Composite Catalysts for Selective Catalytic Reduction of NO_x and Oxidation of Residual NH₃

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Abstract—A comprehensive study has been performed on the catalytic properties of composite catalysts [Mn/support + FeBeta] and their individual components (Mn/support and FeBeta) in the selective catalytic reduction of nitrogen oxides and the ammonia oxidation reaction. It has been shown that mixing the oxide component with the zeolite not only leads to an increase in NO_x conversion, but also improves the selectivity in the oxidation of residual ammonia, thus making it possible to conduct both processes in a single catalytic unit.

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Nitrogen oxides (NO_x) are highly toxic substances formed primarily during the fuel combustion process [1]. Their negative environmental impact, as well as the introduction of stricter regulations on NO_x emissions, necessitates the development of new, highly effective processes for neutralizing these compounds. To date, one of the technologies used for the removal of nitrogen oxides from both industrial (nitric acid production, thermal power plants, etc.) off-gases and motor vehicle exhaust gases is selective catalytic reduction (SCR NO_x) [2, 3], which is carried out on vanadium (V–W–TiO₂) (I), and Cu- or Fe-promoted zeolite catalysts. Ammonia (or urea solution) is typically used as a reducing agent (I), which is introduced with special feeders upstream of an SCR NO_x catalyst system.

$$4NH_3 + 4NO + O_2$$

$$\rightarrow 4N_2 + 6H_2O - \text{standard SCR.}$$
(I)

Despite the fact that the SCR NO_x process is very efficient and is widely used in practice, it nevertheless has some drawbacks. One of these shortcomings is the possible ammonia "slip" due to an overdose of the reducing agent needed to compensate for the abrupt change in the concentration of nitrogen oxides in the effluent gas. To solve this problem, a ammonia slip catalyst is mounted downstream of the NO_x SCR catalyst, a unit that must ensure high selectivity in the oxidation of ammonia to molecular nitrogen [4, 5].

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \tag{II}$$

In [6] we proposed the idea of a catalytic NO_x neutralization system consisting in that an SCR component and a component responsible for the oxidation of residual ammonia are combined in a single unit (by mechanical mixing). Using the composite catalyst [FeBeta + Fe (Mn) MCM-48] as an example, we showed that it is possible to achieve effective removal of nitrogen oxides and residual ammonia in the single catalytic unit by optimizing the ratio between the activities of the SCR-mediating component and the oxidative component.

In this work, we continued the study of the catalytic properties of [oxidative component + FeBeta] composite systems in the SCR NO_x process and the selective oxidation reaction of residual ammonia. Manganese-containing oxide catalysts (Mn/Al₂O₃ and Mn/TiO_2) having high oxidative activity [7] were used as an oxidizing agent. It was shown [8, 9] that the mechanical mixing of the Mn/support component with the zeolite leads to a substantial increase in NO_x conversion over a wide temperature range, but the activity of the [Mn/support + zeolite] composite catalysts in the ammonia oxidation reaction was not studied yet. The catalyst Mn/FeBeta studied in detail [10], in which the oxidizing component (MnO_x) is supported directly onto the outer surface of zeolite microcrystals, was used as a reference and for evaluating the effect of the degree of contact between the oxide and zeolite components on the catalytic properties of the composite system.

EXPERIMENTAL

Catalyst Preparation

Supported manganese catalysts containing 8 wt % Mn were prepared by incipient wetness impregnation of support with a solution of manganese nitrate (Mn(NO₃)₂ · *x*H₂O, Aldrich, 98%). Preliminary calcined (550°C, 4 h) samples of commercial FeBeta (Fe content of ~0.9 wt %, Si/Al = 12.5, Zeolist International), Al₂O₃ ($S_{\text{BET}} = 150 \text{ m}^2/\text{g}$, Sasol), and TiO₂ ($S_{\text{BET}} = 40 \text{ m}^2/\text{g}$, Saint-Gobain) were used as a support. After impregnation, the samples were dried in air at room temperature for 24 h and then calcined in a dry air flow (~300 mL/min) at 550°C for 4 h.

