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NOTE

Mechanistic Implications of Ring-Opening Rate vs Hydrogen Pressure Functions

In a recent paper Jackson *et al.* described hydrogenation reactions of many hydrocarbon molecules over a number of supported platinum catalysts (1). The hydrogenative ring opening of cyclopropane to propane was investigated in detail and it was observed that the ring-opening rate passed through a maximum, as a function of hydrogen pressure over each catalyst. This was interpreted as competition for the active sites between about equally strongly adsorbed hydrocarbon and hydrogen. It means that the molecule in excess repels the other from the surface. Thus, a simple Langmuir–Hinshelwood mechanism applies, and the measured data can be fitted well with the equation applied to a cyclopropane–Pt/SiO_2 system a long time ago (2).

The intention of this note is to show that reaction rate vs hydrogen pressure functions may be used for a better understanding of surface phenomenon, and that they have mechanistic implications, especially for alkyl-substituted cyclopropane–hydrogen systems reacting over supported transition-metal catalysts. Over the years, a substantial amount of experience has been gathered about these systems (3–7) and occasionally unexpected shapes of product formation rate vs hydrogen pressure were found (S1 behavior). Alkyl-substituted cyclopropane may give two products, one resulting from the cleavage of the sterically more hindered ring C−C bond(s), the other from the sterically less hindered ring C−C bond(s). It allows two product accumulation rate vs hydrogen pressure curves to be measured. If the shapes of the two curves for certain molecules over certain catalysts are different (S2 behavior), then they reflect differences in their mechanism of formation.

Examples for both types of behavior can be found in the above-mentioned works. Good candidates are the *cis*- or *trans*-1,2-dimethylcyclopropanes (*c*DMCP or *t*DMCP) over Rh/SiO_2 (3), Pd/SiO_2 (4), Ni/SiO_2 (5), and Cu/SiO_2 (6). A mixture of these hydrocarbons was synthesized according to an established method (8) and was separated by preparative gas chromatography. The reactor was a static circulation system with 1.33 kPa of cyclopropane and varying amounts of hydrogen. Reaction temperatures and reactants were as follows: Rh/SiO_2, 318 K, *t*DMCP; Pd/SiO_2, 373 K, *t*DMCP; Ni/SiO_2, 473 K, *t*DMCP; Cu/SiO_2, 498 K, *c*DMCP. Initial rates were determined and converted to turnover frequencies (TOF in molecules/exp.atoms/s) over these low-dispersion catalysts prepared by impregnation (Rh/SiO_2, Pd/SiO_2, Ni/SiO_2) or precipitation (Cu/SiO_2). The obtained curves are displayed in Fig. 1.

As far as S1 behavior is concerned (3), the product formation vs hydrogen pressure functions go through two extremes: first, a maximum and then at higher hydrogen pressure, a minimum. After the minimum, the reaction rate grows continuously and exceeds the local maximum for both products over Rh/SiO_2.

S2 behavior was observed over the other catalysts (4–6). Over Pd/SiO_2, the formation rate vs hydrogen pressure function of 2-methylbutane goes to saturation with increasing hydrogen pressure, while for the other product the curve passes through a maximum. The situation is reversed over the Ni/SiO_2 and Cu/SiO_2 catalysts. A special property of the Cu/SiO_2 catalyst is that the ring opens predominantly with the cleavage of the sterically more hindered ring C−C bond.

All these observations indicate that a simple Langmuir–Hinshelwood mechanism is not adequate for an appropriate description of the S1 or the S2 behavior. As far as S1 behavior is concerned, the rate enhancement after the minimum with increasing hydrogen pressure clearly indicates that, under hydrogen-abundant conditions, the reaction proceeds with a different mechanism than when hydrogen is scarce. With regards to the S2 behavior, it does not seem possible that the adsorbed precursor of one product of the same starting material is flushed away from the surface by excess hydrogen, while the other is not. It is much more plausible that the two products are formed with different mechanisms.

