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Influence of metal oxides on the catalytic behavior of Au/Al_2O_3 for the selective reduction of NO_x by hydrocarbons

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Abstract

The reduction of NO by propene in the presence of excess oxygen over mechanical mixtures of Au/Al_2O_3 with a bulk oxide has been investigated. The oxides studied were: Co_3O_4, Mn_2O_3, Cr_2O_3, CuO, Fe_2O_3, NiO, CeO_2, SnO_2, ZnO and V_2O_5. Under lean C_3H_6-SCR conditions, these oxides (with the exception of SnO_2) convert selectively NO to NO_2. When mechanically mixed with Au/Al_2O_3, the Mn_2O_3 and Co_3O_4 oxides and, to a much greater extent, CeO_2 act synergistically with this catalyst greatly enhancing its SCR performance. It was found that their synergistic action is not straightforwardly related to their activity for NO oxidation to NO_2. The exhibited catalytic synergy may be due to the operation of either remote control or a bifunctional mechanism. In the later case, the key intermediate must be a short-lived compound and not the NO_2 molecule in gas-phase.

Keywords: Reduction of NO_x by propene; Au/Al_2O_3 catalyst; Mechanical mixtures; Synergy effect

1. Introduction

The need to control NO_x emissions from lean burn engines as well as from stationary sources (without using toxic ammonia), has triggered an intense research effort aiming to the development of efficient catalysts for the selective reduction of NO_x by hydrocarbons under the presence of excess oxygen (HC-SCR). Several studies have shown that the combination of functionally different catalysts, namely of an active catalyst for the HC-SCR of NO with another catalyst active for the NO to NO_2 oxidation, leads to the development of a catalytic system with enhanced performance for this process [1–6]. In this context, Ueda and Haruta [3] have shown that the reduction of NO with C_3H_6 under lean conditions over Au/Al_2O_3 is significantly enhanced by the addition of Mn_2O_3 through mechanical mixing.

In this work, we explore the potential of a number of other oxides to enhance the catalytic performance of the Au/Al_2O_3 catalyst for the lean C_3H_6-SCR of NO, when mechanically mixed with this catalyst. The possible origin of the catalytic synergy exhibited by some of these mechanical mixtures is also discussed.

2. Experimental

2.1. Preparation and characterization of samples

CeO_2 (50 m^2g^{-1}), V_2O_5 (5 m^2g^{-1}), α-Fe_2O_3 (16 m^2g^{-1}), α-Mn_2O_3 (6 m^2g^{-1}) and NiO (4 m^2g^{-1}) oxides were prepared by the decomposition in air at 550 °C for 5 h of $Ce(NO_3)_3·6H_2O$, $V_2(C_2O_4)_5$, $Fe(NO_3)_3·9H_2O$, $Mn(CH_3COO)_2·4H_2O$ and $Ni(NO_3)_2·4H_2O$, respectively. The Cr_2O_3 (23 m^2 g^{-1}), SnO_2 (22 m^2 g^{-1}) and ZnO (8 m^2 g^{-1}) oxides were prepared by subjecting to the above heat treatment the corresponding hydroxides obtained by precipitation from aqueous solutions of $Cr(NO_3)_3·9H_2O$, $SnCl_2·2H_2O$ and $Zn(NO_3)_2·6H_2O$, respectively. In the case of the SnO_2 preparation, the precipitate was repeatedly washed with de-ionised H_2O in order to remove the Cl^- ions. Commercial Co_3O_4 (10 m^2 g^{-1}), CuO (4 m^2 g^{-1}) and γ-Al_2O_3 (174 m^2 g^{-1}) (Akzo) were also subjected to the same heat treatment. The reported specific surface areas of the bulk

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oxides were measured by the BET method and their structure was determined by XRD.

The Au/Al_2O_3 catalyst (0.3 wt% Au, 172 $m^2 g^{-1}$) was prepared by the deposition–precipitation method from aqueous solution of $HAuCl_4 \cdot 4H_2O$ (Alfa) at 70 °C with the pH adjusted to 6. The precipitate was repeatedly washed to eliminate Cl^- ions, dried at 110 °C for 24 h and calcined at 550 °C for 5 h.

