A new class of critical exponents in a dimer-monomer catalytic surface reaction

LETTER TO THE EDITOR

A new class of critical exponents in a dimer–monomer catalytic surface reaction

K Yaldram†‡, K M Khan‡, N Ahmed‡ and M A Khan†

† Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg, France
‡ Pakistan Institute of Nuclear Science and Technology, Post Office Nilore, Islamabad, Pakistan.

Abstract. The critical behaviour of a dimer–monomer ($BC + A \rightarrow \frac{1}{2}C_2 + AB$) irreversible catalytic surface reaction is investigated by means of Monte Carlo simulation technique. On a hexagonal lattice (each site having six nearest neighbours), the reaction exhibits a steady reactive state between two critical concentrations y_A^1 and y_A^2 of A. The critical exponents associated with various order parameters (i.e. coverages) at the second-order phase transition (SOPT) y_A^1 have been obtained. These exponents do not fall in the universality class of Reggeon field theory as is the case of $\frac{1}{2}B_2 + A \rightarrow AB$, the usual dimer–monomer reaction.

The A–B_2 reaction model of Ziff, Gulari and Barshad (ZGB) [1] represented by the reaction scheme $A + \frac{1}{2}B_2 \rightarrow AB$ has been used very extensively for the study of the catalytic oxidation of CO. This model exhibits two irreversible phase transitions which separate a steady reactive state (SRS) from surface saturated or poisoned state. A second-order phase transition (SOPT) separates the B poisoned state from the SRS and a first-order phase transition (FOPT) separates the A poisoned state from the SRS.

Investigating the behaviour near SOPT, Meakin and Scalapino [2] obtained the following expressions for the coverages of A and B:

$$\Theta_A \sim (y_A - y_A^1)^{\beta_A}$$

$$(1 - \Theta_B) \sim (y_A - y_A^1)^{\beta_B}$$

where y_A and $(1 - y_A)$ represent the feed concentrations of A and B respectively, y_A^1 is the critical feed concentration of A at SOPT, Θ_A and Θ_B are the surface coverages of A and B, respectively. β_A and β_B are the critical exponents whose values are obtained as 0.69 and 0.61, respectively. The errors involved in the calculations did not preclude the possibility of $\beta_A = \beta_B$.

Grinstein et al [3], on the basis of field theoretical considerations, have reported that the SOPT of the ZGB model belongs to the universality class of Reggeon field theory (RFT) and directed percolation which yields $\beta = 0.58$. Jensen et al [4] have conducted extensive simulations to show that the continuous phase transition found in the ZGB model definitely belongs to the universality class of directed percolation and RFT. Dickman has tackled the problem via simulations, series expansion and mean field theory [5]. For the various models that he considers he finds a SOPT with RFT critical exponents. The feature of his models is that they all consist of a single component and

a single adsorbing state at the transition point. His results support a conjecture of Grassberger [6] that there would always be a RFT type of transition under these conditions. In fact Grinstein *et al* [3] have extended this conjecture to multiple component systems, requiring a single adsorbing state as the sole criterion for an RFT type of transition.

Kohler and ben Avraham [7] have studied a dimer–trimer model $(A_2 + B_3)$ for heterogenous catalysis. This model always displays a phase diagram similar to that of ZGB model. The numerical results they obtain for the critical exponents of the SOPT differs from the RFT values. They obtain $\beta_A = 0.80 \pm 0.06$ and $\beta_B = 0.63 \pm 0.05$. This dimer–trimer model has an infinite number of adsorbing states near the transition point, thus violating Grinstein's conjecture for an RFT transition.

Recently, Albano [8] studied a model dimer–dimer reaction of the type $\frac{1}{2}A_2 + B_2 \to AB_2$. For the case where he introduces diffusion and consequent recombination of one species, he observes a SOPT. The critical exponents associated with the production of AB_2 and the coverage of B atoms are found to be unity. Furthermore he also obtains other values of β under different conditions of reaction [9].

The models of irreversible surface reactions studied by Kohler *et al* and Albano are quite different from the dimer–monomer (DM) model of ZGB. It is therefore not surprising that they do not belong to the same universality class as the DM model of ZGB.

Recently, Yaldram and Khan [10, 11] studied a DM model similar to that of ZGB with the difference that B_2 is replaced by BC. The reaction proceeds according to the equation: $A + BC \to AB + \frac{1}{2}C_2$. They were mainly interested in the irreversible catalytic surface reaction of CO with NO. This reaction cannot be sustained on a square lattice. On the hexagonal lattice they obtained both SOPT and FOPT. These transitions occur at a critical feed concentration of CO given by $y_{CO} = 0.185 \pm 0.002$ and 0.338 ± 0.002 respectively. The main features of their findings were confirmed later by Brosilow and Ziff [12]. The two transition points obtained on a 32×32 lattice were 0.185 ± 0.005 and 0.354 ± 0.001. While the two studies give the same value at SOPT there is some controversy over the value at FOPT. Since we are interested in the behaviour of the system near the SOPT we believe that the critical concentration of $y_{CO} = 0.185 \pm 0.002$ is fairly well determined.

