

Effect of oxygen concentration on the NO_x reduction with ammonia over V₂O₅–WO₃/TiO₂ catalyst

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Available online 4 January 2006

Abstract

The catalytic reduction of NO_x in the typical operation temperatures and oxygen concentrations of diesel engines has been studied in the presence of V₃W₉Ti in a tubular flow reactor. The results have shown that the selective catalytic reduction is strongly affected by the oxygen concentration in low temperature range (150–275 °C). At higher temperatures, the reaction becomes independent of the O₂ concentration. The rate of the selective catalytic reduction of NO with ammonia may be considerably enhanced by converting part of the NO into NO₂. DRIFT measurements have shown that NH₃ and NO₂ are adsorbed on the catalyst surface on the contrary of NO. The experiments have shown that the decrease in N₂ selectivity of the SCR reaction is mainly due to the SCO of ammonia and to the formation of nitrous oxide.

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Keywords: SCR; Oxygen concentration; Ammonia oxidation; N₂O; Side reactions; DRIFT

1. Introduction

The new generation of diesel engines (common-rail with direct injection) allows one to achieve very high energetic efficiency and quite limited pollutant emissions: both carbon monoxide and unburned hydrocarbons outlet concentrations are in fact lower than those produced in spark ignition engines. However, diesel engines produce specific pollutants that are hazardous for human health: primarily particulate, dangerous due to its potential mutagenic and carcinogenic activity, and nitrogen oxides, which are well-known promoters of acid rain phenomenon and of the so-called photochemical smog. For these vehicles, three-way catalysts are useless due to net-oxidizing conditions of their exhaust streams. NO_x is a by-product of high temperature and high pressure combustion of fuel in air. Its primary component in internal combustion engine exhaust is NO.

The exhaust temperature of a diesel engine is lower, and there are more little HCs remaining in the exhaust compared with a gasoline engine.

On the other hand, diesel engine exhaust contains heavy HCs which are harder to use as a NO_x reducing agent, along with SO₂ that causes catalytic deactivation. These conditions have thwarted practical application of HC–SCR technology to diesel engines.

The selective catalytic reduction (SCR) of nitrogen oxides with N-containing reducing agents is presently considered as the most promising technique for the removal of NO_x from lean exhaust gases of automotive engines. Urea is the preferred reducing agent for toxicological and safety reasons. It can be considered as a solid storage compound for ammonia [1].

Vanadium oxide catalysts are currently used because of their resistance to poisoning by SO₂ and their high activity at low temperatures. Nevertheless, there is still an open area for investigation concerning the use of these catalysts in high oxygen concentration because of the side reactions where N₂O may be formed. Selectivity to N₂O is particularly undesirable because N₂O is approximately 200 times worse than CO₂ as a green house gas and in the upper atmosphere it interferes with ozone.

Specific aims of this study were: for the prepared V₂O₅–WO₃/TiO₂ catalyst, to evaluate the relative contributions of the selective reduction of NO_x and the ammonia oxidation reaction to product formation under different oxygen concentrations (2–6–10–15 vol.%).

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2. Experimental

2.1. Catalyst preparation

The V_2O_5 – WO_3 /TiO₂ has been prepared by the sol–gel method using titania(IV)-bis ethylacetoacetato-isopropylat ($C_{18}H_{32}O_8Ti$, Fluka Chemicals Inc., $\geq 95\%$) as precursor for TiO₂, vanadyl(IV) acetylacetonat ($VC_{10}H_{14}O_5$, Fluka Chemicals Inc., $\geq 97\%$) as precursor for V_2O_5 and NH_4 metatungstate hydrate ($H_{26}N_6O_{41}W_{12}$ aq) as precursor for WO_3 . Acetyl acetone (0.7 g), ethylene glycol (5 g) and water (0.72 g) were added to the ternary mixture. After stirring the mixture for ca. 15 min at ambient temperature, the excess solvent was removed by a first drying on an evaporator at 70 °C followed by an overnight drying at 120 °C. The catalysts were subsequently calcined in air at 400–800 °C for 2 h.

The ternary catalyst contains 3 wt.% V_2O_5 and 9 wt.% WO_3 . WO_3 is employed in larger amount (9 wt.%), it acts both as chemical and structural promoter by enlarging the temperature window of the SCR reaction and by improving the mechanical, structural and morphological properties of the catalyst [2].

BET measurements were performed with a quantochrome autosorb 1C using nitrogen.

