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A “Nitrate Route” for the low temperature “Fast SCR” reaction over a V_2O_5–WO_3/TiO_2 commercial catalyst

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A novel mechanism is proposed for the Fast SCR reaction of NH_3, NO and NO_2 at low temperature involving the formation of ammonium nitrate as intermediate and its subsequent reaction with NO as the rate determining step.

A key feature in the development of SCR catalysts for automotive applications is the enhancement of the DeNOx activity at low temperature. The standard SCR process is based on the following reaction between NH_3 and NO:

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (1)$$

In the early ′80s Kato and co-workers[1] found that the reaction involving an equimolar NO and NO_2 feed, with stoichiometry

$$2\ NH_3 + NO_2 + NO \rightarrow 2\ N_2 + 3\ H_2O \qquad (2)$$

is considerably faster than reaction (1). The importance of the so called Fast SCR reaction (2) has recently much increased, since the possibility to install an oxidation precatalyst upstream of the SCR catalyst, thus incrementing the NO_2/NO_x feed ratio, provides a chance to boost the low temperature deNOx activity of SCR devices for automotive exhaust after-treatment.

In the last few years Koebel, Madia and co-workers have extensively investigated the Fast SCR reaction over $V_2O_5/WO_3/TiO_2$ catalysts, both in powder and in monolith form.[2–6] Concerning the catalytic mechanism, they reported reactivity and spectroscopic experiments showing that NO_2 enhances the reoxidation of vanadia, regarded as the rate determining step of the SCR reaction at low temperatures.[5] Accordingly, they proposed that the Fast SCR should be considered as a standard SCR reaction in which NO_2 plays the role of a more efficient oxidizer for the vanadium sites than oxygen. However, no direct kinetic evidence was offered to prove that the enhanced rate of V^{4+} reoxidation can explain the order-of-magnitude enhancement of the DeNOx rate observed in the presence of equimolar mixtures of NO/NO_2. Besides, this picture does not account for the greater complexity of the chemistry resulting from addition of NO_2 to the SCR reacting system. In fact, on studying the reactivity of the $NH_3/NO/NO_2$ system over V-based catalysts at 150 °C, Koebel *et al.*[6] reported the occurrence of two main reactions not observed with NH_3/NO, namely the formation of NH_4NO_3 from NH_3 and NO_2,

$$4\ NH_3 + 4\ NO_2 \rightarrow 2\ NH_4NO_3 + 2\ N_2 + 2\ H_2O \qquad (3)$$

and the redox decomposition of NH_4NO_3 by NO,

$$2\ NH_4NO_3 \Leftrightarrow 2\ NH_3 + 2\ HNO_3 \qquad (4.a)$$

$$NO + 2\ HNO_3 \rightarrow 3\ NO_2 + H_2O \qquad (4.b)$$

[Reaction (4) is the sum of reactions (4.a) and (4.b)]

$$2\ NH_4NO_3 + NO \rightarrow 3\ NO_2 + 2\ NH_3 + H_2O \qquad (4)$$

According to Koebel *et al.*, reactions (3) and (4) occurred in addition to the Fast SCR, reaction (2). However, we notice that the combination of reactions (3) and (4) already fully accounts for the selective reduction of NO + NO_2 by NH_3: reaction (3) selectively reduces half of NO_2 directly to N_2, the remaining half being converted to nitrate species; such nitrate species can react with NO to form more NO_2 according to the redox reaction (4); the extra formed NO_2 can then react further with more NH_3 according to (3), thus completing the selective reduction of NO_x to N_2. Notice in fact that the sum of reactions (3) and (4) formally results in the stoichiometry of reaction (2). Based on this picture, given an equimolar mixture of NH_3 and NO_x, with $NO/NO_2 = 1/1$, we expect the following situations depending on the relative rates of reactions (3) and (4): a) if (3) is faster than (4), we shall observe the formation/build-up of ammonium nitrate, with only a limited occurrence of the “Fast SCR”, *i.e.* only a partial reduction of NO_x to N_2: this is the situation actually observed by Koebel *et al.*[6] at low temperatures (150 °C); b) if (4) is faster than (3), no formation of NH_4NO_3 will be detected, ammonium nitrate acting as a reactive intermediate, and the occurrence of the “Fast SCR” reaction (2) will be apparently observed, resulting in reality from the simultaneous occurrence of (3) and (4): this is in line with the data reported by Koebel *et al.* at higher temperatures.[6]

We present herein transient low-T reaction experiments performed with $NH_3/NO/NO_2$ mixtures over a powdered commercial V/W/TiO_2 SCR catalysts (160 mg) in a quartz microreactor while analysing the outlet gas concentration profiles by a mass spectrometer, taking into account the response factors and the overlapping fragmentation patterns of all the relevant species.[7] The experiments herein reported were designed to address the role of reactions (3) and (4) in the catalytic mechanism of the Fast SCR reaction. 1% water was added to the feed stream, whereas no oxygen was included in the feed to simplify the mechanistic interpretation: in fact preliminary experiments proved that the O_2 effect on the results herein reported is negligible.

