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ScienceDirect

Catalysis Communications 9 (2008) 664–669

CATALYSIS COMMUNICATIONS

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NO conversion in presence of O_2, H_2O and SO_2: Improvement of a Pt/Al_2O_3 catalyst by Zr and Sn, and influence of the reducer C_3H_6 or C_3H_8

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Received 2 April 2007; received in revised form 2 July 2007; accepted 25 July 2007
Available online 1 August 2007

Abstract

The aim of this work was to improve the SCR activity of a Pt/Al_2O_3 model catalyst by ZrO_2 (20 wt%) and/or SnO_2 (2 wt%) addition. The activity of the catalysts was measured in lean mixture containing C_3H_6 or C_3H_8, O_2, H_2O, CO_2 and SO_2 (0–700 ppm).

With propene, ZrO_2 and SnO_2 addition improve the optimal NO_x conversion (near 250 °C) and decrease the corresponding N_2O selectivity, especially with SO_2 in the feed stream (sulfated catalysts). For higher temperatures, the NO_x conversion decrease is associated with the formation of nitric acid at the reactor outlet (25% nitrate selectivity at 300 °C). With propane, the NO_x conversion is only attributable to the formation of nitric acid, no significant reduction was observed.

Keywords: SCR; C_3H_6; C_3H_8; SO_2; Pt; SnO_2; ZrO_2

1. Introduction

The standards of rejection of the atmospheric pollutants become more and more severe. If the gas mixture contains a large excess of oxygen (e.g. lean-burn gasoline and diesel engines or incinerators), the NO_x reduction in N_2 becomes difficult. Moreover, for some industrial applications, the exhaust gas can contain large amounts of SO_2, until several hundreds ppm. In these conditions, the use of a NO_x-trap catalyst [1] is not possible, because of its high sensitivity to deactivation by sulfate formation [2,3]. Then, the NO_x selective catalytic reduction (SCR) is one possible way to treat these gases [4,5]. Usually, the process involves the NO_x reduction with ammonia or urea [6,7] but there is a risk of ammonia emission. Other reducers like hydrogen [8,9] or carbon monoxide [10] can be used, but they react preferentially with oxygen [11]. Hydrocarbons can lead to interesting results particularly with propene and propane. The optimum NO_x reduction temperature window is narrow but the temperature can be controlled more easily in fixed sources.

NO_x reduction with hydrocarbons was extensively studied on noble metals as on oxides. Platinum is one of the best metallic phases for this reaction but the undesirable N_2O formation can be high [12], depending of the metal dispersion [13] and support acidity [14,15]. The commonly used platinum on alumina catalyst can be further promoted by a wide range of metals and/or oxides [16–18].

A sulfating step or the presence of SO_2 in the mixture can lead to different effects on the NO_x conversion, depending on the catalyst composition and the reducer.

For instance, with alkanes as reducers, a positive effect of sulfating is generally observed. Hamada et al. [19] have pointed out a promoting effect of sulfating for single oxides catalysts such as Al_2O_3, TiO_2 and ZrO_2, in the case of the SCR with propane. The beneficial sulfating treatment of ZrO_2-based catalysts is claimed by several authors. Li et al. have investigated the catalytic performance of

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doi:10.1016/j.catcom.2007.07.034

numerous promoted zirconia samples (Co, Mn, In, Ni) for the SCR of NO with methane. They found that Co exhibited the highest promoting effect on the activity of sulfated zirconia catalysts [20], whereas non-sulfated Co/ZrO_2 was inactive. Positive effects of sulfating were also observed on Ga/ZrO_2 with propane and methane as reducer [21], on Ag/Al_2O_3 [22] with propane, and on Pt/Al_2O_3 with *iso*-butane [23]. On platinum, a decrease of N_2O formation was also observed. On the contrary, Burch et al. [4] have observed an inhibition of the NO SCR with C_3H_8 on a sulfated Pt/Al_2O_3 catalyst which was attributed to the sulfate formation on alumina. In the case of the C_3H_8-SCR, a high SO_2 tolerance of a pre-sulfated 1% Pt/Al_2O_3 catalyst was found by addition of 2% Sn on the catalyst [24].

The results can also be varied with alkenes as reducer. The presence of 20 ppm SO_2 increases the activity of a Ir/SiO_2 catalyst for NO reduction with C_3H_6 [25] while a In/Al_2O_3 catalyst [26,27] is inhibited by SO_2 (100 ppm). On Ag/Al_2O_3, different results were obtained with propene as reducer since a promoting effect of SO_2 was observed by Angelidis et al. [28] while some authors claimed the opposite [29–31]. In opposition with the C_3H_8-SCR results, Burch and Walting [4] have observed no inhibition of SO_2 for the C_3H_6-SCR of NO with a sulfated Pt/Al_2O_3 catalyst. However, the SO_2 resistance of Sn was also demonstrated with propene as reducer [32].

