The dimer-trimer and monomer-trimer models for heterogeneous catalysis: a phase diagram study

2000 J. Phys. A: Math. Gen. 33 L215

(http://iopscience.iop.org/0305-4470/33/25/101)

J. Phys. A: Math. Gen. **33** (2000) L215–L220. Printed in the UK PII: S0305-4470(00)09922-4

LETTER TO THE EDITOR

The dimer–trimer and monomer–trimer models for heterogeneous catalysis: a phase diagram study

K M Khan, A Basit and K Yaldram

Nuclear Physics Division, Pakistan Institute of Nuclear Science and Technology, PO Nilore, Islamabad, Pakistan

Received 24 November 1999, in final form 17 March 2000

Abstract. The phase diagram of the dimer–trimer model has already been studied for Kagome and hexagonal lattices, the detail of which can be found in the literature. Here, we have studied the same model on a square lattice to look into the effect of lattice type on the phase diagram of the system. The steady reactive window width decreases significantly from 0.12 (for hexagonal lattice) to 0.02 for a square lattice. We have also studied a monomer–trimer model through Monte Carlo simulation. The effect of the lattice type on the phase diagram of the system is studied. The phase diagram qualitatively resembles that of the ZGB model. The lattice type has a significant effect on the steady reactive window width.

There has been considerable interest in the study of microscopic models based upon the Langmuir–Hinshelwood mechanism for heterogeneously catalysed reactions [1–14]. Such reactions are of great complexity and they are thus inherently very difficult to deal with. However, the detailed understanding of such reactions is very important in applied research but rarely has such an understanding been achieved either from experiment or from theory. An investigation of lattice models of catalytic surface reactions has been extremely helpful in gaining a better understanding into the kinetics of catalytic processes. Ziff *et al* [1] and Dumont *et al* [13] introduced a monomer–dimer (MD) model, which has been used to study a reaction system of the type $2A + B_2 \rightarrow 2AB$. This reaction mimics the catalytic oxidation of CO. This model is generally known as the ZGB model [1]. In this model a square lattice models the surface. A reservoir containing A and B_2 in a given proportion is in contact with the surface. It is assumed that the supply of the gaseous species is inexhaustible. On striking the surface a monomer (A) adsorbs onto a single vacant site, while a dimer (B_2) adsorbs onto two adjacent vacant sites. Whenever a B atom finds itself sitting next to A, a reaction takes place with the formation of AB that desorbs from the surface, leaving behind two vacant sites. The only parameter in this model is the feed concentration y_A of monomer (A). As a function of y_A, the system exhibits two phase transitions at y_1 (continuous) and y_2 (discontinuous). A second-order phase transition (SOPT) at $y_1 = 0.389 \pm 0.001$ separates a B-poisoned state from a steady reactive state (SRS), while a first-order transition (FOPT) at $y_2 = 0.525 \pm 0.001$ separates an A-poisoned state from an SRS. Within the window defined by $y_1 < y_A < y_2$ the system exhibits an SRS with continuous production of AB.

Meakin and Scalapino [2] investigated the effect of the lattice type on the reactive window of the ZGB model. They found that for a hexagonal lattice (each surface site has six nearest neighbours) the reactive window increases in size compared with the usual square lattice with

0305-4470/00/250215+06$30.00

$y_1 = 0.360 \pm 0.005$ and $y_2 = 0.561 \pm 0.001$. The kinetics of an irreversible dimer–dimer surface reaction of the type $A_2 + B_2 \rightarrow 2AB$ with desorption of dimer B_2 has been studied by Khan *et al* [12] on a square lattice. For a desorption probability (P) of B_2 equal to zero, a single discontinuous transition separating an A + vacancies saturated surface from a B + vacancies saturated surface is obtained at $y_B = 0.50$ (y_B is the feed concentration of dimer B_2). With the increase in P an SRS, which is separated from the poisoned state by two continuous transitions, is obtained for this system. The position of the transition points depends upon the value of P. For $P = 1$, a single continuous transition at $y_B = 0.538$ separates a poisoned state from an SRS. The reactive window width is sensitive to the value of P. With the decrease in P, y_1 remains almost constant, whereas y_2 shifts noticeably towards y_1. At $P \approx 0.20$, the transition points merge, resulting in the disappearance of the reactive window.

