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Multiple steady state in the hydrogenative ring opening of propylcyclobutane over Rh / SiO_2

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During the hydrogenative ring-opening reaction of propylcyclobutane over Rh / SiO_2 bifurcation was observed. On varying the hydrogen concentration in the reactor a catalytic surface with two steady states was formed. This bistability was found over the "working" catalyst and was attributed to the interplay of adsorbed hydrogen, adsorbed propylcyclobutane, the carbonaceous deposits and the surface or close to surface Rh atoms.

Keywords: propylcyclobutane, hydrogenative ring opening, Rh / SiO_2, multiple steady state

1. Introduction

Investigating catalytic reactions occurring over, e.g., supported transition metal catalysts in the function of hydrogen pressure may give valuable mechanistic information about surface events. Reaction rates vs. hydrogen pressure curves most often exhibit a maximum or occasionally they monotonously increase and may go to saturation at high hydrogen pressures. As far as hydrogenative ring-opening reactions are concerned, these curves may also be interpreted as the result of simple competitive (Langmuir–Hinshelwood mechanism) or noncompetitive (Eley–Rideal mechanism) adsorption, respectively. However, even these simple curves may have mechanistic implications if, for instance, the molecule adsorbs irreversibly over the catalyst and the kinetic behavior is still described by maximum curve(s) [1].

Reaction rate vs. hydrogen pressure functions surely reflect surface events when two (or more) different products are formed and for one product the formation rate vs. hydrogen pressure curve passes through a maximum and for the other it is described by a saturation-type or steadily increasing curve [2].

Hydrogen pressure curves with more than one extremum also provide mechanistic information [3]. Curves like these were obtained over the initial as well as over the "working" catalyst when the hydrogenative ring opening of propylcyclobutane was studied over Pt / SiO_2 [4]. However, under similar conditions, but using Rh/ SiO_2 as catalyst, only the initial rates provided smooth activity–hydrogen pressure curves with two extrema (a maximum and a minimum) [5]. Over the working catalyst switches between two steady-state ring-opening rates were observed in the function of hydrogen pressure. Although oscillation reactions over surfaces, which undergo periodic oxidation–reduction cycles are well known and described in detail [6], hydrogenation reactions with non heat or mass transfer related bifurcation are, to the best of our knowledge, unknown. In this contribution we wish to report such an example.

2. Experimental

Propylcyclobutane was obtained from the laboratory of the late O.V. Bragin (Zelinskii Institute, Moscow, Russia). Its purity was checked by ^1H NMR spectroscopy (Bruker AM 400) and the GC-MS (Hewlett-Packard 5970 MS) method. The compound was used without further purification except a couple of freeze–evacuate–thaw cycles right before preparing the reaction mixture. Oxygen-free hydrogen was prepared in a Matheson 8326 generator, operating with a palladium membrane.

A 3.2% Rh / SiO_2 catalyst was made by impregnating a Cab-O-Sil M5 support (BDH product with $241.6\ m^2\ g^{-1}$ BET surface area) with $RhCl_3$ solution, followed by reduction in flowing hydrogen at 773 K for 16 h. The high-temperature hydrogen treatment diminished the chlorine content of the catalyst as revealed by X-ray fluorescence spectroscopy (the quantity of residual chlorine was negligible, it was less than 10 ppm relative to Rh loading). The dispersion of the catalyst (number of exposed Rh atoms / total number of Rh atoms) was determined by H_2 titration in a pulse system at room temperature. The dispersion value, assuming 1 : 1 adsorption stoichiometry, was 0.27.

After the initial reduction, in order to avoid accidental contamination, the catalyst was stored in a closed vial in a vacuum desiccator, separately from the place where the reactions were run. Before each experiment, the cat-

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alyst samples were activated with 26.6 kPa of H_2 at 473 K for 1 h.

