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Routes of formation and composition of NO_x complexes adsorbed on palladium-promoted tungstated zirconia

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Abstract

Surface species obtained during the adsorption of NO and NO/O_2 coadsorption at room temperature on Pd-free (WZ) and Pd-promoted tungstated zirconia (Pd/WZ) are identified by means of in situ FT-IR spectroscopy. The WZ and Pd/WZ samples have a tetragonal structure and contain randomly distributed mesoporous phase. Dispersed palladium(II) species are present in two different environments: (i) Pd^{2+} ions, which have only Zr^{4+} ions in their second coordination sphere and (ii) Pd^{2+} ions, which are linked to both zirconium and tungsten ions via oxygen bridges. On the Pd/WZ sample, NO undergoes oxidation to various NO_x species depending on the temperature. The compounds formed at room-temperature oxidation are adsorbed N_2O_3 and products of its self-ionization, NO^+ and NO_2^-. In this process W(VI) is involved, being reduced to W(IV). At high temperature N_2O_3 decomposes, restoring the W=O species. Under these conditions, NO undergoes oxidation to NO_2 by the Pd(II) ions, which are reduced to Pd(I). The nitrosyls of Pd(I) display high thermal stability and do not disappear upon evacuation at 623 K. During NO/O_2 coadsorption on the Pd/WZ catalyst at room temperature, the amounts of surface nitrates and NO_2/N_2O_4 formed in the gas phase are significantly lower than those observed under identical conditions in the presence of tungstated zirconia. It is concluded that promotion of tungstated zirconia with palladium(II) suppresses the oxidation of NO by molecular oxygen at room temperature due to the elimination of acidic protons involved in the process.

Keywords: NO adsorption; NO/O_2 coadsorption; NO_x adsorbed species; FT-IR spectroscopy; WO_3–ZrO_2; Pd/WO_3–ZrO_2

1. Introduction

Reduction of NO with CH_4 in the presence of oxygen (CH_4-SCR) is an attractive strategy for control of the exhaust from gas engines or turbines fueled with natural gas. Since the first report of Li and Armor [1] on Co-exchanged ZSM-5 catalysts, various zeolites containing transition and non-transition metals have been shown to be active in this reaction [2]. Palladium-exchanged H-ZSM5 and H-Mor catalysts are more attractive because they appear to be less sensitive to steam [3–7]. Nishizaka and Misono [8,9] first reported a high activity of Pd-exchanged H-ZSM-5 catalysts and indicated the direct involvement of protonic acid sites in both palladium dispersion and the mechanism of the CH_4-SCR of NO. Nowadays, it is widely accepted that the Brønsted acid sites of the zeolite are needed to keep palladium(II) highly dispersed and active [4,5,10–20] although the structure of the palladium species (isolated Pd^{2+} ions [10–15] versus highly dispersed PdO [16–20]) is still matter of discussion.

The use of zeolite-based catalysts for the CH_4-SCR of NO presents important drawbacks due to their low thermal stability and deactivation by water or SO_2. It has been shown that simple oxides with strong acidity, such as sulfated and tungstated zirconia, possess the ability to stabilize highly dispersed Pd(II) species analogous to the acidic zeolites [11,12,21–23]. Low-loading palladium catalysts supported on sulfated and tungstated zirconia exhibit catalytic properties in the CH_4-SCR of NO under dry conditions comparable to those of zeolitic catalysts and they show improved selectivity in the presence of H_2O and SO_2 [21–24].

Tungstated zirconia is thermally stable [25] and emerges as a good candidate for the replacement of zeolitic materials.

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Maximum activity in the CH_4-SCR of NO is observed on zirconia catalysts containing up to 16–20 wt.% WO_3 and 0.1–0.17 wt.% Pd [21–24]. Tungstated zirconia is usually prepared by impregnation of hydrated zirconia with ammonium metatungstate, followed by calcination in the 873–1100 K range [25–29]. High density of strong acid sites can also be achieved by simultaneous coprecipitation with ammonia from solutions containing zirconium oxychloride and ammonium metatungstate [30].

Dispersed palladium species on tungstated zirconia have been identified by the appearance of two bands at 1868 and 1821 cm^{-1} in the IR spectra of adsorbed NO [22,23]. Similar bands have been observed on Pd-H-ZSM-5 and Pd-H-Mor and have been attributed to nitrosyls formed on isolated Pd^{2+} ions [3,5,16,17]. Other authors [31] have concluded, based on low-temperature CO adsorption, that the oxidation state of palladium deposited on tungstated zirconia is +3.