Fig. 1 shows a composite transient response run at 170 °C: in a stream of He and 1% H_2O 1000 ppm of NO_2 were first admitted to the reactor (phase A). Upon step addition of 1000 ppm NH_3 (phase

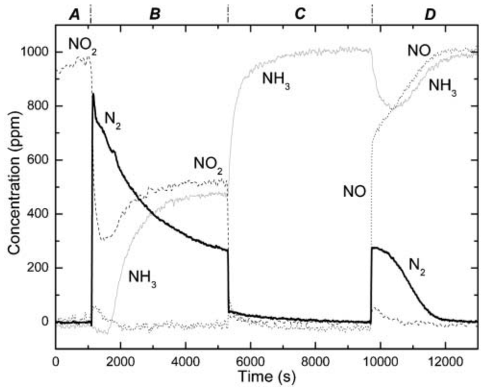

Fig. 1 Ammonium nitrate formation and subsequent decomposition by NO. $T = 170$ °C; GHSV = 90000 h^{-1}; H_2O = 1% in He.

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B), NO_2 and NH_3 were seen to react with formation of N_2. At the end of phase B about 490 ppm of NO_2 and 520 ppm of NH_3 were converted while 250 ppm of nitrogen were produced, in line with the stoichiometry of NH_4NO_3 formation, reaction (3). The build-up of NH_4NO_3 upon the catalyst was confirmed by IR analysis of a catalyst sample discharged immediately after phase B.

After the build-up of NH_4NO_3 on the catalyst obtained by co-feeding NO_2 and NH_3 at 170 °C for about 1 hour (phase B in Fig. 1), the NO_2 feed was shut down at $t = 5300$ s: correspondingly the ammonia level increased to 1000 ppm and nitrogen was no longer detected (phase C): in these conditions no reaction took place. At $t = 9800$ s 1000 ppm of NO were admitted to the reactor: conversion of both NO and NH_3 was readily observed along with the corresponding formation of N_2 (phase D), both phenomena however progressively decaying with time. This is explained observing that according to reaction (4) NO can react with the previously deposited ammonium nitrate producing NO_2 and NH_3. We propose however that NO_2 and NH_3 further react in turn according to (3) to give N_2 and ammonium nitrate. Considering the excess of NH_3 present during phase (D), and assuming reaction (3) to be faster than (4), the following scheme applies:

$$2\ NH_4NO_3 + NO \rightarrow 3\ NO_2 + 2\ NH_3 + H_2O \qquad (4)$$

$$3\ NH_3 + 3\ NO_2 \rightarrow 3/2\ NH_4NO_3 + 3/2\ N_2 + 3/2\ H_2O \qquad (3)$$

[Reaction (5) is the sum of reactions (3) and (4)]

$$1/2\ NH_4NO_3 + NO + NH_3 \rightarrow 3/2\ N_2 + 5/2\ H_2O \qquad (5)$$

Indeed the evolution of NH_3, NO and N_2 in phase D of Fig. 1 agrees exactly with the stoichiometry of (5): NO and ammonia signals are nearly overlapped giving evidence of an equimolar consumption, and eventually rise from about 800 ppm to 1000 ppm, *i.e.* their feed concentration, upon complete depletion of the deposited ammonium nitrate. NO_2 concentration is practically negligible throughout phase D. The N_2 signal exhibits a maximum specular to NH_3, and then decreases as NH_4NO_3 is progressively converted. Notice that the nitrogen peak is of about 300 ppm, being associated with a consumption of 200 ppm of NH_3 and NO, in accord with reaction (5). We emphasize that the overall experiment of Fig. 1 resulted in the conversion of $NH_3 + NO_2 + NO$ to N_2, and this clearly occurred *via* formation/decomposition of ammonium nitrate.

In a dual experiment (not shown), performed at 140 °C, NO alone was admitted to the reactor after NH_4NO_3 build-up. As a consequence, production of NO_2 was observed and no NH_3 was detected. Without excess ammonia in fact the expected reaction scheme, (4) + (3), yields:

$$NH_4NO_3 + NO \rightarrow NO_2 + N_2 + 2\ H_2O \qquad (6)$$

Both the schemes above mentioned suggest that at $T \leqslant 170$ °C reactions (3) and (4) occur sequentially, with reaction (3) significantly faster than (4).

While the data in Fig. 1 agree with the assumption of nitrate intermediates for the Fast SCR reaction (2), one could still speculate that the behavior observed in phase D of Fig. 1 is explained by the reaction of NO with deposited NH_4NO_3, reaction (4), followed by an "independent" Fast SCR, reaction (2). For this to apply, however, the Fast SCR, reaction (2), should be much faster than reaction (4), otherwise a net production of NH_3 and NO_2 should be detected.

