rate constant such as that of dissociation is independent, in principle, of the geometry of the substrate. That geometry, however, has a strong influence on the rate of dissociation through the empty sites fraction, since that rate is equal to $k_5\theta_{NO}\theta_s$. But in the optimisation process by means of the LH model the distinction cannot be made in the product of the rate constant by the fraction of vacant sites, so the calculation assigns to that constant the geometric characteristics of the system. This would therefore mean that the optimum values used in the figures correspond to apparent specific dissociation rate constants.

Fig.1c shows that the kinetic model deviates from the experimental data. The practical difficulty of interpreting kinetics data at moderate and high pressures using k_i constants usually determined under ultrahigh vacuum (UHV) conditions has been called the pressure gap problem.[9] In an interesting recent paper by Zhdanov and Kasemo,[10] they carried out a study that shows the poor agreement obtained by extrapolating the UHV kinetics to moderate pressures (p_{NO} = p_{CO} = 0.01 bar) in the case of the CO–NO reaction on Rh, which is the system of interest in this paper.

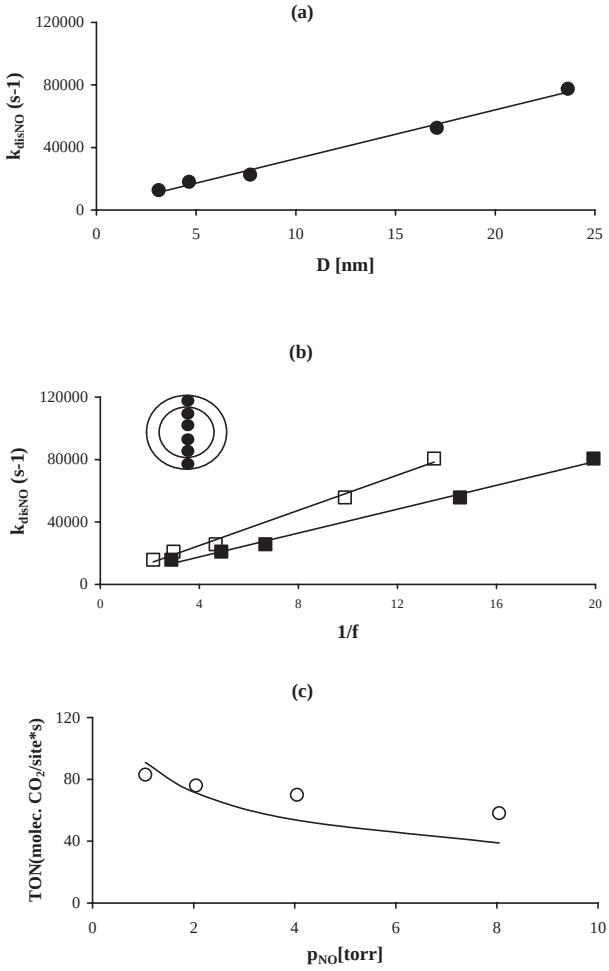

Fig. 1
(a) Optimum specific dissociation rates of NO versus average particle size D for the CO-NO reaction (Table 1).
(b) The same as (a) but versus 1/f. Particle sites are forming a circle (■) (insert figure) or a sphere (□).
(c) Measured and predicted rates of the CO-NO reaction over Rh(111) as a function of the partial pressure of NO. The partial pressure of CO (38 torr) and temperature (523 K) were held constant. ○ Rh(111) ; ——— Model.

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