Discrimination of Surface Storage and Mechanistic Pathways Using Dynamic Pulse Response Experiments

Supplementary Information

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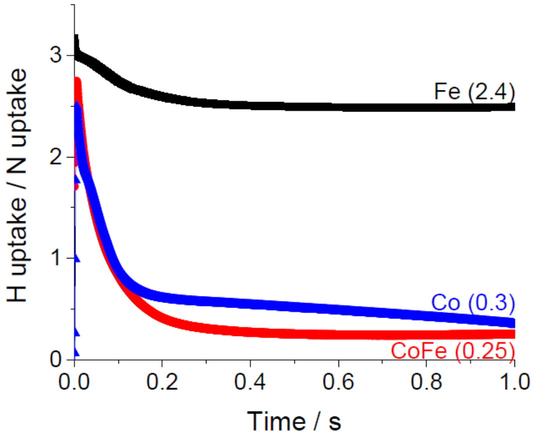
Exit flux is the experimental observable in the vacuum pulse response experiment. The Y-Procedure inverse diffusion method [1-3] is used to calculate the time-dependence of the rate, gas and surface concentration in the active catalyst zone. Dynamic atomic accumulation was calculated from experimentally observed gas concentrations and stoichiometry governing molecular species:

$$H^{Surface} = 3NH_3{}^{Gas} - 2H_2{}^{Gas}$$

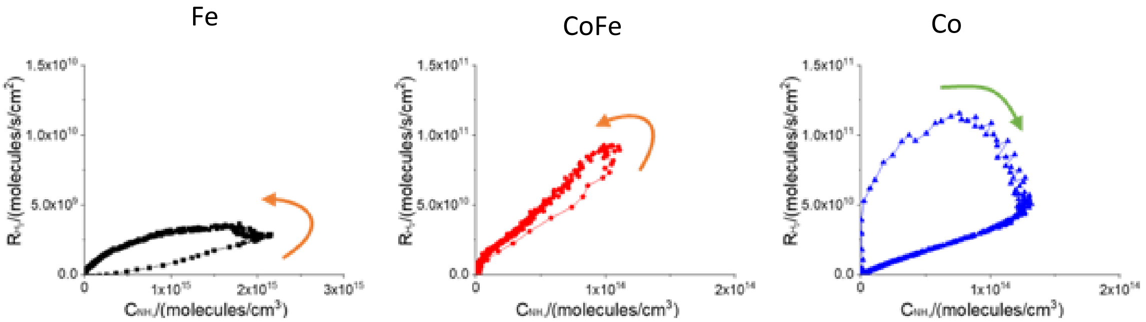
$$N^{Surface} = NH_3{}^{Gas} - 2N_2{}^{Gas}$$

When comparing the pulse response data of ammonia decomposition over Fe, Co and CoFe bimetallic materials, we observed a period of nonsteady state behavior followed by a region of coherent decline in the surface concentration of H and N species (a quasi-steady-state region) [4]:



The higher H/N ratio indicates Fe favors storage of hydrogenated species in comparison to Co and CoFe. This new type of measurement can be useful for benchmark comparison of a series of more complex catalyst preparations.

In the nonsteady state experiment the gas and surface concentrations are decoupled, their dependences can be used to understand microkinetic reaction phenomena. When examining the characteristics of the hydrogen transformation rate as a function of the ammonia gas concentration dynamic we conclude this process is dependent on the surface coverage of H species for Fe and dependent on the ammonia gas concentration for CoFe. On cobalt, however, two H_2 generation processes can be distinguished: one fast process, from direct decomposition of NH_3 and a second, slower process from the recombination of surface H species.



The rate constants of microkinetic reaction steps were quantified and used to build an understanding for why these materials perform differently at a global level:

	Fe	CoFe	Co
k_{NH_3} (1/s)	$4.8 \cdot 10^7$	$4.2 \cdot 10^9$	$3.5 \cdot 10^{10}$
k_{H_2} (1/s)	$1.43 \cdot 10^6$	$5.74 \cdot 10^8$	$7.96 \cdot 10^8$ (low-coverage) $2.3 \cdot 10^8$ (high-coverage)
k_{N_2} (1/s)	0	<0	$1.53 \cdot 10^7$
Active sites (molecules/cm^2)	$3.5 \cdot 10^8$	$2.2 \cdot 10^{10}$	N/A

References

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