where b_{CO} and b_{NO} are the adsorption coefficients for CO and NO. Similarly, treating steps 11 and 12 in combination as rate-limiting, show that the rate equation for mechanism 2 can be written as:

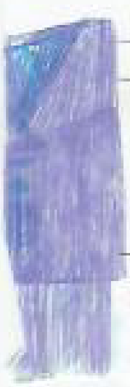
$$r_2 = (k_{11} + k_{12})\left(\frac{b_{NO}\,p_{NO}}{1 + b_{CO}\,p_{CO} + b_{NO}\,p_{NO}}\right)^2 \qquad (14)$$

(d) (*8 marks*) Rates of the reaction of NO with CO have been measured as functions of p_{CO} and p_{NO} over both Pt/Al_2O_3 and Pt/Si_3N_4. When these experimental data are substituted in the theoretical rate equations derived in part (c), a suitable mathematical analysis gives values for the corresponding adsorption coefficients for CO and NO (Table 1). Considering the physical significance of an adsorption coefficient, explain why mechanism 2 can be discounted as a representation of the kinetics of the reaction of NO with CO. (*two or three sentences*) should be +ve

In automobile exhaust streams, the partial pressure of NO is generally substantially lower than that of CO. Using information from Table 1, show that under this condition equation 13 takes a simplified form that is the same for both catalysts. Hence, comment on the effect of CO on the overall reaction rate, and suggest why Pt/Si_3N_4 might be a more efficient catalyst than Pt/Al_2O_3 for reduction of NO by CO. (*two or three sentences*) decrease

$R_2\ b_{NO} p_{NO} / (1 + b_{CO} p_{CO})^2$

Table 1 Adsorption coefficients for CO and NO on Pt/Al_2O_3 and Pt/Si_3N_4 derived on the basis of mechanisms 1 and 2. (The atmosphere (atm) is a non-SI unit of pressure; 1 atm = 101 325 Pa)



Catalyst	Mechanism	b_{CO}/atm^{-1}	b_{NO}/atm^{-1}
Pt/Al_2O_3	1	147	11
	2	−205	−319
Pt/Si_3N_4	1	36	25
	2	−442	−976

lower

(e) (*11 marks*) A sample of the Pt/Al_2O_3 catalyst containing 0.6 g of Pt was found to adsorb 37.2 cm^3 (at stp) of H_2(g) at room temperature. In a specimen of the Pt/Si_3N_4 catalyst, examination by electron microscopy ' the average Pt particle diameter, d, to be 7.8 ... lyst, calculate the specific Pt surface ... of Pt in the catalyst. Assu... en adso... with ev... Pt ... me ... m. For each ca... area, S, per gra... ption ... surface dissociative ... one H atom. (Average are... occupied atom adso... one H atom. (Average are... by a Pt atom on a Pt c... stallite surface, ... 8.42 × 10^{-20} m^2; density of ba... 10 ...

... be considered, commercial applications were ... area re... together with suggest why these sf... area ... world necessitate a high cost of platinum ... of Pt/Si_3N_4 relative to those ... assessment of the mer... (*three or fo... ...es*)

1440 m²/g

V = m/d

Question 2

This question carries 25% of the marks for this assignment, and tests Objectives 1, 2, 6, 8, 9, 10, and 11 of Block 6.

Exposure of a (100) single-crystal surface of the *fcc* metal palladium at 100 K to NO(g) results in the formation of a saturated layer of adsorbed species. The corresponding X-ray photoelectron N(1s) spectrum, generated by photons of energy $h\nu$ = 500 eV obtained from a synchrotron, is shown in Figure 1, together with spectra observed on subsequent heating of the surface to progressively higher temperatures.

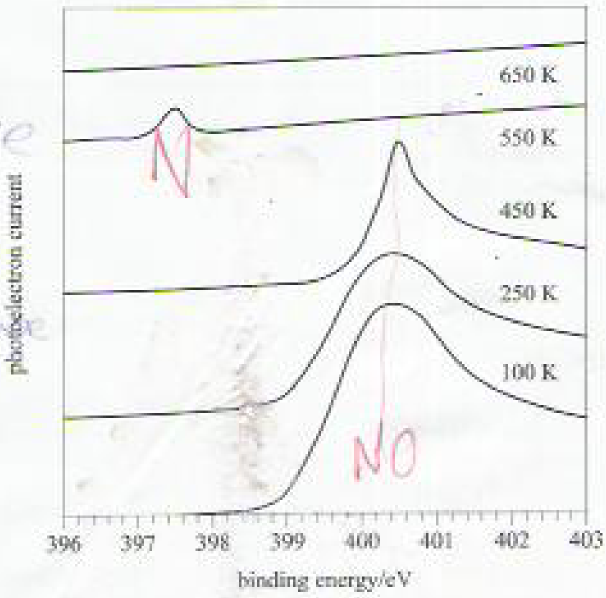


Figure 1 N(1s) XPS spectra of a Pd(100) surface exposed to NO(g) at 100 K and subsequently heated to 650 K; spectra have been displaced vertically for clarity, but the photoelectron current at 396 eV is similar in each case.

(a) (*5 marks*) The peaks in the N(1s) spectra for surface temperatures up to 450 K occur at a binding energy, E_B, of 400.5 eV. For the photoelectrons involved calculate the kinetic energy, E_K, and hence (using Block 6, Figure 3, p. 7) make *rough* estimates of their mean free path and the average number of atomic layers beneath the surface from which they originate (the sep... ...tion between Pd(100) layers is 195 pm).

Discuss bri... the advantage of using 500 eV synchrotron pho...ns rather than those from a conventional X-ray source, such as magnesium K_α ($h\nu$ = 1 254 eV). (*a couple of sentences*) resolution

(b) (*6 marks*) State the nature and origin of the chemical shift effect in XPS. (*one or two sentences*)

In the N(1s) spectrum of the Pd(100) surface at 550 K, the small peak at E_B = 397.5 eV can be assigned to adsorbed atomic nitrogen, N(ad). In terms of chemical shifts, suggest why it is then reasonable to assign a peak observed at 400.5 eV to non-dissociatively adsorbed nitric oxide molecules, NO(ad). Hence, discuss the nature of the species present on the surface at 100 K and the changes taking place in the adsorbed layer on increasing the temperature to 650 K. (*about 150 words*)

E = RT / 1.6E-19