Mechanism of NO_x Reduction with Acetaldehyde over Zeolite-Based Catalysts

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As reported by ***Peden*** et al. in 2001, reduction of nitrogen oxides with acetaldehyd e to N_2 is efficient over catalysts such as Ba/Y or Ba,Na/Y, where Y stands for the faujasi te zeolite Y. Nitrogen yields > 90% are achieved at 200°C, i.e. conditions that are compa tible with the emissions from automotive diesel engines. Most remarkably, no transition metal element is required for this redox catalysis. Our research objective has been to unra vel the mechanism of this multi-step reaction by combining FTIR spectroscopy, kinetic an alysis, flow reactor studies and isotopic labeling.

Since 1847, as first shown by ***Millon,*** it has been well known that ammonium nitri te easily decomposes to $N_2 + H_2O$**.** In 1931 ***Abel*** et al. demonstrated that strong acids cata lyze this process. For reductants other than ammonia, this low activation energy pathway becomes available only if ~ 50% of the NO_x is first reduced ***in situ*** to NH_3. Under diesel exhaust conditions such reduction requires a catalyst of high activity and extraordinary se lectivity.

Our results show that nitromethane is a crucial intermediate in the generation of a mmonia. It is formed from NO_x and acetaldehyde via two parallel reaction paths, one inv olving acetate ions, the other methyl radicals that combine with NO_2. Nitromethane is co nverted to formo-hydroxamic acid, CHO-NH(OH), via a dinitro-methane intermediate. T he steady state concentration of $CH_2(NO_2)_2$ or $O_2N\text{-}CH_2\text{-}NOOH$ is too low for spectrosco pic identification; the existence of such intermediates is, however, obvious from the fast i sotopic exchange of
$CH_3\text{-}^{14}NO_2$ with $^{15}NO_2$. The formo-hydroxamic acid swiftly loses H_2O, forming isocyanic acid, HNCO, which is subsequently hydrolyzed to $NH_3 + CO_2$. The chemistry leading to N_2 is then summarized as:

$$2NH_3 + NO + NO_2 + H_2O \Longrightarrow 2NH_4NO_2 \Longrightarrow 2N_2 + 4H_2O.$$

Adsorbed nitrate ions do not rapidly decompose at 200°C; they could block catalys t sites for nitrite ions. A crucial condition for the above reaction network to be operative at 200°C is, therefore, that nitrates are swiftly reduced to nitrites. Indeed, our data show t hat over Ba,Na/Y catalysts such reduction is efficient when NO is present.