



Hybrid catalysts for the selective catalytic reduction (SCR) of NO by NH₃: Precipitates and physical mixtures



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ARTICLE INFO

Article history:

Received 6 April 2017

Received in revised form 23 June 2017

Accepted 26 June 2017

Available online 28 June 2017

Keywords:

NH₃-SCR

Hybrid catalysts

Physical mixture

Precipitate

ABSTRACT

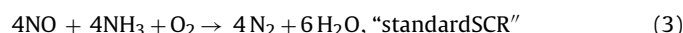
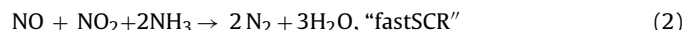
Hybrid catalysts for the selective catalytic reduction of NO by NH₃, which have been introduced as physical mixtures between an oxidation catalyst and an SCR catalyst, have been prepared by precipitation of the former onto the latter. Mn oxide, CeO₂, and CeZrOx have been employed as oxidation components, Fe-ZSM-5 and H-ZSM-5 as SCR components (acidic components). The catalysts have been characterized by XRD, nitrogen physisorption and temperature-programmed reduction after thermal treatments at 623 K or at 923 K, their catalytic behavior has been examined by standard techniques. In the Ce-containing systems, precipitated hybrids were more active than physically mixed hybrids. A reversed ranking in the case of the MnOx/Fe-ZSM-5 system may be due to a particular susceptibility of the corresponding precipitates to deactivation. A lack of correlation between BET surface areas, which indicate accessibility of the zeolite interior, and activity suggests that the reaction does not utilize the whole zeolite crystal. Precipitated hybrids were very prone to thermal deactivation, in particular those containing MnOx or CeO₂. This was ascribed to an increased opportunity for the redox oxides to undergo solid-state ion exchange when deposited onto the zeolite crystals. When the extent of deactivation was more drastic, it was accompanied by a significant decrease of the apparent activation energy of NH₃-SCR. This may support earlier conclusions according to which the reaction mechanism operating in the hybrids comprises a transport step of an unstable intermediate, which might become rate limiting when acidic sites in the vicinity of the oxidation sites are poisoned by solid-state ion exchange.

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1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides remains a key topic in environmental catalysis. While commercialized both for stationary and mobile sources, the technology may benefit from development of catalysts with improved low-temperature behavior [1,2]. Pronounced synergetic effects occurring in physical mixtures of oxidation and SCR catalysts, which were first reported by Stakheev et al. [3–6] may become productive in this search. The synergies in these combined catalysts (or hybrid catalysts) were originally ascribed to a mechanism in which the oxidation component produces NO₂ (Eq. (1)). This enables the

SCR component to operate via fast SCR (2), which would result in an accelerated conversion according to the stoichiometry of standard SCR (3).



Our recent work on these catalysts [7–9], in which various SCR components (Fe-ZSM-5, H-ZSM-5, V₂O₅-WO₃/TiO₂) were combined with a number of oxidation catalysts, has raised, however, doubt about this simple scheme. The synergetic effect was observed to depend strongly on the distance between components, which implies that the species transferring the reaction from one component to the other one is unstable [8]. Comparing reaction rates of fast SCR over the SCR component and standard SCR over hybrids made of this very component, we found conditions where the latter reaction (standard SCR) was faster than the former. Fast SCR

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should therefore not be part of the reaction mechanism of standard SCR over the hybrids [7]. Operating with a transport step of an unstable intermediate, the hybrid catalysts are reminiscent of a system described by us earlier, in which CeO₂ and H-ZSM-5 were combined in physical mixtures or precipitates. These exhibited attractive activities in the SCR of NO by methane [10,11] although none of the components were good for this reaction when applied separately, while Ce-exchanged zeolites operate only with higher hydrocarbons [12].

The short life time of critical intermediates interferes with their easy identification, but it suggests on the other hand that performance of the hybrids may be improved by further decreasing the distance between the components. As exemplified earlier with the CeO₂/H-ZSM-5 system for CH₄-SCR [10,11], this may be achieved by precipitating the oxidation component on the external zeolite surface. While active sites on this surface may be blocked, plenty of sites will remain to be available in the zeolite cavities. The present paper reports on an effort to examine the potential of this approach for the preparation of hybrid catalysts for NH₃-SCR.

2. Experimental

2.1. Catalysts

SCR components employed were H-ZSM-5 and Fe-ZSM-5 in two batches, the Fe content of which was 0.4 and 0.5 wt-% as determined by ICP-OES. Fe-ZSM-5 was made from a NH₄-ZSM-5 (Si/Al ≈ 14) donated by Tricat Zeolites Bitterfeld (now a Clariant company). Fe was introduced into the H form obtained by calcination of the NH₄ form at 773 K by solid-state ion exchange (SSIE) as described in detail by Schwidder et al. [13]. The zeolite was ground with a given amount of FeCl₃·6H₂O, the mixture was heated in inert gas at 573 K for 1 h, the product was washed, dried, and calcined in synthetic air (20% O₂ in He) at 873 K for 2 h.