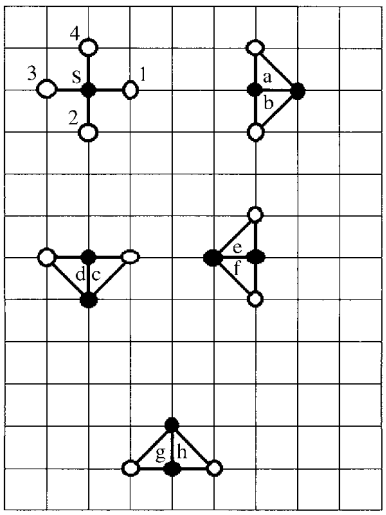

Figure 1. Four nearest neighbours of surface site S are marked as 1, 2, 3 and 4, respectively. Different possible choices of trimer adsorption on a square lattice forming vertices of a right-angled triangle are shown by a–h, respectively. See text for details.

Kohler and ben-Avraham have reported results of a dimer–trimer (DT) model of the type $3A_2 + 2B_3 \rightarrow 6AB$ on a hexagonal lattice [14]. They have observed a phase diagram in which an SRS is separated from a (B + vacancies)-poisoned state by a continuous transition (y_1) and (A + vacancies)-poisoned state by a discontinuous transition (y_2). The phase diagram seems to resemble qualitatively the standard ZGB model with the difference that for $y_A < y_1$ ($> y_2$) in the ZGB model the surface is poisoned with 100% B (A). However, a number of discrepancies can be found in their paper. In figure 1 (shown by them) dimer and trimer coverages are plotted versus values of y_A (where y_A is the concentration of the dimer in the reservoir). In this figure the transitions y_1 and y_2 are shown at approximately 0.34 and 0.66, respectively. On the other hand, in the text of the paper they have quoted these values as 0.3406 and 0.4610, respectively. For the extreme case of $y_A = 1$ their figure shows coverage of dimer ≈ 0.80, whereas in the text of the paper they quote that at $y_A = 1$ there are some isolated vacancies with concentration equal to 0.086. This means that the coverage of a dimer at the extreme case of $y_A = 1$ should be 0.914, which is consistent with the value shown by Meng *et al* [15] for random filling of a dimer on a hexagonal lattice. From these clear discrepancies we conclude that Kohler and ben-Avraham have misquoted some of their results. They have also presented the same results along with extension of the work for the Kagome lattice in another paper [16]. For the Kagome lattice they have observed a phase diagram somewhat like that of a hexagonal lattice. Due to the smaller connectivity of the lattice the dimer-poisoned phase contains a small concentration of trimers, whereas the trimer-poisoned phase contains a small

concentration of dimers. The SRS occurs within a narrow window (≈ 0.014) with $y_1 \approx 0.095$ and $y_2 \approx 0.109$.

Here we have studied the DT model on a square lattice through Monte Carlo simulation. We have taken the lattice size $L = 128$. It is observed that an increase in the lattice size changes the critical values slightly, but the overall qualitative nature of the phase diagram is not affected [12, 17]. Periodic boundary conditions are employed and the simulation starts with a clean surface. The four nearest-neighbouring (NN) sites of a selected site S are shown in figure 1. The only variable in our simulation is the feed concentration of A_2 (y_A). The equilibrium coverages are measured as a function of y_B. In order to locate the critical points ten independent runs, each of up to 50 000 Monte Carlo (MC) cycles were carried out. If the ten runs proceed up to 50 000 MC cycles without the lattice becoming poisoned, the particular point is considered to be in SRS. The poisoning of even a single run is a sufficient criterion for considering the point to be in the poisoned state. If the run does not end up in a poisoned state, then in order to get the coverages in SRS, the initial 10 000 MC cycles are ignored and the system is allowed to run up to 50 000 MC cycles. The values of coverage and the production rate are obtained after every 10 MC cycles, so that the final coverage (production rate) is an average of 4000 points.