X-ray diffraction patterns were obtained with a siemens D-500 powder X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in step mode between 20° and 80°, using a step size of 0.02 step/s.

Mesopores distribution measurements have been obtained by mercury penetration method using a porosimeter Autopore III.

DRIFT measurements were performed with an ATi Mattson Galaxy 5020 FTIR spectrometer.

2.2. Activity measurements

Catalytic activity measurements have been carried out in a quartz tubular fixed bed reactor (i.d. 30 mm). The catalyst V3W9Ti was a coated type (200 mg) supported on a cordierite monolith having a cell density of 64 cells/cm² and a volume of 9.4 cm³. The composition of the feed was 500 ppm NO, 500 ppm NH₃, with varying the oxygen concentration (2, 6, 10 and 15 vol.% O₂). The N₂ being a carrier gas (total flow rate = 2000 ml/min). K-type thermocouples provided the exhaust temperature before the catalyst. The temperature of all gas lines was kept at 150 °C.

Activity data have been collected at different temperatures in the range 150–500 °C, each temperature was maintained until steady-state conditions were reached. The NO_x content have been determined with a CLD 700 EL ht Chemiluminescence detector. NH₃ and N₂O were analysed with non-dispersive IR spectrometry with a siemens Ultramat 5E and Binos 4b.1 devices, respectively. The results of the catalytic tests performed over V3W9Ti catalyst are shown in terms of NO_x conversion $X_{NO_x} = 1 - ([NO_x]_{out}/[NO_x]_{in})$ and N₂ selectivity $S_{N_2} = [N_2]/([N_2] + [N_2O])$, respectively.

Table 1
Morphological properties

Catalyst	T_{calc} (°C)	S_g (m ² /g)	Phase	D_c (Å)	V_p (cm ³ /g)	$r_{p,exp}$ (Å)
V3W9Ti	400	115	A	265	0.036	16.6
	500	77	A	319	0.289	20
	600	22	A	579	0.248	23.2
	800	–	R	783	–	–

The moles of N₂ can be determined from the following atomic nitrogen balance:

$$N_{2out} = (1/2)([NO_x]_{in} - [NO_x]_{out}) + (1/2) \times ([NH_3]_{in} - [NH_3]_{out}) - N_2O_{out}$$

3. Results and discussion

3.1. Characteristics of the prepared catalyst

Table 1 shows the surface area (S_a), the phase composition, the mean crystallite dimensions (D_c) (calculated from XRD measurements), the pore volume (V_p) and the mean pore radius (r_p) obtained from the experimental pore size distribution.

Up to the calcination temperature of 600 °C, the samples of V3W9Ti are monophasic and only anatase polymorph of TiO₂ ($2\theta = 25.3$ – 38 – 48°) is detected. The surface area decreases as the calcination temperature increases. The mean pore radius increases and the pore volume decreases. The anatase to rutile phase transformation ($2\theta = 27.5$ – 36 – 54.5°) is detected starting from 700 °C and is complete at 800 °C (Fig. 1).

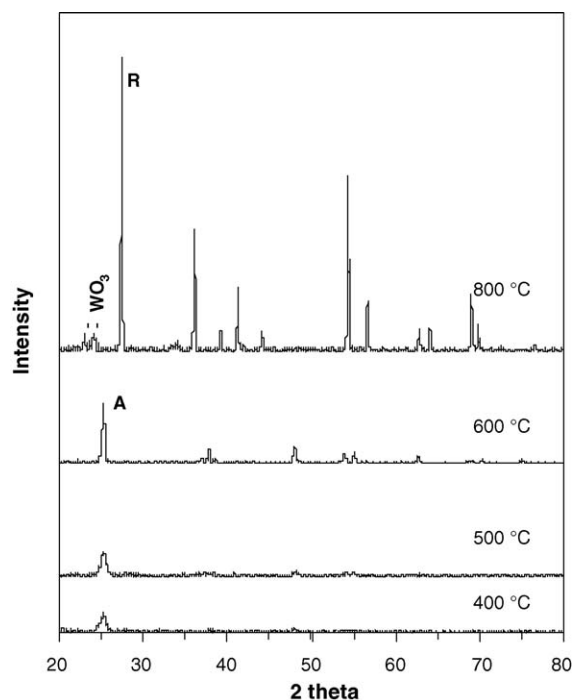


Fig. 1. X-ray powder diffraction patterns of V3W9Ti calcined from 400 to 800 °C.

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