Oxidation components employed were based on CeO₂, Ce-Zr mixed oxide, and manganese oxide. The binary oxides were made by precipitation of the hydroxides from 0.5 M aqueous solutions of Mn(II) and Ce(III) nitrate with ammonia solution (25%, until pH = 8). The precipitates were aged at room temperature for 1 h, washed, dried, and calcined in air at 623 K or at 923 K. Yields of this preparation were very different: 62% for CeO₂, but only 18% for Mn₂O₃. The same procedure was employed to precipitate the oxides onto the external surface of Fe-ZSM-5, with intended weight ratios of oxide/zeolite of 1 and 1/3. Here as well, calcination was performed at 623 K or at 923 K.

CeZrOx was precipitated from a 1 M (in total) solution of Ce(NO₃)₃ and ZrO(NO₃)₂ at a Ce: Zr ratio of 7/3 with dilute NH₃ (1.2 M) at pH = 8.5. The precipitate was aged, washed, dried, and calcined at 623 K or 923 K. This material will be labeled as CeZr(Bo), because for some purposes, a commercial ceria-zirconia mixed oxide donated by Umicore & Co. KG was employed. The latter will be designated as CeZr(U). CeZrO_x was also precipitated onto H-ZSM-5 or onto Fe-ZSM-5 (with 0.4 wt-% Fe; oxide-zeolite ratios – 1 and 1/3) by suspending the zeolites in the above-mentioned solution of the nitrates and precipitating with dilute ammonia solution. The precipitates were calcined at 623 K or 923 K.

For the catalytic studies, the powders were pressed, crushed, and sieved to obtain an appropriate particle size (250–350 μm, 45–60 mesh).

These precipitated hybrid catalysts were compared with physical (or mechanical) mixtures containing both components at a 1:1 weight ratio. The corresponding mixture was thoroughly ground in a mortar before processing it into mixed particles as indicated above. The particles were subjected to calcinations at 623 K and 923 K.

2.2. Characterization

Sample compositions were analyzed by ICP-OES using a UNICAM PU 701 spectrometer. Samples were digested by peroxide fusion (Mn-based materials) or by lithium borate fusion (Ce-containing samples). Textural characterization was obtained from nitrogen adsorption-desorption isotherms measured at 77 K with a NOVA-2000 instrument (Quantachrome). Initially, samples were outgassed at 573 K under a residual pressure of 10⁻³ mbar for 3 h. Surface areas were evaluated from the BET model. Phase compositions of the catalysts were characterized by XRD measurements in reflection geometry with an Empyrean Theta-Theta diffractometer (Panalytical, Almelo) using a Cu anode (λ = 1.54056 Å). The K-beta emission line was suppressed by a Ni Filter. Samples were scanned in the 2–70° 2θ range at ambient temperature.

Selected catalysts were also studied by temperature-programmed reduction (TPR), which was made by heating the samples in 4.5 vol-% H₂ up to 1123 K at 5 K/min, with a 1 h isothermal period at this temperature. The effluent gas was analyzed by a Hydros thermal conductivity detector (Fisher-Rosemount).

2.3. Catalytic measurements

Reaction rates of standard SCR were measured in flow regime (microflow quartz reactor, 4.2 mm i.d.) at atmospheric pressure and temperatures between 423 and 873 K. Gas lines after and before the reactors were kept at 350 K to avoid water condensation. The GHSV was 300,000 h⁻¹ for the hybrid catalysts (catalyst mass – 25 mg) while 600,000 h⁻¹ (catalyst mass – 12.5 mg) were employed for individual components in order to identify their possible contribution to the behavior of the hybrid systems. The feed consisted of 1000 ppm NO, 1000 ppm NH₃, 2 vol-% O₂, balanced with He. In the steady state, NO and NH₃ concentrations were determined on-line using an XStream X2 Gas Analyzer (Rosemount Analytical; Emerson) which combines non-dispersive infrared and ultraviolet spectrometry for quantitative analysis. The same instrument was used to check for NO₂ while N₂O formation was examined with an ABB Advanced Optima Continuous Gas Analyzer (A02000 Series). Conversions were calculated according to: $X_i (\%) = \frac{c_{i,in} - c_{i,out}}{c_{i,in}} \times 100$ (i – NO or NH₃).

3. Results

3.1. Characterization

3.1.1. Composition

Compositions achieved in the precipitation preparations are given in Table 1 where the labels of the samples are presented as well. They consist of the targeted wt-% of oxide (denoted as “Mn”, “Ce”, or “CeZr”) in the sample in parentheses, the kind of zeolite (Fe- or H-ZSM-5) and the temperature of calcination. Initial P or MM differentiates between precipitates and physical (mechanical) mixtures.

While the intended oxide/zeolite ratios were nearly achieved with Ce-based preparations, the Mn-based precipitates deviate strongly from the targeted values. This parallels the low yield in the preparation of Mn₂O₃ and seems to be due to a relatively high solubility of Mn²⁺ at the pH employed. However, important results were achieved also with these samples, while there was no indication that increased Mn content could improve the performance (see below). Precipitates with higher Mn content were therefore not prepared. In the mixed oxide catalysts, the targeted 70/30 atomic ratios between Ce and Zr was nicely met (see footnotes to Table 1), but the oxide content of the precipitates was somewhat smaller than intended.

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