



Selective catalytic reduction of NO with NH₃ on iron zeolite monolithic catalysts: Steady-state and transient kinetics

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ABSTRACT

An experimental study of steady-state and transient selective catalytic reduction (SCR) of NO with NH₃ on both commercial and in-house synthesized Fe-ZSM-5 (MFI type) monolith catalysts is presented. The reaction system was studied in a bench-flow reactor spanning a range of temperature, space velocity and washcoat thickness, affording an assessment of activity and selectivity, reaction pathways, temperature window, mass transport and pore diffusion effects. Experiments included NH₃ uptake and temperature-programmed desorption, steady-state and transient NO and NH₃ oxidation and standard SCR (NO + NH₃ + O₂) reaction studies. Differential kinetics studies were performed for the standard SCR reaction and NO oxidation reaction systems to determine reaction orders and activation energies. In the temperature range of 200–300 °C the standard SCR reaction was found to be nearly first-order and half-order with respect to NO and O₂, respectively, but moderately negative-order (−0.3) with respect to NH₃. Agreement in the kinetics for both reaction systems suggests that the oxidation of NO is the rate determining step, in line with recent literature studies. Rate inhibition by ammonia appears to be the result of blockage of NO oxidation reaction sites; a necessary step for the standard SCR reaction. Water is shown to inhibit the oxidation of NO significantly and of NH₃ to a moderate extent, while having only a negligible effect on the standard SCR reaction. A mechanistic-based kinetic model is proposed in which NH₃ reacts with surface bound NO₂ and nitrous acid via a NH₄NO₂ intermediate. A mechanism in which gaseous NO reacts with adsorbed oxygen (Eley Rideal like reaction) cannot be ruled out. In the absence of NH₃ these surface species inhibit the adsorption of NO and/or O₂ during NO oxidation. Both external mass transfer limitations and washcoat diffusion limitations were ruled out for moderate temperature conditions (≤300 °C). However, experiments on monoliths with different washcoat thicknesses conclusively show the appearance of washcoat diffusion limitations at higher temperatures.

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1. Introduction:

The mono- and di-oxides of nitrogen, NO and NO₂, commonly referred to as NO_x, are produced during the internal combustion of fuels. NO_x is a precursor of ground-level ozone, a primary constituent of urban air pollution. NO₂ may also react to form nitric acid and participate in the formation of fine particulate matter, both of which also pose health risks. As a result, the emission standards for NO_x from both stationary and vehicular sources are becoming more stringent.

While great strides have been made in the aftertreatment of vehicular pollutants, the elimination of NO_x from diesel vehicles is difficult. The primary reason is that diesel combustion is a fuel-lean process, so there is significant unreacted O₂ in the exhaust. The

reduction of NO_x to N₂ is poor when using conventional three-way catalysts (TWC) developed for stoichiometric gasoline vehicles. Several methods are at different stages of development that utilize advanced catalytic processes for abating diesel NO_x. These include NO_x storage and reduction (NSR) and selective catalytic reduction using ammonia as the reductant (SCR). A detailed review of the main features of NSR and SCR and associated modeling recently appeared [1]. The current paper focuses on kinetics and performance of SCR catalysis.

SCR is the most efficient aftertreatment technology for converting NO_x into molecular nitrogen in the presence of oxygen from the lean exhaust of stationary sources and vehicles. The two most common SCR catalysts in development for vehicular applications are Fe- and Cu-based zeolites [2,3]. The common point-source SCR catalyst, V₂O₅/TiO₂/WO₃, has insufficient activity at lower temperature and inadequate durability at higher temperatures for mobile applications (>400 °C). Both Cu- and Fe-exchanged ZSM-5 have attracted recent interest given their higher activity and lower cost.

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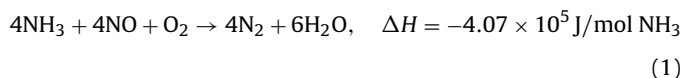
E-mail address: mharold@uh.edu (M.P. Harold).

Nomenclature

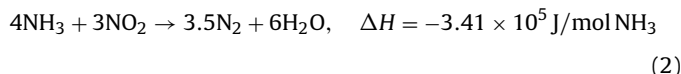
$A_{\Omega 1}$	channel cross-sectional area open to flow;
$A_{\Omega 2}$	washcoat cross-sectional area;
$P_{\Omega 1}$	channel perimeter open to flow;
D_f	diffusivity of a species in fluid phase;
D_e	effective diffusivity of a species in the washcoat;
$D_{e,c}$	effective diffusivity in the zeolite crystallite;
$R_{\Omega 1}$	effective transverse diffusion length scale;
$R_{\Omega 2}$	effective washcoat thickness;
$R_{\Omega 3}$	radius of a single zeolite crystallite particle;
τ_e	transverse diffusion or external mass transfer time;
τ_c	convection time;
$\tau_{d,w}$	characteristic diffusion time in the washcoat;
L	length of the monolith;
u	velocity;
r_{obs}	observed rate of reaction;
R_{SCR}	rate of standard SCR reaction;
R_{NO}	rate of NO oxidation reaction;
k_{eq}	equilibrium constant;
θ_v	mole fraction of vacant sites S_1 ;
σ_v	mole fraction of vacant sites S_2 ;
C_i	concentration of species i ;
ψ	Weisz-Prater modulus;

Cu-ZSM-5 has the higher of the two low temperature activities [4].

