Propane dehydrogenation on Cr_2O_3: kinetics and mechanism of the reaction and catalyst deactivation

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Highlights
- The complete mechanism of propane dehydrogenation on $Cr_2O_3(0001)$ is calculated using first-principles methods.
- Kinetic simulations reveal the reaction rates and the effect of varying conditions.
- Deactivation of the catalyst due to cracking and coke formation is kinetically described.
- Surface of the catalyst is initially covered with H*, but C* and CH_3CC* form upon coking.

Introduction
Despite the increased global demand for propylene, this important chemical is still most often produced in petroleum refineries with steam cracking and fluid catalytic cracking. Propane dehydrogenation is a viable alternative since it represent a more responsible and sustainable use of natural resources as opposed to its use as fuel. Industrially, propane dehydrogenation proceeds on chromium oxide supported on alumina (the Catofin® process), avoiding the use of critical or expensive raw materials (noble metals, rare-earth elements *etc.*). Although understood empirically [1,2], the reaction mechanism, kinetics and especially the nature of catalyst deactivation lack a clear theoretical explanation.

In this work, we devise a full reaction network of non-oxidative propane dehydrogenation on $Cr_2O_3(0001)$ using first-principles methods. First, all possible elementary reaction steps including adsorptions, desorptions, simple dehydrogenations, deep dehydrogenations and C-C bond breaking, have been investigated with density functional theory (DFT). No prior limitations as to the feasibility of the reactions were considered. Included were also all relevant cracking and coking reactions. After having obtained a complete potential energy surface for the reaction, extensive kinetic Monte Carlo simulations were carried out at different, industrially relevant conditions.

Methodology
The catalyst was modelled as a $Cr_2O_3(0001)$ surface of 12 alternating oxygen and chromium layers with the bottom six layers frozen to their bulk position with 15 Å of vacuum above the slab. Due to the limitations of DFT in describing the dispersion interactions, the Grimme D3 method was used. To account for strong correlation effects of the *3d* states of chromium, a GGA functional (PW91) was complemented with the Hubbard $+U$ correction (D–J = 4 eV). The dimer method was used to locate the transition states. The Kinetic Monte Carlo method was used to simulate the kinetics. The kinetic parameters were determined from the transition state theory from the DFT data. A lattice of 800 sites (a 20 x 20 configuration with 2 distinct sites per unit cell) sufficed for well converged results with ~10^7 events per simulation.

Selected Results

The dehydrogenation of propane over C_2O_3 has the apparent activation barrier of 1.37 eV, which is close to the experimental value of 1.47 eV. Subsequent dehydrogenation to propyne is ~10-times slower and has a larger activation barrier of 1.57 eV. Both reactions are first-order. Hydrogen, a by-product of the process, modestly slows down the reaction. Even at a considerable build-up of hydrogen in the reaction vessel (~50 %), the reaction is impeded by less than 20 %. This is the consequence of low hydrogen coverage, which stays well below 0.10 even at the highest investigated pressures (10 bar). Propane and propyne in the feed have a stronger inhibitory effect on the reaction rate. When keeping the partial pressure of propane constant, a co-presence of propene slows down the reaction for up to a factor of ~2.7. On the other hand propyne, on account of its stronger interaction with the catalyst, inhibits the reaction for up to two orders of magnitude and its surface coverage increases considerably. Both also decrease the selectivity. If the temperature is increased above 900 K, considerable coking occurs. This is due to an increased rate of the C-C bond breaking. Particularly susceptible to the breaking are $CH_3CH_2CH_2^*$, CH_3CHCH^* and $CH_3CCH_3^*$. First CH_3CC^* and later C^* begin to form on the catalyst, both representing mechanistic dead-ends, irreversibly poisoning the catalyst. The rate of deactivation can be described with Arrhenius parameters $A = 1.66 \cdot 10^{10}$ s^{-1} and E_a = 270 kJ mol^{-1}.
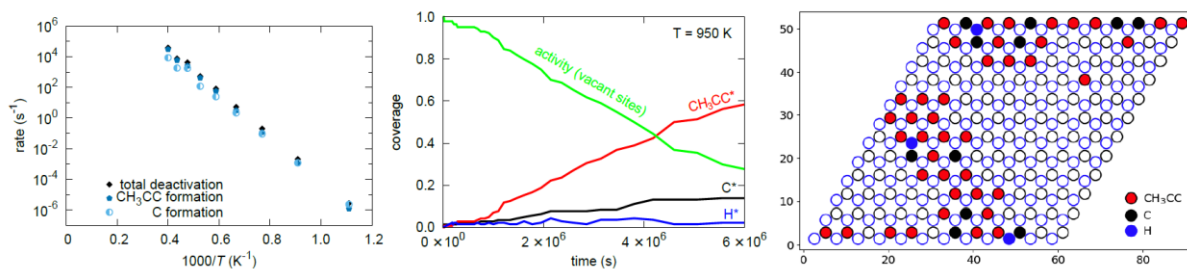

Figure 1. Arrhenius plot for catalyst deactivation at 5 bar propane (left), temporal evolution of the catalytic sur face at 950 K (centre), a lattice snapshot after $3 \cdot 10^6$ seconds (right).

Key Conclusions

Propane dehydrogenation mostly starts with an Eley-Rideal activation due to the weak interaction of propane with the catalyst. The reaction predominantly follows the most probable reaction route: C_3H_8 → $CH_3CHCH_3^*$ → CH_3CHCH_2 → $CH_3CCH_2^*$ → CH_3CCH. At elevated temperature, cracking occurs due to the reactions $CH_3CH_2CH_2^* → CH_3CH_2^* + CH_2^*$. Coking and a subsequent catalyst deactivation is the consequence of the build-up of C^* and CH_3CC^* on the surface. The deactivation rate is strongly dependent on the temperature and hinders the use of the catalyst above 900 K.

Literature Cited

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