In my view, these observations, which reflect the mechanism(s) of surface transformations, can be interpreted as follows. The maximum of the curve represents the most favorable conditions for the formation of dissociatively adsorbed species, that is adsorbed intermediates formed through the rupture of C−H bond(s). It is known that concomitant C−C bond cleavage also takes place in the ring, since deuterated cyclopropane could not be obtained during H−D exchange (9). Further increase in hydrogen pressure inhibits the scission of the C−H bond, the reaction slows down or even stops. However, under hydrogen-rich conditions new adsorbed species emerge over the Rh/SiO_2

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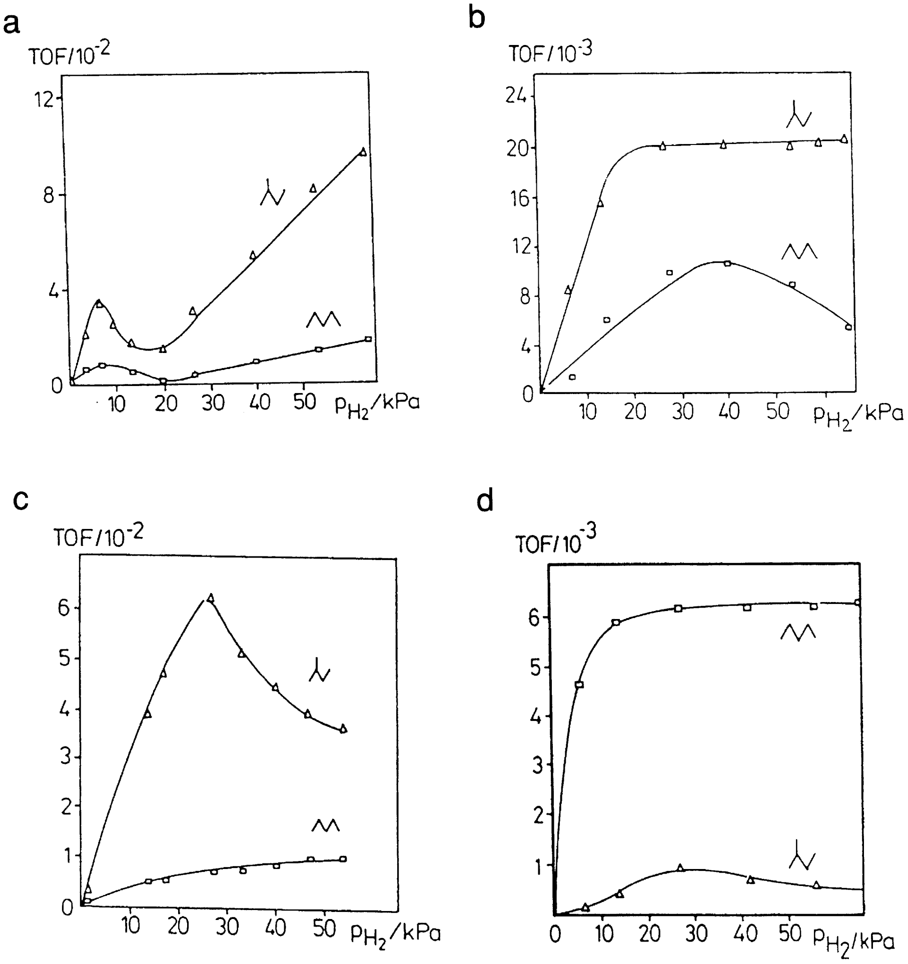

FIG. 1. Product formation rate (TOF: molecules/exp. atoms/s) vs hydrogen pressure in the hydrogenative ring opening of *t*DMCP over (a) Rh/SiO_2, (b) Pd/SiO_2, (c) Ni/SiO_2, and of *c*DMCP over (d) Cu/SiO_2.

catalyst, the formations of which are not influenced by hydrogen pressure. Here too, however, a hydrogen pressure increase helps product desorption (without hydrogen there is no ring opening). Adsorbed species not influenced by hydrogen are suggested to form via scission of the ring C–C bond.

The use of product formation vs hydrogen pressure curves for describing surface events for alkyl-substituted cyclopropane derivatives can be further justified by the findings of many authors (9, 10). It was found that cyclopropane and various alkyl-substituted cyclopropanes adsorb irreversibly, that is the ring opens on the first contact with the metal surface. It is also known that the introduction of alkyl substituents into the cyclopropane ring enhances the adsorption strength (10, 11).

Based on the above observations and considerations, let me propose that hydrogen pressure functions are useful for drawing mechanistic conclusions about the hydrogenative ring opening of cyclopropane and their alkyl-substituted derivatives even when the formation of both products is described with maximum or saturation type curves (see examples in (3–7) and especially Ref. (7) for the Pt/SiO_2 catalyst). However, this may be true only for a certain number (and size) of substituents, since the hydrogenative ring opening properties of the crowded 1,1,2,2-tetramethylcyclopropane may be described well by a Langmuir–Hinshelwood mechanism. An extension of the method to hydrogen related reactions of other compounds may work, but only after careful considerations.

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