The composite catalysts $[Mn/Al_2O_3 + FeBeta]$ and $[Mn/TiO_2 + FeBeta]$ were obtained by thorough grinding in a mortar of the oxide $(Mn/Al_2O_3 \text{ or } Mn/TiO_2)$ and zeolite (FeBeta) components in a weight ratio of 3 : 1.

Instrumental Study of Catalysts

Examination of the samples by temperature-programmed reduction with hydrogen (H_2 -TPR) was performed on a semiautomatic flow unit with a thermal conductivity detector. Prior to reduction, the sample (100 mg) was heated under argon at 325°C for 1 h and cooled to room temperature. The reduction was carried out in a flow of 5 vol % H_2/Ar gas mixture (30 mL/min) with a temperature rise to 820°C at a rate of 10°C/min. To remove water formed upon reduction, a trap cooled with dry ice in ethanol to -70° C was placed between the reactor and the detector. The detector was calibrated using data on the temperature programmed reduction of CuO (Aldrich-Chemie GmbH, 99%) taken in an amount of 0.8 to 11 mg. Deconvolution of TPR peaks was performed using the program Ekokhrom.

The microstructure of the samples was studied by field-emission scanning electron microscopy (SEM) with a Hitachi SU8000 electron microscope. The analytical measurement conditions were optimized in accordance with the approach described previously [11]. Before measurements, the samples were mounted on a 25 mm aluminum specimen stub, fixed with a conductive adhesive tape, and then coated with a conductive metal layer (Au/Pd, 60/40) of a 7 nm thickness by magnetron sputtering deposition. Images were acquired in the secondary electron detection mode at an accelerating voltage of 2 kV and a working distance of 4 to 5 mm. The morphology of the samples was studied taking into account possible influence of metal coating on the surface [12].

Catalytic Experiments

The activity of the composite catalysts and the individual components in both the SCR process and

the NH_3 oxidation reaction was measured in a flow unit with a quartz reactor (internal diameter 4 mm).

The reaction mixtures had the following compositions:

NH₃SCR: 580 ppm NH₃, 500 ppm NO, 10 vol % O₂, 6 vol % H₂O in nitrogen.

NH₃ oxidation: 580 ppm NH₃, 10 vol % O_2 , 6 % H₂O in nitrogen.

Excess of ammonia ($NH_3/NO > 1$) was used to provide ~80 ppm residual NH_3 at the reactor outlet during the SCR reaction (for ammonia "slip" detection).

The measurements were made in the temperature range of $100-500^{\circ}$ C at a GHSV of 270000 h^{-1} with a catalyst loading of 0.04 g (fraction 0.2–0.4 mm), unless otherwise indicated. The feed gas mixture and the reaction products were analyzed using a Gasmet FTIR analyzer (Temet Instruments Dx-4000). To avoid condensation of water vapor, all gas lines were heated (180° C).

The conversions of NO_x (X_{NO_x}) and NH₃ (X_{NH_3}) were calculated as follows:

$$=\frac{C_{\text{in,NO}} - (C_{\text{out,NO}} + C_{\text{out,NO}_2} + 2C_{\text{out,N}_2\text{O}})}{C_{\text{in,NO}}},$$
 (1)
$$=\frac{C_{\text{in,NO}} - (C_{\text{out,NH}_3} - C_{\text{out,NH}_3})}{C_{\text{in,NH}_3}},$$
 (2)

$$X_{\rm NH_3} = \frac{C_{\rm in, NH_3} - C_{\rm out, NH_3}}{C_{\rm in, NH_3}},$$
 (2)

where $C_{\rm in}$ and $C_{\rm out}$ are the concentrations of the respective gases at the inlet and outlet of the reactor, respectively.

RESULTS AND ITS DISCUSSION

Scanning Electron Microscopy

The character of distribution of the oxide and zeolite components in the catalytic systems prepared on their basis was evaluated using scanning electron microscopy. The micrographs in Fig. 1 clearly show that a very homogeneous distribution of the components can be achieved by mechanical mixing. The images obtained before (Fig. 1a) and after (Figs. 1b, 1c) mixing FeBeta with the oxide components distinctly display large (~0.4 mm), regular shaped zeolite microcrystals. The micrographs of the composite catalysts (Figs. 1b, 1c) show that the zeolite microcrystals are in contact with smaller particles of the oxide component (Mn/TiO₂ or Mn/Al₂O₃).