Mechanical mixtures, with various compositions, of the Au/Al_2O_3 catalyst with each of the aforementioned oxides were prepared from suspensions of the calcined Au/Al_2O_3 and oxide powders (particle size in the region $90 < d_p < 150$ μm) in isopropanol. After evaporation of isopropanol at ambient temperature the mixtures were dried at 120 °C for 5 h.

2.2. Catalytic activity measurements

All specimens were tested for their catalytic performance in the selective reduction of NO with C_3H_6, in excess O_2, at the temperature region of 200–550 °C in a conventional flow, fixed-bed reactor at atmospheric pressure. The particle size of the catalytic samples was in the region $90 < d_p < 150$ μm in order to avoid significant pressure drop and internal concentration and temperature gradients over the catalyst bed. The composition of the feed (100 cm^3/min, corresponding to GHSV = 2×10^4 h^{-1} cm^3/g_{cat}, unless stated otherwise) was 0.1% NO, 0.1% C_3H_6 and 10% O_2 in N_2. On-line mass spectrometry and gas chromatography were used for the analysis. Due to the large excess of N_2 (used as a carrier gas), the NO conversion to N_2 was not calculated from the expression $\{2[N_2]/[NO]_{in}\} \times 100$ but from the measured values of [NO], $[NO_2]$ and $[N_2O]$ in the effluent stream, using the equivalent relation:

$$\{\text{NO conversion to } N_2\}\% = \left\{ \frac{([NO]_{in} - [NO] - [NO_2] - 2[N_2O])}{[NO]_{in}} \right\} \times 100$$

where $[NO]_{in}$ is the inlet concentration of NO. Under our experimental conditions, N_2O was not detected.

3. Results and discussion

3.1. Bulk oxides

Among the oxides studied under our SCR conditions, only γ-Al_2O_3 and SnO_2 convert part of NO to N_2; all the other bulk oxides convert, with various activities but selectively, NO to NO_2. This is in general agreement with previous reports in literature. Thus, it is known that γ-Al_2O_3 is active for the SCR of NO with hydrocarbons under lean conditions, exhibiting high selectivity for N_2 at elevated (>400 °C) temperatures [7–10]. Indeed, our γ-Al_2O_3 sample exhibited high N_2 yields (60–74%) in the temperature region of 475–525 °C. The maximum NO conversion to N_2 achieved over the SnO_2 sample was only 14% at 350 °C. The relatively poorer SCR performance of SnO_2, as compared to that of γ-Al_2O_3, has also been reported by Moriya et al. [11], when propane was used as the reductant. Bulk Co_3O_4, Fe_2O_3, V_2O_5 and CuO oxides were found totally inactive for the NO reduction to N_2 when either propane [12] or propene [13] was used as reducing agent. Both Mn_2O_3 [1,3] and CeO_2 [12] have been reported to convert selectively NO to NO_2 under the HC-SCR conditions. Finally, it has been reported that Cr_2O_3 exhibits only a very low activity for NO reduction to N_2 when the reductant is propane [12], but none (as in our case) when propene is used [13].

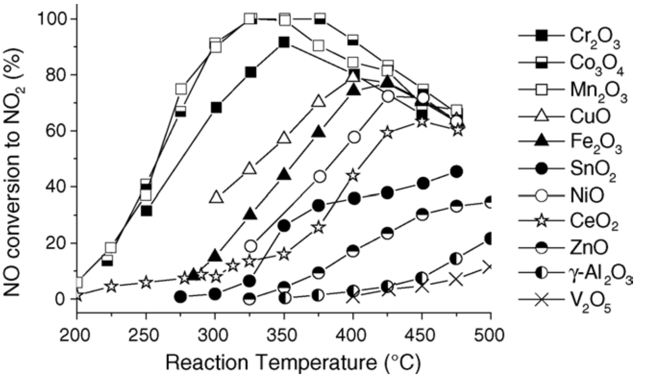

Fig. 1. Conversion of NO to NO_2 over the bulk oxides as a function of reaction temperature. *Feed*: 0.1% NO, 0.1% C_3H_6 and 10% O_2 in N_2. GHSV = 2×10^4 h^{-1} cm^3/g_{cat}.