Then, contradictory results can be found in the literature about the SO_2 impact on the NO SCR. They can be attributed to different protocols (steady-state measurement or continuous increase of the temperature from room temperature) and different reaction mixtures. Often, they are not always fully representative, with no CO_2 and especially with no water in the feed stream. Moreover, there is no study with high SO_2 contents as it can be found in some industrial applications.

The aim of this work was to improve the SCR activity of a Pt/Al_2O_3 catalyst tested under severe conditions, with a lean mixture containing C_3H_6 or C_3H_8, O_2, H_2O, CO_2 and SO_2 (0–700 ppm). Thus, the Pt/Al_2O_3 catalyst was modified by ZrO_2 (20 wt%) and/or SnO_2 (2 wt%), both being promising promoting compounds.

2. Experimental

2.1. Catalyst preparation

The Pt/ZrO_2/Al_2O_3 catalyst (noted Pt/ZrAl) was prepared using the following method. A γ-alumina powder (BET surface area: 102 $m^2\,g^{-1}$) was impregnated with a solution of $Zr(O(CH_2)_3CH_3)_4$, in order to obtain 20 wt% ZrO_2 on alumina. After drying at 120 °C for 12 h, the powder was calcined at 600 °C for 4 h in synthetic air. The resulting ZrO_2/Al_2O_3 support was then impregnated with a $Pt(NH_3)_2(NO_2)_2$ solution in order to obtain 1 wt% Pt. For the bimetallic Pt–Sn/ZrO_2/Al_2O_3 catalyst (noted Pt–Sn/ZrAl), the ZrO_2–Al_2O_3 support was co-impregnated with H_2PtCl_6 and $SnCl_4$ solutions in order to obtain 1 wt% Pt and 2 wt% Sn, respectively. After drying and calcination (600 °C, 4 h), the catalyst was reduced at 450 °C for 4 h under pure H_2, and finally activated at 600 °C for 4 h under a 10% H_2O–N_2 mixture. Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts (noted Pt/Al and Pt–Sn/Al, respectively) were prepared following the same way. The BET area of Pt/Al, Pt/ZrAl, Pt–Sn/Al and Pt–Sn/ZrAl are 104, 103, 94 and 88 $m^2\,g^{-1}$, respectively. These catalysts are named fresh catalysts.

In the sulfating process, the catalyst sample was exposed to a 700 ppm SO_2, 5% O_2, 5% H_2O, 10% CO_2 and N_2 mixture at 500 °C for 1 h. Then, the sample was treated at 500 °C under a 10% O_2, 10% H_2O and N_2 mixture for 30 min in order to eliminate the platinum sulfates. Chemical analysis of the samples before and after the sulfating treatment did not show significant changes in platinum and tin loading. The sulfur content was evaluated by H_2 temperature programmed reduction (TPR) from room temperature up to 800 °C. Assuming that one sulfate needs four H_2 ($*\text{-SO}_4 + 4H_2 \rightarrow *\text{-S} + 4H_2O$ or $*\text{-SO}_4 + 4H_2 \rightarrow *\text{-O} + H_2S + 3H_2O$, where $*$ is an adsorption site), the TPR comparison between fresh and sulfated catalysts allows to calculate the sulfur content. Results are summarized in Table 1. Note that (i) the theoretical sulfur content is 2 wt% if all the sulfur were deposited, (ii) same results are obtained after 4 h under the sulfating mixture and (iii) the sulfur content after test is not significantly modified.

The increase of the sulfating rate with ZrO_2 addition is attributed to stronger basic sites on zirconia compared to alumina. The H_2-TPR profile of Pt/Al exhibits a maximum near 460 °C, whereas it is shifted to 540 °C for Pt/ZrAl. The decrease of the sulfur content after Sn addition seems to be linked to the decrease of the specific area (−12% and −14%, respectively).

2.2. Catalytic activity measurements

Catalytic activity was measured using a fixed bed reactor. The reaction gas mixture contained 1000 ppm NO, 1000 ppm C_3H_6 or C_3H_8, 5% O_2, 5% CO_2, 5% H_2O and SO_2 (0–700 ppm) diluted in N_2. The total flow rate was 10 L h^{-1} and GHSV = 10,000 h^{-1}.

Prior to each experimental run, the catalyst was pretreated in-situ under 5% O_2, 5% CO_2, 5% H_2O and N_2 for 30 min at 500 °C. After cooling, the catalytic activity was measured by steps of 25 °C or 50 °C from 200 °C to 400 °C, after a 30 min stabilization. Before analysis, the outlet gas was dried first in a trap at 0 °C and then with a membrane dryer. NO_x were analyzed with a chemilumi-

Table 1
Sulfur content (wt%) of the sulfated and tested catalysts

Sulfur content (wt%)	Pt/Al	Pt/ZrAl	Pt–Sn/ZrAl
Sulfated catalyst	1.06	1.33	1.17
Tested catalyst[a]	1.10	1.34	1.22

[a] Propene as reducer, 50 ppm SO_2 in the feed stream.