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The Mechanism of Reduction of NO with H₂ in Strongly Oxidizing Conditions (H₂-SCR) on a Novel Pt/MgO–CeO₂ Catalyst: Effects of Reaction Temperature¹

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Abstract—Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments using on-line Mass Spectrometry (MS) and in situ Diffuse Reflectance Infrared Fourier-Transform Spectroscopy (DRIFTS) have been performed to study essential mechanistic aspects of the Selective Catalytic Reduction of NO by H₂ under strongly oxidizing conditions (H₂-SCR) in the 120–300°C range over a novel 0.1 wt % Pt/MgO–CeO₂ catalyst. The N-path of reaction from NO to the N₂ gas product was probed by following the ¹⁴NO/H₂/O₂ \longrightarrow ¹⁵NO/H₂/O₂ switch (SSITKA-MS and SSITKA-DRIFTS) at 1 bar total pressure. It was found that the N-pathway of reaction involves the formation of two active NO_x species different in structure, one present on MgO and the other one on the CeO₂ support surface. Inactive adsorbed NO_x species were also found on both the MgO–CeO₂ support and the Pt metal surfaces. The concentration (mol/g cat) of active NO_x leading to N₂ was found to change only slightly with reaction temperature in the 120–300°C range. This leads to the conclusion that other intrinsic kinetic reasons are responsible for the volcano-type conversion of NO versus the reaction temperature profile observed.

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1. INTRODUCTION

In order to meet strict emission regulations, removal of NO_x from stationary polluting sources, such as power plants, industrial boilers and furnaces, gas turbines, biomass incinerators, and gasifiers is required [1]. The SCR of NO_x with the use of ammonia (NH_3 – SCR) was first introduced in the early 1970s [1], and since then it has become a widely practiced NO_x control technology in many industrial combustion facilities [2]. However, many problems are encountered in the use of NH_3 –SCR technology [2, 3], namely NH_3 -slip (emissions of unreacted toxic NH_3), catalyst deterioration, ash odor, fouling of air heaters, and a high running cost.

Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) under strongly oxidizing conditions has been extensively studied and reported as recently reviewed [4–6]. However, the latter technology exhibits several problems such as catalyst deactivation in the presence of H₂O and SO₂ and low N₂-selectivities at $T < 200^{\circ}$ C [7]. Moreover, in the case of external addition of HC for NO_x control of stationary polluting sources, the excess of HC required results in polluting the environment with HC or CO₂, if the former is burnt [8]. These drawbacks could be considered as the main reasons for the HC-SCR technology not yet being able to become commercially available.

The today's emerging needs for the development and use of green technologies that lead to reduced emissions of CO₂ and NO_x demand that suitable non-carbon-containing reducing agents for the catalytic elimination of NO_x from industrial flue gas streams, preferably at low temperatures ($T < 200^{\circ}$ C), be found. In this direction we have focused our efforts over the past few years on the development of novel catalytic systems for the selective catalytic reduction of NO_x by hydrogen (H₂-SCR) [9–14]. Until full transition to a hydrogen economy and zero emissions of greenhouse gases are achieved, the H₂-SCR can be considered as a breakthrough NO_x control technology in favor of the present NH₃-SCR.

In the present work, important kinetic and mechanistic aspects of the H₂-SCR of NO towards N₂ have been investigated over the novel 0.1 wt % Pt/MgO– CeO₂ catalyst [12–14] by SSITKA experiments (use of ¹⁵NO) coupled with Mass Spectrometry and DRIFTS. In particular, the chemical structure of adsorbed *active* and *inactive* (spectators) NO_x species and the surface

¹ The text was submitted by the authors in English.



Fig. 1. (a) SSITKA–DRIFTS spectra recorded over the 0.1 wt % Pt/MgO–CeO₂ catalyst after 30 min of 14 NO/H₂/O₂/Ar (—) and 15 NO/H₂/O₂/Ar (- -) reaction at 120°C; (b) Deconvolution of the SSITKA–DRIFTS spectra recorded in the 1400–1150 cm⁻¹ range.

concentration of *active* NO_x under H₂-SCR working conditions in the 120–300°C range were determined.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation and Characterization

The catalyst support consisting of MgO and CeO₂ was prepared via the sol-gel method according to the experimental procedures reported elsewhere [15]. Mg(EtO)₂ (Aldrich) and Ce(NO₃)₃ · H₂O (Aldrich) were used as metal precursors of Mg and Ce, respectively, so as to yield 50 : 50 (w/w) MgO : CeO₂. The supported-Pt catalyst (0.1 wt % Pt/MgO–CeO₂) was prepared by the incipient wetness impregnation method using the H₂Pt(IV)Cl₆ (Aldrich) metal precursor. After water evaporation and drying overnight at 120°C, the solid residue was ground and calcined in air at 600°C for 2 h. Prior to any experiment, the catalyst sample was

calcined in $5\%O_2$ /He at $600^{\circ}C$ for 2 h and then reduced in $10\%H_2$ /He at $300^{\circ}C$ for 2 h.