The activities of our bulk oxides for the NO conversion to NO_2 are shown in Fig. 1. As seen from this figure, Mn_2O_3, Co_3O_4 and Cr_2O_3 were the most active bulk oxides for the oxidation of NO to NO_2, while V_2O_5 and γ-Al_2O_3 were the least active. The dependence of the exhibited activity for the C_3H_6 consumption (Fig. 2) on the nature of the bulk oxide follows in general the same trend with that for the NO_2 production. We may, thus, sort these oxides by their activity for both the C_3H_6 consumption and the NO oxidation to NO_2 as follows:

$$\{Co_3O_4, Mn_2O_3, Cr_2O_3\} > CuO > Fe_2O_3 > \{NiO, CeO_2, SnO_2\} > ZnO > \gamma\text{-}Al_2O_3 > V_2O_5$$

3.2. Mechanical mixtures

In order to explore the potential of the studied bulk oxides to enhance the performance of the Au/Al_2O_3 catalyst we formed

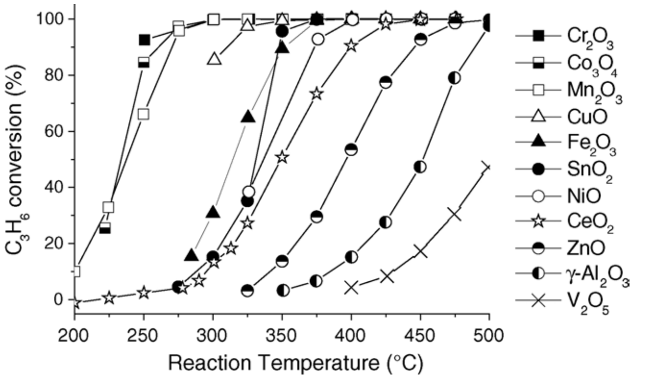

Fig. 2. Conversion of C_3H_6 over the bulk oxides as a function of reaction temperature. *Feed*: 0.1% NO, 0.1% C_3H_6 and 10% O_2 in N_2. GHSV = 2×10^4 h^{-1} cm^3/g_{cat}.

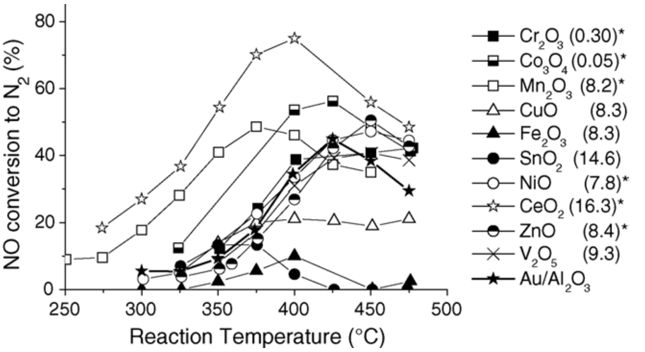

Fig. 3. Conversion of NO to N_2 over the Au/Al_2O_3 catalyst and the mechanical mixtures of Au/Al_2O_3 with the bulk oxides as a function of reaction temperature. The composition of the mixtures is given in parentheses as wt% of oxide. Compositions marked by an asterisk are the determined optimum compositions. *Feed*: 0.1% NO, 0.1% C_3H_6 and 10% O_2 in N_2. GHSV = 2×10^4 h^{-1} cm^3/g_{cat}.