In the case of FeBeta with 8 wt % manganese supported by impregnation (Mn/FeBeta sample), it was possible to achieve more intimate contact between MnO_x and FeBeta, as well as uniform distribution of the oxide and zeolite components. Comparison of the micrographs of the FeBeta and Mn/FeBeta



Fig. 1. Scanning electron microscopy micrographs of (a) FeBeta, (b) $[Mn/TiO_2 + FeBeta]$, (c) $[Mn/Al_2O_3 + FeBeta]$, and (d) Mn/FeBeta samples.

(Figs. 1a, 1d) shows that MnO_x clusters decorate the surface of the FeBeta zeolite microcrystals (Figs. 1a, 1d).

Temperature-Programmed Reduction

In the H_2 -TPR spectra of the Mn/FeBeta, Mn/TiO₂, and Mn/Al₂O₃ catalysts (Fig. 2), two pronounced peaks of hydrogen absorption at low (330-360°C) and high temperatures (425-525°C) are distinguishable. In the literature, the presence of these two peaks is associated with the consecutive reduction of manganese oxides, wherein the first step is the reduction of MnO_2 to Mn_2O_3 and the second step is the reduction of Mn_2O_3 to MnO [13, 14]. The total hydrogen uptake is 0.93, 0.99, or 0.68 mmol/g_{cat} for Mn/FeBeta, Mn/TiO₂, or Mn/Al₂O₃, respectively. These values indicate that most of the manganese in the Mn/FeBeta and Mn/TiO₂ samples occurs as MnO_2 , whereas a significant portion of the manganese in the Mn/Al_2O_3 sample is in the form of Mn_2O_3 and/or nonstoichiometric MnO_x.

In the case of composite catalysts $[Mn/Al_2O_3 + FeBeta]$ and $[Mn/TiO_2 + FeBeta]$, in addition to the above two peaks, the H₂-TPR spectra exhibit a low-temperature signal at 200°C (Fig. 2), which can be explained by reduction of finely divided MnO_2 to Mn_2O_3 [15]. At the same time, the total absorption of hydrogen turns to be 0.92 mmol/g_{cat} for [Mn/Al₂O₃ + FeBeta] and 0.96 mmol/g_{cat} for [Mn/TiO₂ + FeBeta],

which is comparable with the value of hydrogen uptake for the Mn/FeBeta catalyst and suggests the prevalence of MnO_2 .



Fig. 2. Profiles of temperature-programmed reduction with hydrogen for (*I*) Mn/FeBeta, (*2*) Mn/TiO₂, (*3*) Mn/Al₂O₃, (*4*) [Mn/TiO₂ + FeBeta], and (5) [Mn/Al₂O₃ + FeBeta].



Fig. 3. Temperature dependence of NO_x conversion on (1) Mn/Al₂O₃, (2) Mn/TiO₂, (3) FeBeta, (4) [Mn/Al₂O₃ + FeBeta], (5) [Mn/TiO₂ + FeBeta], and (6) Mn/FeBeta catalyst samples.

Catalytic Measurements

Catalytic properties of the individual components $(Mn/Al_2O_3 \text{ and } Mn/TiO_2)$ and the composite catalysts on their basis were tested in both the selective catalytic reduction of NO_x and the ammonia oxidation reaction.

Activity of Catalysts in NO_x SCR

Samples of the individual components Mn/Al_2O_3 and Mn/TiO_2 have a low NO_x SCR activity (Fig. 3). The NO_x conversion in both cases increases with the increasing temperature; however, after reaching the maximum (27% for Mn/TiO_2 or 51% for Mn/Al_2O_3), it sharply decreases because of the reaction of complete oxidation of ammonia and the formation of additional amounts of NO_x .

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (III)$$

The activity of the zeolite component is relatively low (<75% at 500°C), since the mass of FeBeta used in the individual test was the same as in the composite catalysts (space velocity, ~1075000 instead of 270000 h⁻¹).