2.2. Transient Mass Spectrometry Studies

Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments following the switch 14 NO/H₂/O₂/Ar/He (30 min, T) \rightarrow 15 NO/H₂/O₂/He (t, T) were conducted in a specially designed transient gas-flow system and a quartz microreactor [16, 17]. The amount of catalyst used was 0.15 g, and the total flow rate was 30 NmL/min. An on-line quadrupole mass spectrometer (MS) (Omnistar, Balzers) was used for the chemical analysis of the gas effluent stream from the reactor. Standard gas mixtures were used for calibrating the signals obtained by MS. The H₂-SCR feed gas mixture consisted of 0.25 vol% NO, 1 vol % H₂, and 5 vol % O_2 and He as the balance gas.

2.3. Transient DRIFTS Studies

In situ DRIFTS spectra were obtained using a Perkin-Elmer GX FTIR spectrophotometer (resolution of 2 cm^{-1}) coupled with high temperature/high pressure temperature controllable DRIFTS cell (Harrick Scientific) equipped with ZnSe IR windows. We used 30 mg of solid catalyst in powder form, and the total flow rate of feed gas was 50 NmL/min. For FTIR single-beam background subtraction, the IR spectrum of the solid was recorded in Ar flow. DRIFTS spectra were collected at the rate of 1 scan/s in the 3000–800 cm⁻¹ range and then analyzed using the instrument's Spectrum for Windows software. IR absorption bands due to adsorbed NO_x were assigned based on well-documented literature [18–20, 22].

3. RESULTS AND DISCUSSION

3.1. SSITKA–DRIFTS Studies

The chemical structure of the active NO_x species participating in the nitrogen reaction path of the H₂-SCR of NO was determined by SSITKA-DRIFTS experiments. Initially, DRIFTS spectra were recorded after 30 min of reaction in ¹⁴NO/H₂/O₂. The feed stream was then switched to the equivalent isotopic ¹⁵NO/H₂/O₂ gas mixture, and DRIFTS spectra were recorded after 30 min of reaction. Figure 1 shows DRIFTS spectra recorded over the 0.1 wt % Pt/MgO- CeO_2 catalyst at 120°C in the 2000–1150 cm⁻¹ range as explained above. The IR bands that shifted to lower wave numbers after the isotopic switch correspond to active adsorbed intermediate NO_x species formed during the NO/H₂/O₂ reaction that eventually lead to N_2 and N₂O [20]. After appropriate deconvolution and curve fitting of the range of the spectrum (see Fig. 1a, vertical dotted lines) where an isotopic shift was noticed [20], it was found that two IR bands shifted from 1560 to 1540 cm^{-1} and from 1250 to 1210 cm^{-1}



Fig. 2. Deconvolution of the SSITKA–DRIFTS spectra recorded in the 2450–2000 cm⁻¹ range over the 0.1 wt % Pt/MgO–CeO₂ catalyst for the H₂-SCR at 120°C. Thick solid line: 14 NO/H₂/O₂; dashed line: 15 NO/H₂/O₂.

(see Fig. 1b). These IR bands correspond to the asymmetric and symmetric vibrational modes, respectively, of bidentate nitrates (NO_3) formed on MgO [20], after performing similar SSITKA-DRIFTS studies on 0.1 wt % Pt/MgO and 0.1 wt % Pt/CeO₂ catalysts. In Fig. 1b the spectrum obtained under $^{14}NO/H_2/O_2$ reaction conditions was best deconvoluted by two IR bands centered at 1370 and 1310 cm⁻¹, and two IR bands centered at 1250 cm⁻¹. The former two bands correspond to nitrito and/or chelating nitrite (NO_2^-) species [18–20, 22] which are considered as inactive NO_x intermediates since no red isotopic shift was observed. One of the two IR bands centered at 1250 cm⁻¹ corresponds to an active bidentate nitrate species (dotted curve) as discussed above, whereas the second IR band (solid curve) corresponds to an inactive species but the same in structure (different location on the support). The latter assignment is based on recent transient DRIFTS-H₂ reaction experiments to be reported elsewhere [21]. It was found that not all bidentate nitrates (1250 cm⁻¹ IR band) were able to be reduced by hydrogen (no further change in the band integral intensity was observed after 10 min in H₂/Ar mixture). This result was explained as due to the limited distance of H diffusion on the MgO support surface [21]. As the reaction temperature increased above 200°C, the chemical structure of the active NO_x formed on MgO was that of chelating nitrite (NO₂⁻) [20, 21].