In this letter we report the investigation of the critical behaviour of various coverages for the $A + BC$ reaction considering a complete dissociation of BC. It is interesting to determine whether these critical exponents belong to the same universality class as the $A + B_2$ reaction.

The model to represent the irreversible catalytic surface reaction of A with BC and the simulation procedure have been described in detail elsewhere [10]. We give here a brief description. The simple oxidation of A and the simultaneous reduction of BC (where B may be an oxygen atom) is known to proceed via the following Langmuir–Hinshelwood mechanism, when a complete dissociation of BC into B and C is assumed:

$$A(g) + AS \to A^S \tag{1}$$

$$BC(g) + 2S \to B^S + C^S \tag{2}$$

$$C^S + C^S \to C_2(g) + 2S \tag{3}$$

$$A^S + B^S \to AB(g) + 2S. \tag{4}$$

Here (g) and S represent the gas phase and an active site respectively. A^S means that an atom A is adsorbed at a site S. This simple model is simulated in the following
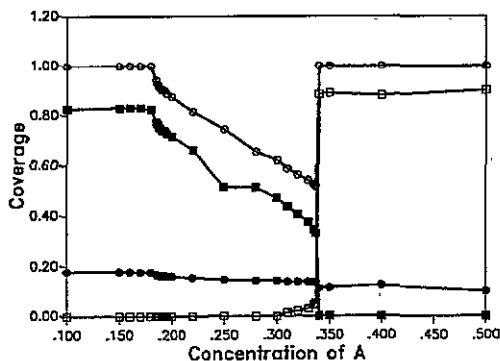
Figure 1. Coverages of $A(\square)$, $B(\blacksquare)$, $C(\bullet)$ and total ($\bigcirc$) as a function of the concentration of A for complete dissociation of BC.

way: the concentration of BC and A in an infinite reservoir is normalized to unity ($y_A + y_{BC} = 1$). The hexagonal surface is mapped onto a square 40×40 lattice, the periodic boundary conditions are used. The colliding reactant is chosen to be A with probability y_A and BC with probability $1 - y_A$. If the colliding atom is A the following steps are taken: (i) a site on the lattice is chosen at random; (ii) if the site is empty, A adsorbs (equation 1) else the trial ends; (iii) the nearest neighbours of this A are checked randomly for the presence of a B atom; (iv) if B is present, $AB(g)$ is formed which desorbs leaving behind two empty sites (equation (4)).

If the colliding molecule is BC, then two neighbouring empty sites are randomly located. B and C are adsorbed on each of these by a random selection (equation 2). After adsorption the nearest neighbours of both C and B are randomly scanned for either the presence of another C or an A atom respectively. The presence of C or A will lead either to the formation of $C_2(g)$ or $AB(g)$. In either case two empty sites are left vacant by the desorbing gas molecules.

We have studied the critical behaviour of this model system. To locate the SOPT point which separates the steady reactive state from the poisoned state we carried out five independent runs for each value of A concentration (y_A) close to the transition point, each for 50 000 Monte Carlo cycles. If all the runs continued for the full 50 000 Monte Carlo cycles we assumed that particular point to belong to the steady reactive
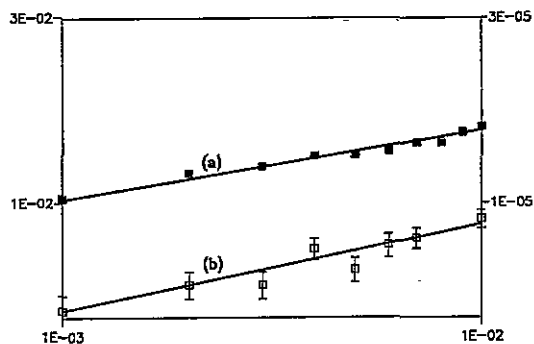

Figure 2. $|\Theta_A - \Theta_A^{sat}|$ (curve b represented by the right vertical axis) and $|\Theta_C - \Theta_C^{sat}|$ (curve a represented by left vertical axis) plotted versus ($y_A - y_A'$) on a log-log scale. Where error bars are not indicated the errors lie within the size of the markers.
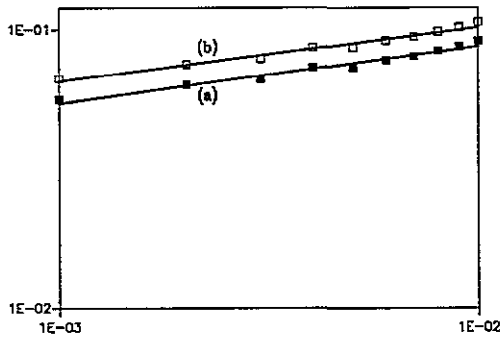
Figure 3. $|\Theta_B - \Theta_B^{sat}|$ (a) and Θ_S (b) plotted versus $(y_A - y_A^1)$ on a log–log scale. The errors in coverages lie within the size of the markers.

state. Even a single run leading to poisoning of the lattice was sufficient criteria for placing that point in the poisoned state. The critical point y_A^1 is found to be 0.185 ± 0.002.