The reactions were carried out in a conventional closed circulation reactor at 373 K (for more details concerning the experimental setup, see ref. [7]). The analysis of samples withdrawn from the reaction mixture was performed with a Carlo Erba Fractovap 2150 gas chromatograph equipped with a flame ionization detector. Either a 4 m or a 3.6 m long glass column filled with 5% bis(methoxyethyl)adipate/Chromosorb PAW or 20% squalane/Chromosorb PAW, respectively were used for analysis. The quantity of the catalyst (10 mg) and the circulation rate was chosen to avoid diffusion resistance.

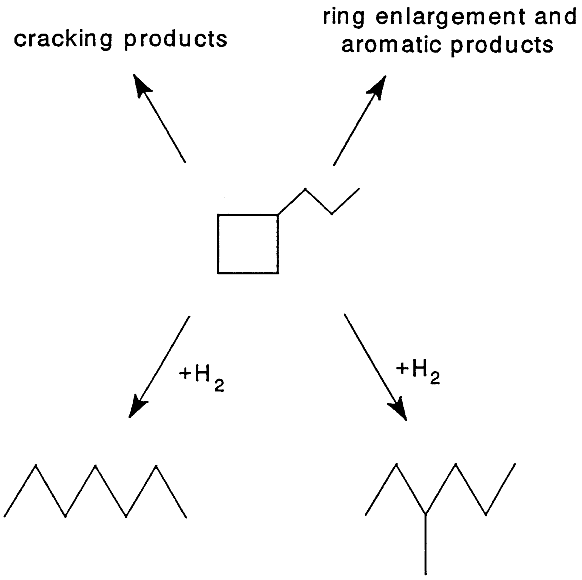
Reactants (1.33 kPa of hydrocarbon and various amounts of hydrogen) were premixed in the circulation part of the system before the reaction. Product yield vs. time functions were always measured over a fresh sample of catalyst (10 mg). The curves could be modeled by two straight lines. The first was typical for the initial catalyst, the second one characterized the "working" surface. The slope of the second part was determined and was converted to turnover frequency data (TOF: molecules s^{-1} (exp. atom)$^{-1}$). From these and the hydrogen pressure values TOF vs. hydrogen pressure curves were constructed.

3. Results and discussion

Systems with multiple steady states, often revealed in autonomous oscillation of reaction rates in time, are well known in heterogeneous catalytic systems and over model surfaces as well. Detailed studies of such systems are available in large number throughout the catalytic and surface science literature and the topic has also been reviewed frequently [6,8–12]. The most popular model reaction for studying oscillation behavior is the oxidation of CO over Pt surfaces. Well-established explanations for oscillation are the alternating oxidation and reduction of the surface [13,14], the formation and autocatalytic oxidation of carbon [15,16], and reconstruction of surface structure [17,18]. In most cases, instabilities were observed vs. time.

Multiple steady states which are not exhibited in rate or selectivity oscillations vs. time are much less frequent. In the aqueous oxidation of ethanol over Pt/C a transition between two steady states was reported recently upon changing the ethanol or the oxygen feed concentration [19]. Bifurcation was also found in the hydrogenation of ethene over Pt/boehmite catalyst in a flow system [20]. Here the effect was observed upon changing the temperature. However, it was not attributed to the kinetic behavior, but rather to heat transfer instabilities.

In our system we could observe a bifurcation upon changing the hydrogen concentration, but only over the "working" catalytic surface.



Scheme 1. Possible transformation routes in the transition metal catalyzed hydrogenative reactions of propylcyclobutane.

As far as reactions and products are concerned propylcyclobutane may undergo several types of transformations, such as hydrogenative ring opening, cracking, ring enlargement and aromatization (scheme 1). At 373 K only hydrogenative ring opening takes place giving *n*-heptane from the rupture of the sterically more hindered ring C–C bond (1,2 C–C bond scission) and 3-methylhexane when the sterically less hindered ring C–C bond is broken (2,3 C–C bond scission).

On varying the hydrogen pressure two sets of rates could be measured for both products. Virtually all points representing the TOF values fall on two "smooth" curves (figures 1 and 2). The system seems to choose between two steady states in the function of hydrogen pressure.