Figure 2 presents the IR spectrum obtained in the 2450-2000 cm⁻¹ range over the 0.1 wt % Pt/MgO-CeO₂ catalyst under the ¹⁴NO/H₂/O₂ feed gas mixture and its deconvolution into three IR bands. The IR band centered at 2220 cm⁻¹, which corresponds to one of the three IR bands obtained after deconvolution, was the only one shifted to 2180 cm⁻¹ at the isotopic switch (Fig. 2). This band corresponds to an active nitrosyl NO^+ species coadsorbed with nitrate (NO_3^-) species on adjacent cerium cation-oxygen anion sites on the ceria support [20]. The same result was also obtained at higher reaction temperatures (up to 300°C). The other two IR bands obtained after deconvolution, which do not give the isotopic shift, about 2360 and 2120 cm^{-1} . correspond to the asymmetric vibrational mode of adsorbed NO₂⁺ and NO⁺, respectively on MgO and/or CeO₂ support surface [19, 20, 22]. The latter species appear, therefore, to be considered as inactive reaction intermediates of the H₂-SCR of NO.

3.2. SSITKA–Mass Spectrometry Studies

The surface concentration of the *active* NO_x reaction intermediates of the H₂-SCR in the 120–300°C range were determined by SSITKA–MS experiments. Figure 3



Fig. 3. Transient response curves of ${}^{14}N_2$, ${}^{14}N^{15}N$, and Ar obtained following the isotopic switch ${}^{14}NO/H_2/O_2$ (*T*, 30 min) \longrightarrow ${}^{15}NO/H_2/O_2$ (*T*, *t*) at 120°C (a) and 300°C (b) over the 0.1 wt % Pt/MgO–CeO₂ catalyst.

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Fig. 4. Concentration (μ mol/g, curve 2) and surface coverage (θ , curve 1) of active NO_x that lead to N₂ as calculated from SSITKA–MS experiments.

presents transient isotopic response curves of N₂ obtained after the switch ¹⁴NO/H₂/O₂ (30 min) \rightarrow ¹⁵NO/H₂/O₂ (*t*) at 120°C (Fig. 3a) and 300°C (Fig. 3b). The results are expressed in terms of the dimensionless concentration Z, which corresponds to the fraction of the ultimate change (giving Z = 0) as a function of time. Thus, Z is defined by

$$Z(t) = \frac{y(t) - y_{\infty}}{y_0 - y_{\infty}}.$$
 (1)

The subscripts 0 and ∞ refer to the values of y (mole fraction) at the time of isotopic switch (t = 0) and long after that $(t = \infty)$. The decay of Ar gas concentration (Fig. 3) was used to monitor the gas phase holdup of the system [20]. As seen in Fig. 3, the ¹⁴N-containing isotopic product is mainly ¹⁴N¹⁵N (very little ¹⁴N₂ was produced by the catalyst after comparing ${}^{14}N_2$ and Ar responses). As the reaction temperature increases, two peaks in the ¹⁴N¹⁵N response curve are seen clearly (Fig. 3b). This result reflects the different reduction kinetics of the two active NO_x species, the nature of which depends on the reaction temperature (see Section 3.1). The concentration of active NO_x that truly participates in the nitrogen reaction path to form N₂ gas was calculated by integrating the transient response curves of ${}^{14}N^{15}N$, and that of ${}^{14}N_2$ with respect to the Ar curve. The results obtained in terms of mol/g and surface coverage (θ) as a function of reaction temperature are shown in Fig. 4. The surface coverage θ is referred to the exposed surface Pt atoms (mol Pt/g). Values of θ greater than unity indicate that at least part of the active NO_x cannot reside on Pt. Figure 4 shows that in the whole temperature range of $120-300^{\circ}$ C, θ takes values significantly larger than unity. On the other hand, only a slight change in the concentration of active NO_x with reaction temperature is noticed. Thus, the

volcano-type of activity versus reaction temperature profile reported in previous works [11, 13, 14] cannot be explained by the results of Fig. 4. It is suggested that the significant combustion of H₂ at temperatures higher than 150°C [13, 14] and the partial oxidation of Pt crystallites are the main reasons for this behavior.

4. CONCLUSIONS

The following conclusions related to the H_2 -SCR of NO over the Pt/MgO–CeO₂ catalyst can be derived from the results of the present work:

(a) The active NO_x intermediate species were found to be formed on the MgO and CeO_2 support, whereas their chemical structure was found to depend on reaction temperature (120–300°C).

(b) The concentration (mol/g) of the active NO_x intermediate species that lead to N_2 formation was found to be practically independent of the reaction temperature (120–300°C) and significantly larger than one equivalent monolayer of surface Pt. The former result cannot explain the volcano-type behavior of the catalytic activity versus the reaction temperature observed [13, 14, 21].

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