In figure 1 we reproduce the full phase diagram (i.e. coverages as a function of A concentration). In the steady reactive state the sum of various coverages do not add up to unity. In fact the presence of vacancies and pair of vacancies is necessary to sustain a continuous reaction.

Near the SOPT we can express the power law behaviour as

$$\Theta_X - \Theta_X^{sat} = a_X (y_A - y_A^1)^{\beta_X}. \tag{5}$$

Here X represents A, B, C or the surface site S. Θ_X^{sat} is the saturated coverage of different species at the critical point, β_Xs are the critical exponents and a_X are constants. Moreover we have also studied the power law behaviour of the production rates of C_2 and AB near y_A^1. There we have two more βs through the relations

$$R_Z = a_Z (y_A - y_A^1)^{\beta_Z} \tag{6}$$

where R_Z is the production rate of Z (AB or C_2) which is zero at y_A^1. The log–log plots of $(\Theta_X - \Theta_X^{sat})$ and R_Z versus $(y_A - y_A^1)$ are sketched in figures 2, 3 and 4.

Figure 2 shows $\log|\Theta_A - \Theta_A^{sat}|$ and $\log|\Theta_C - \Theta_C^{sat}|$ versus $\log(y_A - y_A^1)$. The coverage of A is about 10^3 times smaller than that of C. The right hand coverage axis shows the values of $\log|\Theta_C - \Theta_A^{sat}|$. Due to very small coverage of A (figure 2(b)) we obtain a large
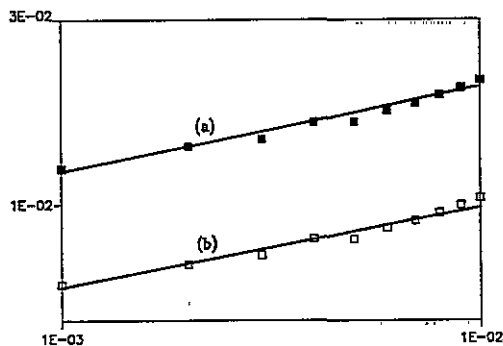

Figure 4. Production rate of C_2 (b) and AB (a) as a function of $(y_A - y_A^1)$ plotted on a log–log scale.

Table 1. The errors in all values are ± 0.02 except for A which is ± 0.05.

X	A	B	C	S	AB	C_2
β_X	0.20	0.20	0.21	0.22	0.22	0.21

scatter in the simulation results, but the least square fit to these values is very much parallel to the least square fit for the C coverage. In figure 3 we show $\log|\Theta_B - \Theta_B^{\text{sat}}|$ (figure 3(a)) and $\log(\Theta_S)$ (figure 3(b)) versus $\log(y_A - y_A^1)$. These two lines are very close to each other and have nearly the same slope. Finally, figure 4 shows the production rates of C_2 (curve a) and AB (curve b) versus $(y_A - y_A^1)$ on a log–log scale. Again we obtain two parallel lines with the same slope as the previous ones. All these slopes have been tabulated in Table 1. As for the values of different species at y_A^1, only B and C have non-zero coverages: 0.839 ± 0.001 and 0.161 ± 0.001, respectively, whereas the other species and the production rates give a saturated coverage.

In view of the errors involved in obtaining the coverages near the critical point y_A^1, it can be concluded that all the exponents β are approximately $\frac{1}{5}$ in the present dimer–monomer reaction. This puts this reaction in an entirely different class as compared to the usual dimer–monomer reaction of the type $A + \frac{1}{2}B_2 \rightarrow AB$ (i.e. CO–O$_2$). As for the dimer–trimer model of Kohler and ben Avraham [7] and the dimer–dimer model of Albano [8] we obtain an infinite number of adsorbing states near the transition point. Grinstein's criteria of a single adsorbing state near the transition is thus violated. It is thus not surprising that we do not obtain an RFT type of transition. To our knowledge none of the systems so far studied and displaying multiple adsorbing states at the transition point fall in the category of RFT. The diversity and richness of the A–BC type of reactions has already been illustrated in the case of NO–CO type of reactions [10–12]. This reaction should be further studied through other approaches for a better understanding.

References

[1] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
[2] Meakin P and Scalapino J 1987 *J. Chem. Phys.* **87** 731
[3] Grinstein G, Lai Z W and Browne D A 1989 *Phys. Rev. A* **40** 4820
[4] Jensen I, Fogedby H L and Dickman P 1990 *Phys. Rev. A* **41** 3411
[5] Dickman R 1989 *Phys. Rev. B* **40** 7005
[6] Grassberger P 1992 *J. Phys. B: At. Mol. Phys.* **47** 465
[7] Kohler J and ben-Avraham D 1991 *J. Phys. A: Math. Gen.* **24** L621
[8] Albano E V 1992 *J. Phys. A: Math. Gen.* **25** 2557
[9] Albano E V 1992 *Stat. Phys.* **69** 643
[10] Yaldram K and Khan M A 1991 *J. Catal.* **131** 369
[11] Yaldram K and Khan M A 1992 *J. Catal.* **136** 279
[12] Brosilow B J and Ziff R M 1992 *J. Catal.* **136** 275