DYNAMIC ACCUMULATION AS A TOOL FOR MATERIALS CHARACTERIZATION

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Dynamic Experiments reveal how the individual steps of the reaction mechanism work together: the sequence of steps, how fast each step proceeds and the dependence on concentration. It is difficult however to obtain temporal information regarding surface intermediates at reaction temperatures. The Temporal Analysis of Products (TAP) reactor is a unique experimental device which produces non-steady state gas information with millisecond time resolution [1, 2]. Recently, a new strategy for calculating dynamic rate and concentration from TAP exit flux data was developed [3, 4]. The time-dependence of the reactant and product gas phase reaction rates enables the calculation of dynamic accumulation on the active surface. This type of observation is new (in particular for atomic accumulation) and is more sensitive (nmol resolution) than microbalance or thermogravimetric methods.

In the decomposition of ammonia at 550 °C over polycrystalline iron, cobalt and a bimetallic preparation of the two, the dynamic accumulation is presented to understand how these materials regulate surface species. Within the dynamic pulse response experiment a region of quasi-steady state behavior was identified. In this region a constant value of atomic hydrogen and nitrogen species were observed, *Figure 1*A. From the observed H/N ratio different quasi-steady state assumptions were tested to reduce the complexity of the reaction mechanism. We found that ZNH and ZN were the most abundant surface species for cobalt material while the bimetallic preparation and iron samples supported ZNH_3 and ZN as the most abundant surface species. From quasi-steady state testing the reduced mechanism is deduced:

$NH_3 + Z \leftrightarrow ZNH_3$
$ZNH_3 \leftrightarrow ZNH + H_{2,fast}$
$2ZNH \leftrightarrow 2ZN + H_{2,slow}$
$2ZN \leftrightarrow N_2 + 2Z$

From the dynamic data we present rate constants of these simple reaction steps as a function of surface coverage, *Figure 1*A, B and C. This characterization, enabled by the observation of dynamic accumulation, provides a new tool for understanding why materials perform different at a global level.

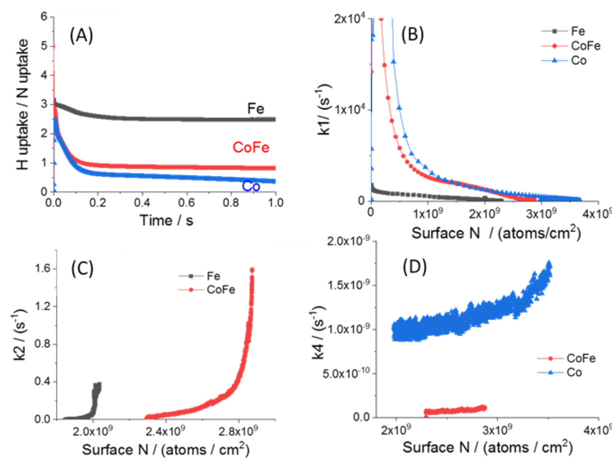

Figure 1: Pulse response experiments of ammonia decomposition at 550 °C in the TAP reactor over iron, cobalt and a bimetallic (CoFe) preparation. (A) Dynamic atomic accumulation of H and N species over different iron; (B) Rate constant for $NH_3 + Z \leftrightarrow ZNH_3$; (C) Rate constant $ZNH_3 \leftrightarrow ZNH + H_2$; (D) Rate constant for $2ZN \leftrightarrow N_2 + 2Z$; as a function of atomic nitrogen surface coverage.

References

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