The mechanical mixing of the components Mn/support and FeBeta leads to a sharp increase in the catalytic activity (Fig. 3) as compared to the individual components. Thus, the composite catalysts [Mn/Al₂O₃ + FeBeta] and [Mn/TiO₂ + FeBeta] at low temperatures ($T < 350^{\circ}$ C) are almost as good ($T_{50} = 225^{\circ}$ C for Mn/FeBeta, ~255^{\circ}C for [Mn/Al₂O₃ + FeBeta], or ~240^{\circ}C for [Mn/TiO₂ + FeBeta]) as the reference sample Mn/FeBeta in catalytic properties. The observed synergistic effect can be explained by the occurrence of the SCR reaction via the bifunctional mechanism proposed in [8, 9]. According to this

mechanism, close contact between the oxide and zeolite components facilitates rapid transfer of reaction intermediates from one component to another, thereby enhancing the reaction. During the two-step process, NO_2 produced on the oxide component (IV), diffuses to the zeolite surface, on which it is reduced along with NO by ammonia via fast SCR reaction (V).

 $2NO + O_2 \leftrightarrow 2NO_2$ on oxide component (IV)

$$\frac{NO + NO_2 + 2NH_3}{2N}$$
(V)

$$\rightarrow 2N_2 + 3H_2O$$
 on zeolite component.

The decrease in the NO_x conversion (71% on Mn/FeBeta and 36% on the composite catalysts at 500°C) observed at T > 350°C can be due to side reaction of ammonia oxidation (III), as evidenced by the absence of ammonia in the gas stream at the reactor outlet (residual NH₃ concentration did not exceed 10 ppm).

Activity of the Catalysts in the NH₃ Oxidation Reaction

Testing the samples in the ammonia oxidation reaction revealed that the individual components (Mn/support) and the composite catalysts based on them ([Mn/support + FeBeta]) almost do not differ in activity (Fig. 4a). The oxidation reaction begins at $T \approx 300^{\circ}$ C and the NH₃ conversion at $T > 400^{\circ}$ C is 94–99% on all of the Mn-containing samples, including the reference sample Mn/FeBeta. The only exception is FeBeta, on which the ammonia conversion does not exceed 12%. These data lead to the conclusion that the activity of the catalysts in the oxidation of NH₃ is primarily determined by the Mn component and the contribution of the zeolite component is insignificant.

However, the introduction of the zeolite component results in a drastic change in selectivity of the process. The main products of the reaction on the individual oxide components are NO, NO₂, and N₂O (Fig. 4b), whereas mixing the Mn component with FeBeta zeolite leads to substantial inhibition of the formation of undesirable nitrogen oxides at temperatures above 350°C. For example, the maximal concentrations of NO_x on the composite catalysts [Mn/Al₂O₃ + FeBeta] and [Mn/TiO₂ + FeBeta] at 500°C are about ~50 and ~130 ppm (versus ~320 ppm on Mn/Al₂O₃ and ~410 ppm on Mn/TiO₂), respectively.

The increase in the ammonia oxidation selectivity is apparently due to the involvement of NO, produced on the oxide component (III), in standard SCR reaction (I) on the zeolite [8]. The general scheme of the process can be described by the following combination of the reactions discussed above:

$$4NH_3 + 5O_2 \tag{III}$$

$$\rightarrow 4NO + 6H_2O \text{ on Will component}$$

$$2NO + O_2 \leftrightarrow 2NO_2$$
 on Mn component (IV)

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Fig. 4. (a) Temperature dependence of NH₃ conversion on (1) Mn/Al₂O₃, (2) Mn/TiO₂, (3) FeBeta, (4) [Mn/Al₂O₃ + FeBeta], (5) [Mn/TiO₂ + FeBeta], and (6) Mn/FeBeta samples; (b) formation of NO_x during the ammonia oxidation reaction on (1) Mn/Al₂O₃, (2) Mn/TiO₂, (3) FeBeta, (4) [Mn/Al₂O₃ + FeBeta], (5) [Mn/TiO₂ + FeBeta], and (6) Mn/FeBeta samples.

$$NO + NO_2 + 2NH_3$$

$$\rightarrow 2N_2 + 3H_2O \text{ on zeolite component.}$$
(V)

It should be noted that the lowest NO_x concentration was obtained on the Mn/FeBeta sample (<20 ppm), thereby indicating that the prevalence of the zeolite component in the catalyst increases the probability of reaction (V).

