A comparative study of the selective catalytic reduction of NO by propylene over supported Pt and Rh catalysts

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Abstract

The catalytic performance of Pt and Rh catalysts for the selective catalytic reduction (SCR) of NO by propylene in the presence of excess oxygen has been investigated over catalysts supported on six different metal oxide carriers (CeO_2, Al_2O_3, TiO_2, YSZ, ZrO_2 and W^{6+}-doped TiO_2). It has been found that the nature of the dispersed metal affects strongly the light-off temperature of propylene, the maximum NO conversion to reduction products and the selectivity towards nitrogen. For a given support, Pt catalysts are always more active for both NO reduction and propylene oxidation, but are much less selective towards N_2, compared to Rh catalysts. Rhodium catalysts are able to selectively reduce NO even in the absence of oxygen in the feed. However, their activity is suppressed with increasing oxygen feed concentration possibly due to the formation of less reactive rhodium oxides. In contrast, oxygen promotes the *de*-NO_x activity of platinum catalysts but decreases selectivity towards nitrogen. Results are explained by considering the effects of the nature of the metallic phase and the support on the elementary steps of the propylene-SCR reaction. It is concluded that the catalytic performance of both metals may be improved by proper selection of the support.
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1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by hydrocarbons (HC) has received worldwide attention as a potentially effective method for the elimination of NO_x in the exhaust gases of lean-burn and diesel fueled vehicles [1–4]. The reaction has been studied extensively over zeolite catalysts in the presence of excess oxygen and has given promising results in terms of high activities for NO reduction and relatively wide temperature windows of operation [5–8]. The main disadvantage of zeolite-based catalysts, which limits their potential use in practical applications, is their poor hydrothermal stability. Metal oxide catalysts supported on base oxides, such as alumina [9–12], have also attracted attention due to their high activity and hydrothermal stability, but are active at relatively high temperatures and an inhibition effect is usually observed in the presence of SO_2 [13,14]. Supported noble metals catalysts, in particular platinum group metals (PGM), seem to be the most promising candidates for the HC-SCR of NO_x because of their high reduction activity at relatively low temperatures [1–4,15], their enhanced resistance against SO_2, compared to the metal oxide catalysts [16,17], and their tolerance towards steam [18]. Among the noble metal catalysts investigated, platinum is the most active at low temperatures and, therefore, widely studied. However, Pt-based catalysts are characterized by low selectivity towards N_2, which is typically less than 30%. In contrast, Rh-containing catalysts exhibit superior behavior as far as selectivity to N_2 is concerned but require higher operating temperatures, compared to Pt [3,15,16].

Concerning the mechanism of the HC-SCR reaction of NO_x over supported PGM catalysts under lean-burn conditions, several schemes have been proposed, which have been recently reviewed [11,19]. Most researchers agree that the reaction involves dissociative adsorption of NO on the active metal sites followed by recombination of the adsorbed species to yield N_2 or N_2O [11,19–21]. The chemical state of the noble metal under reaction conditions seems to play a crucial role because active sites for NO dissociation are believed to be reduced surface atoms, such as Pt^0 or Rh^0 [2,3,22–24]. The role of the reductant

is to scavenge adsorbed oxygen atoms and regenerate the catalytically active sites. According to other mechanisms, adsorbed NO_2 or other intermediates, such as organo-nitro and related species [25–27], play an important role in the *de*-NO_x reaction. Experimental evidence has also been provided for the intermediacy of cyanide (–CN) and/or isocyanate (–NCO) surface species [28–31].

In our previous studies, we have investigated in detail the reduction of NO by CO [23,24,28,32] over Rh catalysts as well as the SCR of NO by propylene over Rh [22,33–35] and Pt [36] catalysts. In the present work, the effects of the nature of the active metallic phase (Pt and Rh) and the support (CeO_2, TiO_2, $TiO_2(W^{6+})$, YSZ, ZrO_2 and Al_2O_3), and also of the oxygen feed concentration on the catalytic performance for the title reaction are investigated. Results are used to extract information related to the mechanism of the reaction over Pt and Rh catalysts, to elucidate the chemical state of the active metal sites and to identify the parameters which determine catalytic activity and selectivity.