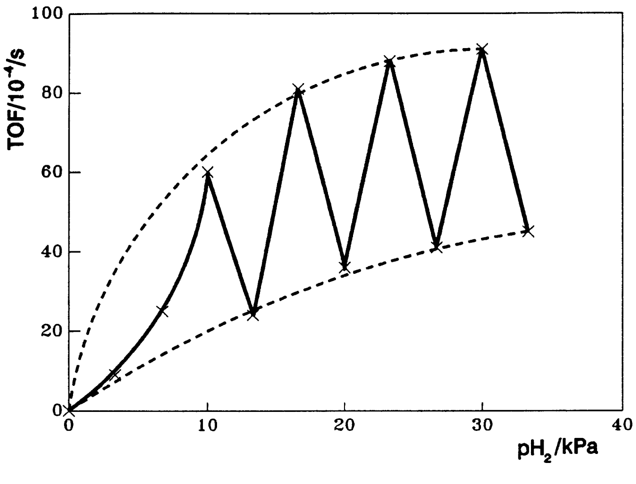


Figure 1. Formation rates of 3-methylhexane vs. H_2 pressure in the hydrogenative ring opening of propylcyclobutane over the "working" Rh/SiO_2 catalyst at 373 K.

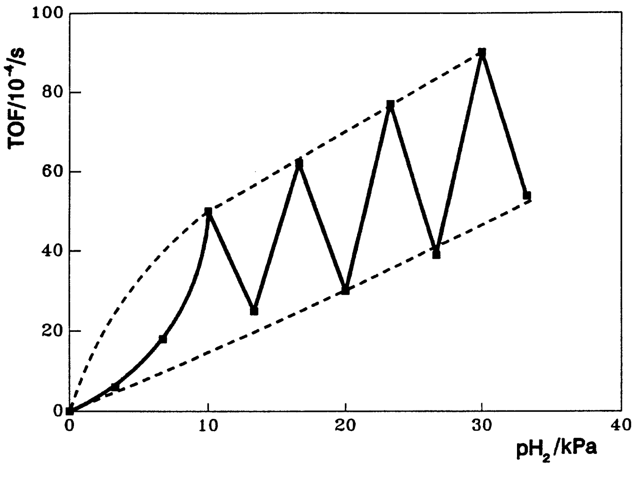


Figure 2. Formation rates of *n*-heptane vs. H_2 pressure in the hydrogenative ring opening of propylcyclobutane over the "working" Rh/SiO_2 catalyst at 373 K.

A comparison of the two curves also reveals that in the more active steady state (upper dashed curve) 2,3 C–C ring scission predominates at most hydrogen pressures, while over the less active one (bottom dashed curve) the ring opens in both directions with about the same rate.

Let us point out again that the phenomenon is connected to the "working" surface and was not observed (however, slightly indicated by the two extrema in the hydrogen pressure curves) over the initial surface [5]. This means that the presence of hydrogen, the hydrocarbon and the metal are not enough for producing the bistability. It is known that during hydrocarbon reactions, when the "working" catalyst is established, carbonaceous deposits of various forms decorate the surface in various ways [21]. We propose that in our system bistability is resulting from two stabile configurations of carbonaceous deposits. At the configuration when the higher rate was measured the carbonaceous moieties may cover parts of the support and the interface between the support and the Rh crystallite. In the less active state fewer active metal atoms (sites) are exposed, leading to smaller activity, but the relative quantities of interfaces are higher, therefore the ring opening selectivity shifts, that is the portion of 1,2 C–C scission ring opening route increases.

This bistability seems to be specific to Rh/SiO_2, since the phenomenon was not observed over Pt/SiO_2 [4], Pd/SiO_2 [22] or Ni/SiO_2 [23]. Adsorbed hydrogen, adsorbed propylcyclobutane, the carbonaceous deposits and the surface or close to surface Rh atoms together produce the surface with two steady states. The phenomenon is an interplay of the listed components and they are not related to heat or mass transfer problems.

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