mechanical mixtures of these oxides with this catalyst. Having determined that the optimum composition of the Mn_2O_3 + Au/Al_2O_3 mixtures corresponds to an atomic ratio of Mn/Au = 77, we studied first the behavior of M_xO_y + Au/Al_2O_3 mixtures with M/Au = 77. With this composition, only the Mn_2O_3 + Au/Al_2O_3 and the CeO_2 + Au/Al_2O_3 mixtures exhibited improved SCR performance compared to that of the Au/Al_2O_3 catalyst. Then, we determined the optimum composition of the mechanical mixtures of Au/Al_2O_3 with the bulk oxides of Cr_2O_3, Co_3O_4, NiO, CeO_2 and ZnO. The results, namely the NO conversion to N_2, are shown in Fig. 3. For comparison, the behavior of the Au/Al_2O_3 catalyst is also presented. As seen from this figure, besides the well-known case of Mn_2O_3, Co_3O_4 and, to a much greater extent, CeO_2 act synergistically with Au/Al_2O_3, when mechanically mixed with this catalyst, greatly enhancing its performance. This is evidenced by the increased NO reduction activity and the enlargement of the operational temperature window, especially at lower temperatures. For example, while the NO conversion to N_2 at 350 °C is zero over bulk CeO_2 and only 9% over Au/Al_2O_3, it is 54% over the best CeO_2 + Au/Al_2O_3 mixture. The mechanical mixtures with Cr_2O_3, NiO and ZnO, having the optimum for each case composition, exhibited practically the same NO reduction activity with the Au/Al_2O_3 catalyst, with the exception of a slight increase observed at 450–475 °C. Finally, for the mechanical mixtures with composition corresponding to M/Au = 77, it can be seen that the addition of CuO, Fe_2O_3 and SnO_2 deactivates the Au/Al_2O_3 catalyst while the addition of V_2O_5 has not any significant influence on its NO reduction activity.

Having in mind the gentle way followed for the formation of all the above mixtures, the catalytic synergy exhibited in the case of Mn_2O_3-, Co_3O_4- and CeO_2-containing mixtures cannot be attributed either to the formation of a common phase or to textural synergy. Moreover, these mixtures consist of a low specific surface area bulk oxide and a material where a very low loading of gold is dispersed on a high surface area porous support; a fact that minimizes the number of direct contacts between oxide and supported Au particles. Thus, the a priori possible explanations for the exhibited catalytic synergy are limited to the mechanisms of remote control and of bifunctional catalysis.Yokoyama and Misono [1,2] combined bulk oxides active for the NO oxidation with a HC-SCR catalyst and showed that the mechanical mixing of Mn_2O_3 or CeO_2 with Ce-ZSM-5 considerably enhances the lean NO reduction by C_3H_6 of the Ce-ZSM-5 catalyst. They also showed that, in contrast, mixing with Cr_2O_3 or CuO strongly deactivates the Ce-ZSM-5 catalyst. In order to explain the catalytic synergy exhibited by these mechanical mixtures these authors proposed a bifunctional mechanism in which Mn_2O_3 or CeO_2 accelerates the oxidation of NO to NO_2 and the subsequent reaction steps between NO_2 and C_3H_6 proceed on the Ce-ZSM-5 catalyst. Ueda and Haruta [3] also proposed, for the case of the Mn_2O_3 + Au/Al_2O_3 mechanical mixture, that NO is oxidized with molecular oxygen over Mn_2O_3 to form NO_2 in the gas-phase, which then reacts with C_3H_6 adsorbed on the surface of gold particles. Finally, a similar bifunctional mechanism involving the gas-phase transport of NO_2 was also proposed by Yan et al. [4] for explaining the synergy exhibited by mechanical mixtures of Co/Al_2O_3 with H-zeolites for the CH_4-SCR of NO.

Our present results, however, suggest that the catalytic synergy exhibited by the M_xO_y + Au/Al_2O_3 mixtures is not straightforwardly related to the activity of the M_xO_y bulk oxide for the NO oxidation to NO_2. Indeed, while mixing of Au/Al_2O_3 with CeO_2 resulted to the greatest enhancement of catalytic performance of Au/Al_2O_3 observed in the present study, not any significant enhancement was observed when NiO was used, although NiO oxide exhibited similar to CeO_2 activity for the NO to NO_2 oxidation. Moreover, comparable oxidation activities were also observed in the case of Co_3O_4, Mn_2O_3 and Cr_2O_3 bulk oxides, but in contrast to Co_3O_4 and Mn_2O_3 oxides, Cr_2O_3 could not improve appreciably the SCR performance of Au/Al_2O_3 when mechanically mixed with this catalyst.