2. Experimental

Catalysts were prepared employing the wet impregnation method [36] with the use of $(NH_3)_2Pt(NO_2)_2$ or $Rh(NO_3)_3 \cdot 2H_2O$ as metal precursor salts and the following commercial metal oxide powders as supports: Al_2O_3, TiO_2, CeO_2, YSZ and ZrO_2. Titanium dioxide doped with W^{6+}-cations, denoted in the following as $TiO_2(W^{6+})$, has been also used as catalyst support. This material was prepared by the method of solid-state diffusion, using TiO_2 P-25 (Degussa) and $(NH_4)_{12}W_{12}O_{41} \cdot 5H_2O$ (Alfa) as starting materials. Diffusion of the dopant cation into the crystal matrix of TiO_2 has been achieved by calcination of the sample at 900 °C, following a procedure which has been reported previously [35]. The nominal metal loading of all catalyst samples thus prepared was 0.5 wt.%. The specific surface area of the supports has been determined employing nitrogen physisorption at the temperature of liquid nitrogen (BET method). Metal dispersion and mean crystallite size were obtained employing H_2 chemisorption (CO chemisorption for Pt/CeO_2) at room temperature, following a procedure described elsewhere [36]. Results of catalyst characterization are summarized in Table 1. It should be noted that the chemisorption capacity of Pt is significantly suppressed when it is supported on TiO_2 doped with higher valence cations (e.g. W^{6+}), compared to undoped TiO_2, whereas

the opposite is true for Rh ([37] and Refs. therein). This may explain the relatively low values of Pt dispersion estimated for $Pt/TiO_2(W^{6+})$ and the relatively high values of Rh dispersion estimated for $Rh/TiO_2(W^{6+})$, compared to Pt/TiO_2 (Table 1).

The catalytic performance of the prepared samples for the SCR of NO by propylene was investigated in the temperature range of 150–550 °C using a feed composition consisting of 0.1% NO, 0.1% C_3H_6 and 5% O_2 (balance He). The effects of inlet oxygen partial pressure on catalytic activity and selectivity have been investigated with the use of variable feed compositions containing 0–10% O_2. In all cases, the mass of catalyst loaded to the quartz reactor was 60 mg and the total volumetric flow rate was 200 cm³/min ($W/F = 0.018$ g s cm^{-3}). On-line analysis of reactants and products was accomplished with the use of a gas chromatograph (Shimadzu GC-9A) and a NO/NO_x analyzer (Teledyne 911/912). Chromatographic separation of N_2, O_2 and CO has been achieved using a molecular sieve 5A column while N_2O, C_3H_6 and CO_2 were analyzed using a Porapak-Q column. The concentrations of NO and NO_2 at the effluent of the reactor were continuously monitored with the use of the NO_x analyzer. High purity reaction gases were obtained from Meisser-Griesheim. Details on the apparatus and procedures employed can be found elsewhere [35,36].

3. Results

3.1. De-NO_x performance of Pt and Rh catalysts under lean-burn conditions

Typical results of catalytic performance tests obtained over Al_2O_3-supported Pt and Rh catalysts are presented in Fig. 1A and B, respectively, where the conversions of NO (X_{NO}) and C_3H_6 ($X_{C_3H_6}$) as well as the yields of N_2, N_2O and NO_2 are plotted as functions of reaction temperature. It is observed that conversion of propylene over Pt/Al_2O_3 catalyst (Fig. 1A) increases sharply with increasing reaction temperature above ca. 200 °C and reaches completion at ca. 265 °C. This is accompanied by a parallel increase of the yields of N_2 and N_2O which pass through maxima at ca. 270 °C, i.e., at temperatures somewhat higher than the light-off temperature of propylene, defined here at the temperature at which $X_{C_3H_6}$ exceeds 90%. Under these conditions, conversion of NO to reduction products (N_2 and N_2O) reaches a maximum value of 34% and then progressively decreases upon further increase of temperature.

Table 1
Characteristics of the supported Pt and Rh catalysts investigated

Support material		Pt catalysts (0.5 wt.%)		Rh catalysts (0.5 wt.%)	
Metal oxide	Specific surface area (m²/g)	Pt dispersion (%)	Mean Pt crystallite size (Å)	Rh dispersion (%)	Mean Rh crystallite size (Å)
CeO_2	3	46	22	43	25
Al_2O_3	83	60	17	80	13
TiO_2	50	85	12	88	12
YSZ	12	64	16	100	10
$TiO_2(W^{6+})$	15	30	34	100	10
ZrO_2	4	65	15	35	31