The different steps involved in the simulation procedure are as follows. A surface site is chosen at random, if it is already occupied the trial ends else a neighbouring surface site is also picked at random. If this site is occupied the trial ends. In case both sites are vacant A_2 is picked with a probability y_A. This then is adsorbed onto the two empty sites in its atomic form. The adsorption trial for B_3 is made with probability $(1 - y_A)$. For this purpose in addition to the randomly selected site S two more vacant sites are also required. The choice of these two sites is also made at random in such a way that the three sites constitute the vertices of a right-angled triangle (figure 1). If all three sites are empty, then B_3 is adsorbed in atomic form on them. The adsorption of a trimer on triplets of linear vacancies is not allowed. There are two sets of linear triplets of vacancies as shown by (1, S, 3) and (2, S, 4) in figure 1. Atoms A and B sitting next to each other form AB that desorbs from the surface, leaving behind two vacant sites. This simulation procedure gives a phase diagram which is qualitatively very similar to that observed by Kohler and ben-Avraham for a hexagonal lattice. The continuous and discontinuous phase transitions (y_1 and y_2) are observed at $y_A = 0.403 \pm 0.001$ and 0.422 ± 0.001, respectively (figure 2). Only in the range $y_1 < y_A < y_2$ does the system exhibit an SRS. For $y_A < y_1$, a B + vacancies saturated phase is observed, whereas for $y_A > y_2$, we get an A + vacancies saturated phase. For the extreme case of $y_A = 1$ the coverage of the dimer ≈ 0.90, which

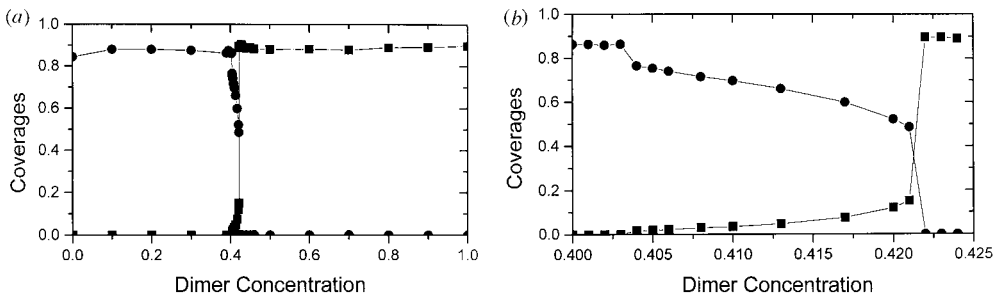

Figure 2. Coverages of trimer (circle) and dimer (square) as a function of the dimer concentration for the dimer–trimer model on a square lattice (*a*). A blown-up portion of the steady reactive state is also shown (*b*).

is consistent with the value shown by Albano [5] for random filling of a dimer onto a square lattice. For the other extreme case of $y_A = 0$ the coverage of the trimer ≈ 0.84. If random filling of the dimer gives a coverage ≈ 0.90, then it is very clear that random filling of the trimer should give a smaller coverage. This is because if dimer random filling gives isolated vacancies having a concentration ≈ 0.10 then trimer random filling should give isolated, double and even triple linear vacancies and thereby the coverage of vacancies ≈ 0.16. The same fact also holds true for a hexagonal lattice. However, surprisingly figure 1 in the paper of Kohler and ben-Avraham shows that for a hexagonal lattice the coverage of dimer random filling ≈ 0.80, whereas that of trimer random filling ≈ 0.91. This gives extra evidence that they have quoted the wrong figures in their paper. For the cases $0 < y_A < y_1$ and $y_2 < y_A < 1$ the coverage of vacancies is almost constant, having values ≈ 0.08 and ≈ 0.09, respectively. As for the ZGB model in this case also the lattice type has a significant effect on the reactive window of the system. The reactive window width of ≈ 0.12 (as shown by Kohler and ben-Avraham for the hexagonal case) has been significantly reduced to ≈ 0.02 for a square lattice.

We have also studied a monomer–trimer (MT) model of the type $3A + B_3 \rightarrow 3AB$, which is symbolically represented by following three equations:

$$A(g) + S \rightarrow A^s \tag{1}$$

$$B_3(g) + 3S \rightarrow 3B^s \tag{2}$$

$$A^s + B^s \rightarrow AB(g) + 2S. \tag{3}$$

Here (g) and S indicate the gas phase and an active surface site, respectively.

