

Tutor Marked Assignment

Make sure you know how to complete and send in your TMA and PT3 form: detailed instructions are given in *Completing TMA and CMA forms* in your *Student Handbook*.

Covering: **Blocks 5 and 6**
and Topic Study 2

Cut-off date:

Friday 8 August 2003

You should refer to the 'General advice for S342 TMAs' given on the front of the first Assignment Booklet before you tackle this TMA.

Question 1

This question carries 40% of the marks for this assignment, and tests Objectives 1, 3, 6, 19, 21 and 23 of Block 5.

Supports for heterogeneous catalysts are not necessarily inert and, as in the case of dual-function catalysts (Block 5, Section 4), may contribute chemically to the catalytic process. Alternatively, they may interact with the metal component of the catalyst either electronically to influence its reactivity or physically to control particle size. This question considers such possibilities in relation to the substitution of silicon nitride, Si_3N_4 , for Al_2O_3 in the three-way catalytic converter as a means of enhancing performance for reduction of NO by CO.

(a) (6 marks) State the assumptions underlying the Langmuir-Hinshelwood models for the kinetics of heterogeneously catalysed reactions, noting briefly the limitations of this approach. (100–150 words)

(b) (8 marks) For competitive non-dissociative adsorption of two reactants, A and B, on a surface with N sites, write an expression for the number of sites remaining vacant at any moment. Then, by equating appropriate expressions for the equilibrium rates of adsorption and desorption of A, show that the fractional coverage of A, θ_A , is given by

$$\theta_A = b_A p_A (1 - \theta_A - \theta_B) \quad (1)$$

where b_A is the adsorption coefficient of A, p_A is the equilibrium partial pressure of A, and θ_B is the fractional coverage of B. Combine equation 1 with its equivalent for θ_B to obtain

$$\theta_B = \theta_A (b_B p_B / b_A p_A) \quad (2)$$

and then use this expression and equation 1 to show that

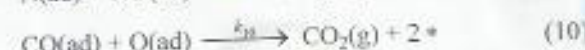
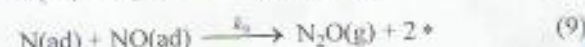
$$\theta_A = b_A p_A / (1 + b_A p_A + b_B p_B) \quad (3)$$

Finally, using equations 1 and 3, show that the fraction of sites vacant, θ^* , can be written as

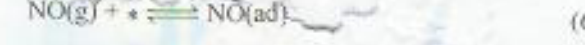
$$\theta^* = 1 / (1 + b_A p_A + b_B p_B) \quad (4)$$

(c) (7 marks) Two possible mechanisms for reduction of NO by CO are shown below, where $*$ represents a vacant surface site, b is an adsorption coefficient and k is a rate constant of the form appropriate for surface reactions. Both mechanisms involve competitive non-dissociative adsorption of CO and NO (steps 5 and 6). In mechanism 1, the rate-limiting step is taken to be the dissociation of an adsorbed NO molecule (step 7), the N(ad) and O(ad) formed reacting rapidly to give the gaseous products N_2 , N_2O (nitrous oxide) and CO_2 (steps 8–10). In mechanism 2, the slowest process is assumed to be the bimolecular reaction between two NO(ad) species, taking place via two parallel pathways (steps 11 and 12), at rates that are of a similar order of magnitude.

Mechanism 1



Mechanism 2



Assuming that a Langmuir-Hinshelwood kinetic model applies, and noting that the rate of step 7 will depend on the fraction of sites vacant, θ^* , use appropriate expressions from part (b) to show that the rate equation for mechanism 1 can be written as:

$$r_1 = k_7 \frac{b_{\text{NO}} p_{\text{NO}}}{(1 + b_{\text{CO}} p_{\text{CO}} + b_{\text{NO}} p_{\text{NO}})^2} \quad (13)$$