The data obtained by studying the oxidation of NH₃ also allow the following explanation of the higher NO_x conversion observed on the Mn/FeBeta catalyst at high temperatures (330-500°C, Fig. 3). Ammonia participates simultaneously in two reactions on the composite systems [oxide component + FeBeta] or the Mn/FeBeta catalyst. The selectivity of the ammonia oxidation process in this case will depend on the ratio of the rates of reactions (III) and (V), which in turn are directly related to the ratio between the oxide and zeolite components in the composite catalyst. Thus, the higher the proportion of the oxide component in the catalyst ($[Mn/Al_2O_3 + FeBeta], [Mn/TiO_2 +$ FeBeta]), the greater the amount of ammonia oxidized via reaction (III) and the greater will be the concentration of NO_x in the products. An increase in the zeolite content (Mn/FeBeta) will lead to involvement of NO_x in fast SCR NO_x reaction (V).

In addition, it should be taken into account that the standard catalytic reduction reaction (I) on the FeBeta component, whose proportion is much higher in Mn/FeBeta, plays a significant role in the overall SCR process in the temperature range of 300–500°C.

Thus, the comparison of the experimental data on the catalytic activity of the catalysts in the SCR NO_x process and the NH₃ oxidation reaction shows that the decline in the NO_x conversion on $[Mn/Al_2O_3 + FeBeta]$ and $[Mn/TiO_2 + FeBeta]$ is due to the beginning of domination of the ammonia oxidation reaction over the composite catalysts at temperatures above 350°C to form nitrogen oxides, most of which are not reduced to nitrogen via the standard SCR reaction because of a small zeolite content (three times below that in the Mn/FeBeta sample).

CONCLUSIONS

It has been shown that composite catalysts consisting of an oxidative component (MnO_x) and a zeolite (FeBeta) have high activity in both the selective catalytic reduction of NO_x and the selective oxidation of ammonia. The feasibility to integrate the two catalytic functions in one unit will make it possible to reduce not only costs, but also the size of the nitrogen oxides neutralization system as a whole, which is especially important for addressing environmental challenges of the automotive industry.

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REFERENCES

1. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide: Global *Update 2005,* Geneva: World Health Organization, 2006).

- 2. A. Alessandro and R. D. Ana, Energy 34, 348 (2009).
- 3. T. Johnson, Platinum Met. Rev. 52, 23 (2008).
- M. Jabłońska and R. Palkovits, Appl. Catal., B 181, 332 (2016).
- 5. S. M. Lee and S. C. Hong, Appl. Catal., B 163, 30, (2015).
- A. Yu. Stakheev, D. A. Bokarev, A. I. Mytareva, et al., Mendeleev Commun., No. 24, 313 (2014).
- Z. Wu, N. Tang, L. Xiao, Y. Liu, H. Wang, J. Colloid Interface Sci. 352, 143 (2010).
- A. Yu. Stakheev, G. N. Baeva, G. O. Bragina, et al., Top. Catal. 56, 427 (2013).

- A. Yu. Stakheev, A. I. Mytareva, D. A. Bokarev, et al., Catal. Today, No. 258 (Part I), 183 (2015).
- 10. D. S. Krivoruchenko, A. V. Kucherov, N. S. Telegina, et al., Izv. Akad. Nauk, Ser. Khim., No. 2, 389 (2014).
- V. V. Kachala, L. L. Khemchyan, A. S. Kashin, et al., Usp. Khim. 82, 648 (2013).
- 12. A. S. Kashin and V. P. Ananikov, Izv. Akad. Nauk, Ser. Khim., No. 12, 2551 (2011).
- 13. X. Lou, P. Liu, J. Li, and K. He, Appl. Surf. Sci. 307, 382 (2014).
- 14. J. Liu, C. Y. Yu, P. Q. Zhao, and G. X. Chen, Appl. Surf. Sci. 258, 9096 (2012).
- 15. A. Zhang, Z. Zhang, J. Chen, et al., Fuel Process. Technol. **135**, 25 (2015).

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