3.3. Layered mixtures

In order to explore this point further we investigated, for the Mn_2O_3 + Au/Al_2O_3 and CeO_2 + Au/Al_2O_3 mechanical mixtures, the catalytic behavior of the corresponding ‘layered mixtures’. In this case, the two components, namely the metal oxide and the Au/Al_2O_3, are physically separated inside the reactor by a thin layer of quartz powder, which is totally inactive for this reaction [7,13]. The results, for the case of the CeO_2-containing mechanical and layered mixtures, are presented in Fig. 4. Similar results were also obtained for the case of Mn_2O_3-containing mixtures. It can be seen that in the absence of an intimate contact between the two phases, and regardless of whether the reaction feed contacts first the oxide or the Au/Al_2O_3 catalyst, there is not any synergistic behavior. This is consistent with the operation of a remote control mechanism. Indeed a contact is needed in order for the surface-mobile (‘spillover’) species generated in one phase to surface-migrate on the other phase, and control the number or kind of its catalytically active centers. Performing similar experiments, Chen et al. [5] have shown that the synergy exhibited in the case

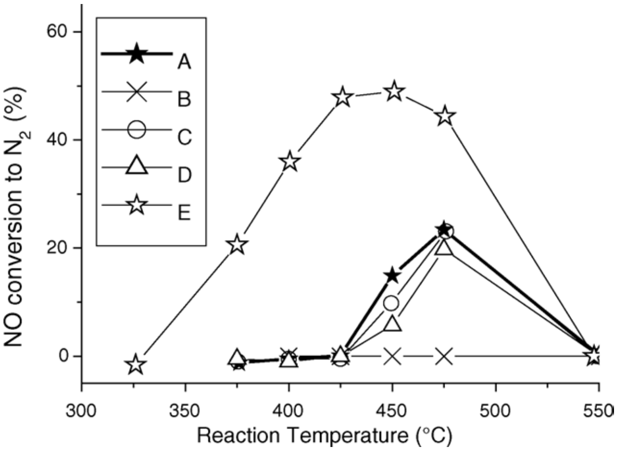

Fig. 4. Conversion of NO to N_2 over Au/Al_2O_3 (A), CeO_2 (B), layered arrangements of Au/Al_2O_3 and CeO_2 with the feed contacting first Au/Al_2O_3 (C) or CeO_2 (D) and mechanical mixture $CeO_2 + Au/Al_2O_3$ (E). *Feed*: 0.1% NO, 0.1% C_3H_6 and 10% O_2 in N_2. GHSV = $8.6 \times 10^4\ h^{-1}\ cm^3/g_{cat}$.

of C_3H_6-SCR of NO over mixtures of Mn_2O_3 and spinel Ni–Ga oxide is not manifested in the absence of an intimate contact between these two oxides. According to these authors, the spillover of adsorbed NO_2 and C_xH_y species from Mn_2O_3 to the neighboring Ni–Ga oxide is an important step for the cooperation of these oxides.

If a bifunctional mechanism is at the origin of the exhibited synergy in the case of our $CeO_2 + Au/Al_2O_3$ and $Mn_2O_3 + Au/Al_2O_3$ mixtures, then our results show that the key intermediate product should be an unstable, short-lived, compound and not, as previously suggested [1–3], the NO_2 molecule in the gas-phase. This interpretation is further corroborated by Liese et al. [6] who also observed that the synergetic interaction of CeO_2 + H-ZSM-5 mixture for the CH_4-SCR of NO could only be manifested when the components of this mixture are in close contact. They proposed a bifunctional mechanism for this synergetic behavior based on short-lived organo-nitro or organo-nitroso intermediates excluding the possibility of the bifunctional interaction to be mediated by a long distance transport step as would be the gas-phase transport of NO_2.

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