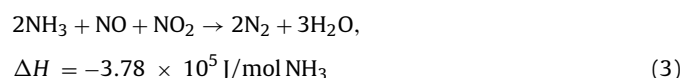
The overall SCR chemistry is generally well established and qualitatively similar for V_2O_5 - WO_3 /TiO₂, Cu-zeolite and Fe-zeolite catalysts. The NO_x emitted from diesel engines is mainly composed of NO, some of which is oxidized to NO₂ upstream of the SCR reactor. It is well established that the ammonia (obtained from urea hydrolysis) reacts with NO and NO₂ in the presence of O₂ at different rates. The reaction between NO and NH₃ involving O₂ is the “standard SCR” reaction and is given by



The reaction between NO₂ and NH₃ is given by



This reaction is sometimes called the NO₂ SCR reaction and has sometimes been referred to as the “slow SCR” reaction. In an historical context, the “slow” descriptor refers to the fact that its rate is typically slower than the reaction between NH₃ and an equimolar mixture of NO and NO₂, often referred to as the “fast SCR” reaction, which is given by

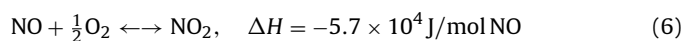


While each of the three overall reactions produces N₂ and H₂O as products, the mechanistic pathways are different.

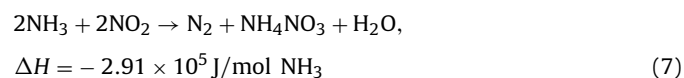
One must consider several side reactions that occur along with the standard, fast, and NO₂ SCR reactions. The extent of byproduct formation varies with the operating conditions such as the feed composition and temperature. The first is the oxidation of NH₃ by gas phase O₂ to either N₂ or N₂O:



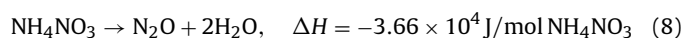
These reactions are undesired because they involve the consumption of the NH₃ reductant [5–11]. The oxidation of NO may also occur:



This reaction is desirable since NO₂ as a co-reactant with NO generally reacts faster with NH₃ [12–14]. The presence of NO₂ in the feed is mainly responsible for the formation of ammonium nitrate and N₂O [5,15]:



In the absence of NO₂, there is negligible formation of N₂O since the main route for its formation is via decomposition of ammonium nitrate:



An overall mechanistic picture has been proposed by Tronconi and coworkers [5,6,16,17] for the reduction of NO_x by NH₃ on vanadia-based catalysts. This picture explains differences in the reduction rate between the standard and fast reaction pathways. During the standard SCR reaction, the oxidation of reduced vanadia sites by gas phase O₂ is considered the rate determining step. The oxidized sites may also lead to the formation of NO₂, which is considered to react with vanadyl species, forming surface nitrates. These nitrates then react with adsorbed ammonia, forming N₂ or N₂O, the latter via NH₄NO₃. This pathway is distinctive to NO₂, and is faster than the standard pathway involving catalyst reoxidation and reaction with NH₃.

The kinetics of the V₂O₅-WO₃/TiO₂ catalyst are also fairly well established. The standard and fast SCR reactions are generally considered to involve reaction between adsorbed NH₃ and gas phase NO and/or NO₂; i.e. Eley-Rideal (ER) kinetics [18,19]. This is because ammonia binds more strongly than NO which has much less adsorption under similar conditions. Nova et al. [16,17] reported an inhibiting effect of ammonia on the standard SCR rate and proposed a redox kinetic model for the NO_x reduction on V-based catalysts. This feature was attributed to the blocking of active sites by spillover of NH₃ from adjacent adsorption sites. Other researchers [20,21] have proposed a Langmuir-Hinshelwood kinetics for the standard SCR reaction considering the co-adsorption of NO and NH₃ on the SCR catalyst.

Compared to the vanadia system, there have been fewer kinetic studies of the Fe-based zeolitic catalysts. Sjøvall et al. [11,22] presented a global kinetic model for SCR reaction over Cu-ZSM-5 and commercial Fe-zeolite monolith catalysts. Iwasaki et al. [21] reported kinetics for both standard and fast SCR reactions on Fe-ZSM-5 powder catalyst. Reaction orders of standard SCR reaction were 0.81–0.88 for NO, 0.29–0.34 for O₂ and –0.21 to –0.11 for NH₃. Following earlier results for the vanadia catalyst system, they proposed NO oxidation as the rate determining step during the standard SCR chemistry. Huang et al. [23] carried out similar studies on powdered Fe-ZSM-5 catalyst and reported that the SCR reaction orders are 0.88–0.94 for NO, 0.36–0.41 for O₂ and –0.15 to –0.11 for NH₃. Similar kinds of studies of reaction orders on other powder catalysts have been reported in the literature [24–26].

This work is a part of a larger project aimed at developing steady-state and transient kinetic models of SCR reactions taking place on zeolite-based monolithic catalysts. The objective of the current study is to carry out differential and integral flow reactor experiments of NH₃ based SCR of NO on Fe-ZSM-5 monolith catalysts. As mentioned, most previous studies involved powder catalysts and only a few reports of kinetics have appeared. In addition to reporting apparent reaction orders and activation energies for the standard SCR and NO oxidation reactions, we reconcile key reaction

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