The relative partial pressures or concentrations of A and B_3 are y_A and $1 - y_A$, respectively. We consider both a square as well as hexagonal lattices for this study. We take the lattice size $L = 128$. The general features of the simulation procedure are the same as discussed in the DT model. The simulation proceeds as follows. A surface site is chosen randomly. There are two possibilities. Either the site is occupied or it is empty. If the selected site is occupied the trial ends. If the selected site is empty then a monomer (A) adsorption trial is made with probability y_A. The adsorption trial for B_3 is made with probability $1 - y_A$. For this purpose in addition to this selected site two more vacant sites are also required. The choice of these two vacant sites is also made at random in such a way that three vacant sites constitute the vertices of a right-angled triangle for the square lattice and that of an equilateral triangle for the hexagonal lattice. After successful adsorption of A or B_3, we proceed towards the reaction step. A and B atoms sitting next to each other form AB that desorbs from the surface leaving behind two vacant sites.

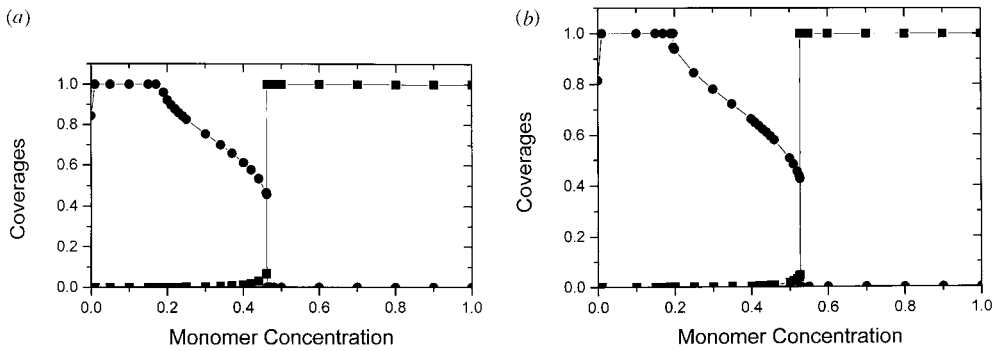

Figure 3. Coverages of trimer (circle) and monomer (square) as a function of monomer concentration for the monomer–trimer model for a square lattice (*a*) and for a hexagonal lattice (*b*).

Our simulations reveal a phase diagram which is very similar to that of the ZGB model. Like the ZGB model the only parameter is the feed concentration y_A of monomer (A). As a function of y_A, the system exhibits continuous and discontinuous phase transitions. Figure 3 shows coverages plotted as a function of y_A. For a square lattice the SOPT at $y_1 = 0.190 \pm 0.005$ separates a B-poisoned state from the steady reactive state, while a FOPT at $y_2 = 0.465 \pm 0.005$ separates an A-poisoned state from an SRS. Within the window defined by $y_1 < y_A < y_2$ the system exhibits an SRS with continuous production of AB. Like ZGB, for all non-zero values of y_A the poisoned phases have 100% B and 100% A coverages, respectively. However, in this case the window width is almost double the value (≈ 0.265) of the ZGB model. For the extreme case of $y_A = 1$, the adsorption of only a monomer is attempted. All the lattice sites are occupied by monomer, resulting in 100% coverage of A. For the other extreme case of $y_A = 0$, the adsorption of only a trimer is attempted. The coverage of B for this case is ≈ 0.84. For the region $0 < y_A < y_1$, the vacancy coverage is zero contrary to dimer–trimer or dimer–dimer models. In this range all lattice sites are occupied by B. This is because in this case a single vacancy can be picked by A for adsorption, which burns B and thus results in triplets of NN empty sites for B_3 adsorption. Due to the high partial pressure (concentration) of trimer all the monomer is burnt and the lattice gradually poisons with B. The production of AB increases with increase in y_A, becomes maximum close to y_2 and then decreases rapidly to zero at y_2. This trend is similar to that obtained in the ZGB model. If we plot AB production (R) versus y_A, it shows a polynomial fit with equation $R = -0.025 - 0.038(y_A) + 1.21(y_A)^2$, as shown in figure 4. For a hexagonal lattice the coverages are plotted as a function of y_A in figure 3. It is observed that by moving from a square to a hexagonal lattice the general features of the phase diagram remains the same. The value of y_2 shifts to the higher value of feed concentration $y_A = 0.528$, whereas that of y_1 remains almost constant. This value of y_2 is exactly the same as obtained in the ZGB model for a square lattice. The steady reactive window width increases significantly to 0.34. The AB production (R) shows a behaviour of the type $R = -0.007 - 0.276(y_A) + 1.485(y_A)^2$.