Since the dispersion of Pd(II) is favored by non-microporous materials [12], in this study we used Pd-free and Pd-promoted tungstated zirconia containing mesoporous phase. By means of in situ FT-IR spectroscopy we have identified the surface species, obtained during the adsorption of NO and NO/O_2 coadsorption on these materials. The samples have been characterized by XRD and DR-UV–vis spectroscopy. The localization of the Pd^{2+} species on the surface of tungstated zirconia has been studied by room-temperature adsorption of CO. The interaction of the surface NO_x complexes with methane can throw a light about the potentials of Pd-promoted tungstated zirconia containing mesoporous phase as a catalyst for the reduction of NO and the mechanism of the reaction. The results of this study will be reported separately.

2. Experimental

2.1. Sample preparation

Tungstated zirconia (notation WZ) was prepared by coprecipitation of aqueous solutions of $ZrOCl_2{\cdot}8H_2O$ (Merck) and ammonium metatungstate (Aldrich) with ammonia using polyvinyl alcohol (Aldrich) as a template according to a procedure described in detail in the literature [32]. The gel obtained was dried at 473 K for 24 h in air. The dried material was heated for 2 h at 673 and 923 K in an inert atmosphere (carbonization steps) followed by calcination at 773 K for 5 h. After fusion with $KHSO_4$ and dissolution in deionized water, the tungsten content was determined spectrophotometrically at $\lambda = 402$ nm using $TiCl_3$, $SnCl_2$ and NH_4SCN as chromogenic agents [33,34]. The WZ sample contained 18.6 wt.% WO_3.

The zirconia was synthesized by the same method [32], without the addition of ammonium metatungstate solution. The final carbonization temperature was 873 K. After that the material was calcined at 773 K for 5 h.

Palladium-promoted tungstated zirconia was prepared impregnating the WZ sample with a solution of $Pd(NO_3)_2{\cdot}2H_2O$ (Merck-Schuchardt) ensuring 0.1 wt.% of nominal palladium content. The sample was dried and calcined at 773 K for 5 h. For this sample the notation Pd/WZ is used.

The physico-chemical characteristics of the materials are summarized in Table 1.

2.2. Surface area measurements, X-ray diffraction and DR-UV–vis spectroscopy

The BET surface areas of the samples (dehydrated at 523 K) were measured by nitrogen adsorption at 77 K using a Monosorp apparatus from Quantachrome. XRD analysis was performed on a Rigaku Miniflex diffractometer with Ni-filtered Cu Kα radiation under ambient conditions. Crystallite sizes were calculated from the peak broadening of principal peaks with the Scherrer formula [36]. DR-UV–vis spectra were obtained under ambient conditions with a fiber optic spectrometer AvaSpec-2048 (Avantes) using WS-2 as a reference.

2.3. FT-IR spectroscopy

The FT-IR spectra were recorded on a Bomem MB 102 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} (128 scans). The self-supporting discs were activated in the IR cell by heating for 1 h in a vacuum at 773 K, and in oxygen (13.3 kPa, passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 773 K. A specially designed transmission IR cell (Xenonum Scientific, USA) equipped with BaF_2 windows allowed recording of the spectra at elevated temperatures. The sample holder of the cell can be moved up and down relative to the light beam, giving the possibility of recording the gas phase spectrum. All of the FT-IR spectra presented (except those in Fig. 3A) were obtained by subtracting the spectra of the activated samples from the spectra recorded.

The CO (99.95%, BOC) used was passed through a trap cooled by liquid nitrogen before admission to the IR cell. The purity of the NO gas was 99.9% (Air Products).

Table 1
Physico-chemical characteristics of the samples

Sample	BET surface area (m^2/g)	WO_3[a] (wt.%)	Pd[b] (wt.%)	WO_3 (nm^2)	WO_3 coverage[c] (monolayer)
ZrO_2	96	–	–	–	
WZ	153	18.6	–	2.6	0.5
Pd/WZ	145	18.6	0.1	2.7	0.5

[a] Analytical content.

[b] Nominal content.

[c] Estimated by using the maximum packing density of planar WO_3 species of 0.21 g WO_3/100 m^2 [35].