In order to compare the rates of reactions (2), (3) and (4), more transient runs were performed in the simultaneous presence of NH_3, NO and NO_2. Fig. 2 presents a typical experiment where 1000 ppm of NH_3 were fed to the reactor at 170 °C (phase A), then 500 ppm of NO and 500 ppm of NO_2 were added to the feed stream (phase B). At the end of phase B 450 ppm of NH_3, 110 ppm of NO, 340 ppm of NO_2 were consumed producing 330 ppm of N_2. These levels are in agreement with the simultaneous occurrence of the Fast SCR reaction (2), which converted 220 ppm of NH_3, 110 ppm of NO and 110 ppm of NO_2 generating 220 ppm of N_2, and the reaction of NH_4NO_3 formation (3), which consumed the remaining 230 ppm of ammonia and 230 ppm of NO_2 producing 110 ppm of nitrogen. This means that during phase B ammonium nitrate was being accumulated onto the catalyst; at the same time the Fast SCR was progressing to an extent directly reflected by the NO conversion level.

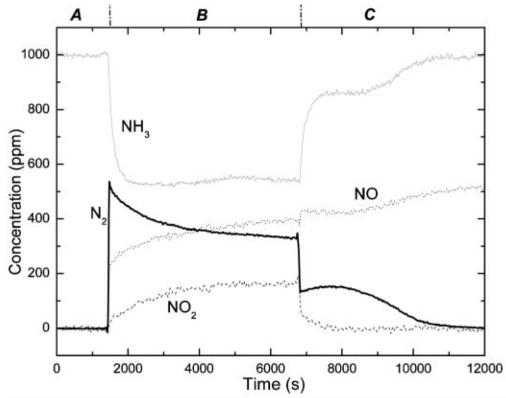

Fig. 2 Rate comparison between Fast SCR (2) and reaction of NH_4NO_3 with NO (4): $T = 170$ °C; GHSV = 90000 h^{-1}; $H_2O = 1\%$ in He.

During the second part of the run, phase C in Fig. 2, the NO_2 feed was shut down thus stopping nitrate formation. Nevertheless NH_3 and NO consumption as well as nitrogen production were still noticed, in analogy with what observed in Fig. 1, phase D: this indicates the occurrence of reaction (4) between the stored nitrate and NO. The most important result shown in Fig. 2 is that the NO conversion level remained practically unaltered† in going from phase B to phase C: this proves that the Fast SCR (during phase B) and the reaction between NO and NH_4NO_3 (during phase C) progressed at the same rate, which rules out the hypothesis that reaction (2) is consecutive to the nitrate decomposition, reaction (4). On the contrary, this result is strongly suggestive of a scheme where the Fast SCR, reaction (2), results from the sum of reactions (3) and (4), reaction (4) acting as the rate determining step at the investigated low temperatures. According to this picture, thus, ammonium nitrate is not a terminal species, but behaves as an intermediate of the Fast SCR reaction.

Sachtler and co-workers[8,9] recently proposed a nitrite intermediate for the Fast SCR reaction but ruled out a route *via* nitrate because of the well known stability of NH_4NO_3. However this conclusion does not consider the possibility of a reaction between NH_4NO_3 and NO, which in this work was demonstrated to be active over a V/W/TiO_2 catalyst already at low temperature.

Notes and references

† The small increase in the NO concentration level could be explained by the influence of NH_3 concentration on the equilibrium (4.a): during phase C the increment of the ammonia concentration shifts the equilibrium to the left causing a decrease of the available HNO_3, inhibiting reaction (4.b).

1 A. Kato, S. Matsuda, T. Kamo, F. Nakajima, H. Kuroda and T. Narita, *J. Phys. Chem.*, 1981, **85**, 4099.
2 M. Koebel, M. Elsener and G. Madia, *Ind. Eng. Chem. Res.*, 2001, **40**, 52.
3 G. Madia, M. Koebel, M. Elsener and A. Wokaun, *Ind. Eng. Chem. Res.*, 2002, **41**, 3512.
4 G. Madia, M. Koebel, M. Elsener and A. Wokaun, *Ind. Eng. Chem. Res.*, 2002, **41**, 4008.
5 M. Koebel, G. Madia, F. Raimondi and A. Wokaun, *J. Catal.*, 2002, **209**, 159.
6 M. Koebel, G. Madia and M. Elsener, *Catal. Today*, 2002, **73**, 239.
7 C. Ciardelli, I. Nova, E. Tronconi, B. Konrad, D. Chatterjee, K. Ecke and M. Weibel, *Chem. Eng. Sci.*, 2004, DOI: 10.1016/j.ces.2004.07.016.
8 Q. Sun, Z. Gao, B. Wen and W. M. H. Sachtler, *Catal. Lett.*, 2002, **78**, 1.
9 Y. H. Yeom, B. Wem, W. M. H. Sachtler and E. Weitz, *J. Phys. Chem. B*, 2004, **108**, 5386.