We have studied the DT model on a square lattice. It is seen that a change of lattice coordination has a significant effect on the width of the steady reactive window. The steady window width ≈ 0.12 for a hexagonal lattice, whereas it has significantly decreased to 0.02 for a square lattice. We have also seen that a change of lattice coordination also has a significant effect on the width of the steady reactive window in the MT model. For the MT model, the steady window width ≈ 0.265 for a square lattice (double the value of the ZGB model), whereas it has significantly increased to 0.33 for a hexagonal lattice. The change in lattice

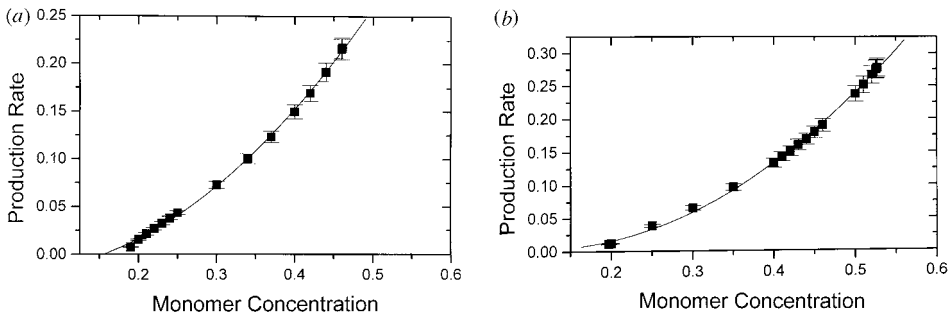

Figure 4. Production rates of AB as a function of monomer concentration for the monomer–trimer model for a square lattice (a) and for a hexagonal lattice (b). A second-degree polynomial ($Y = a + bX + cX^2$) fits the data. The values of a, b and c are given in the text.

coordination does not affect the value of SOPT (y_1). The value of y_1 is almost the same for the two lattices. However, with the increase in lattice coordination FOPT (y_2) is significantly shifted towards higher values of y_A. It has a value ≈ 0.34 for a square lattice, whereas it increases to 0.527 (± 0.001) for a hexagonal lattice. It is also interesting to note that this value is the same as obtained in the ZGB model for a square lattice. However, in the ZGB model lattice coordination has an effect on the values of both y_1 and y_2. The features of the phase diagram of the MT model are qualitatively similar to that obtained in the ZGB model.

References

[1] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
[2] Meakin P and Scalapino D J 1987 *J. Chem. Phys.* **87** 731
[3] Yaldram K and Khan M A 1991 *J. Catal.* **131** 369
[4] Khan M A, Yaldram K, Khalil G K and Khan K M 1994 *Phys. Rev.* E **50** 2156
[5] Albano E V 1992 *J. Phys. A: Math. Gen.* **25** 2557
[6] Khan K M, Yaldram K and Ahmed N 1998 *J. Chem. Phys.* **109** 5054
[7] Yaldram K, Khan K M, Ahmad N and Khan M A 1994 *J. Catal.* **147** 96
[8] Yaldram K and Sadiq A 1987 *J. Phys. A: Math. Gen.* **22** 1925
[9] Albano E V 1992 *Phys. Rev. Lett.* **69** 656
[10] Khan K M and Yaldram K 1999 *Sur. Sci.* at press
[11] Khan K M, Khalifeh J, Yaldram K and Khan M A 1997 *J. Chem. Phys.* **106** 8890
[12] Khan K M, Yaldram K and Ahmed N 1998 *J. Chem. Phys.* **109** 5054
[13] Dumout, Poriaux M and Dagonnier P 1986 *Sur. Sci.* **169** L307
[14] Kohler J and ben-Avraham D 1991 *J. Phys. A: Math. Gen.* **24** L621
[15] Meng B, Weinberg W H and Evans J W 1993 *Phys. Rev.* E **48** 3577
[16] ben-Avraham D and Kohler J 1991 *J. Stat. Phys.* **65** 839
[17] Khan K M, Yaldram K, Ahmad N and Qamar-ul-Haque 1999 *Physica* A **268** 89