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Structural sensitivity of NO decomposition over a V-O-W/Ti(Sn)O_2 catalyst

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Abstract

NO decomposition at 673 K as a function of contact times over a V-O-W/Ti(Sn)O_2 catalyst obtained by sol–gel method and pretreated at 673 K in helium stream was investigated and compared with that over a Cu-ZSM-5 catalyst. Feed containing 4% NO in a helium stream was used in both the cases.

The V-O-W/Ti(Sn)O_2 catalyst showed higher activity as well as higher selectivity to dinitrogen than the Cu-ZSM-5 catalyst over the whole range of used contact times (0.375–15 g s cm^{-3}).

The highest activity of the V-O-W/Ti(Sn)O_2 catalyst, especially at higher normalised contact times ($\tau/\tau_{max} > 0.25$), was shown to result from vanadia-like surface layer formation with high tungsten content. It was also shown that the decrease in activity as contact time decreased is connected with tungsta monolayer formation on the V-O-W hybrid crystallites composed of tungsta, V-W oxide bronze and vanadia.

Keywords: Rutile-supported vanadia-tungsta catalyst; Nitrogen oxide decomposition; Surface species structure

1. Introduction

Anatase-supported vanadia-tungsta catalysts are commonly used to remove nitric oxide from flue gases of stationary sources of emission, e.g., power and heat plants, nitric acid factories, waste incinerators and stationary diesel engines [1–4]. NO removal in the presence of oxygen occurs via selective catalytic reduction by ammonia, according to the reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Ammonia is used as a selective NO reducer, as it does not undergo oxidation by oxygen present in flue gases. Unfortunately, it is corrosive, relatively expensive and poisonous.

Direct NO decomposition could be the best way to remove NO in the presence of dioxygen as it allows for the elimination of secondary pollutants.

NO decomposition was investigated mainly on supported precious metals: Pt-Ni [5], Pt [6,7], Rh, Ir and Ru [8] and on Cu in a zeolite structure [9,10]. To this point, the best catalysts for NO decomposition have been Cu-zeolites [9], especially Cu-ZSM-5 [10]. Poor performance of the catalyst based on supported precious metals was due to competitive adsorption of oxygen (released by decomposition or contained in the feed gas) on the active sites responsible for the reaction. The zeolite catalysts have advantage in comparison to the supported precious metals. This can be explained by the fact that desorption of the oxygen released by decomposition from the surface of the zeolite catalyst is not rate determining step in the overall reaction mechanism. However, with increasing concentration of oxygen contained in the feed gas conversion of NO to N_2 over Cu-ZSM-5 decreased, as already reported [11].

Efficient NO decomposition in the presence of oxygen was earlier observed [12] over unsupported V-O-W catalyst (V:W = 2:9) with the use of a feed containing 1% nitric oxide and 4% oxygen in helium. Miyamoto et al. [13] observed some NO decomposition in a stream not containing oxygen over V_2O_4. Very effective NO decomposition in a He stream

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containing 150 ppm NO over $Ti(Sn)O_2$-rutile-supported V-O-W catalyst deposited on fecralloy construction has been observed by Najbar et al. [14].

The aim of this study was to compare the activity in NO decomposition on the V-O-W/$Ti(Sn)O_2$ catalyst with that on the Cu-ZSM-5 one and to determine the structure of the species active in this reaction on the former one.

2. Experimental

2.1. Synthesis of the V-O-W/$Ti(Sn)O_2$ and Cu-ZSM-5 catalysts

$Ti(Sn)O_2$ support as well as $Ti(Sn)O_2$-supported catalyst were obtained using sol–gel method. $VO(C_3H_7O)_3$ (Johnson Matthey), WCl_6 (Aldrich), $SnCl_4$ (Aldrich), $Ti(C_3H_7O)_4$ and C_3H_7OH (Aldrich) were applied as substrates.

A mixture of a solution of $SnCl_4$ in isopropanol and titanium isopropoxide (Ti:Sn = 80.2:19.8) was used to synthesize the support. A mixture of the WCl_6 solution in isopropanol and vanadyl isopropoxide as well as sol solution of $Ti(Sn)O_2$ support (V:W:Ti:Sn = 1:9:72:18) were used to synthesize the catalyst. Details of these syntheses are described elsewhere [14–16]. The BET surface area of the freshly pretreated catalyst was equal to 67 $m^2\,g^{-1}$. A 0.315–0.5 mm-size fraction was used for the catalytic tests.

H/ZSM-5 zeolite (Si/Al = 54), supplied by Degussa, was used to synthesize Cu-ZSM-5 catalyst. Before the copper ion exchange step, the parent H/ZSM-5 (10 g) was washed with 0.5 dm^3 of diluted $NaNO_3$ solution (1 M), then filtered and dried at 373 K. An aqueous solution of cupric acetate (0.01 M) was used to obtain a final Cu-ZSM-5 zeolite catalyst. Ion exchange was performed for several hours at room temperature. The pH value of the initial cupric acetate solution was 6.4 and the pH of the equilibrium solution after exchange was 6.2. The obtained catalyst was washed and dried overnight at 373 K. The degree of ion exchange was ca. 70%. Pure zeolite powder containing copper was then pressed into tablets under the pressure of 3.1 t cm^{-2}, crushed and sieved. For the catalytic experiments the 0.315–0.5 mm size fraction was used. Negative values of the corresponding BET constants have been obtained indicating that the BET equation was not suitable for the calculation of the specific surface area of Cu-ZSM-5, probably due to micropore filling in the low-pressure region of a nitrogen adsorption isotherm. Therefore, specific surface area of the zeolite catalyst was estimated on the basis of the Langmuir adsorption model. The Langmuir surface area of the catalyst pretreated in He for 2 h was equal to 395 $m^2\,g^{-1}$.

2.2. Pretreatment of catalysts and determining surface species structure

Before catalytic testing of the V-O-W/$Ti(Sn)O_2$ catalyst in NO decomposition, pretreatment at 673 K in helium flow (40 $cm^3\,min^{-1}$) was performed for 1 h. Cu-ZSM-5 was also pretreated in helium before testing its activity in NO decomposition. The surface species structures of the V-O-W/$Ti(Sn)O_2$ catalysts (freshly prepared and used in NO decomposition as well as pretreated in a different atmosphere) were determined by Raman spectroscopy.

To check how the surface species structure and thus initial catalyst activity in NO decomposition depend on the pretreatment conditions, the NO conversion (at 423 K and normalised contact time (τ/τ_{max}) equal to 0.5) in a He stream containing 200 ppm NO, or 200 ppm NO and 10% oxygen, was investigated over the catalyst pretreated at 723 K in the feed or in flowing oxygen (40 $cm^3\,min^{-1}$).

The surface structure was determined by FT Raman spectroscopy. The spectra were registered using a Bio-Rad spectrometer with a Spectra Physics Nd:YAG laser (λ = 1064 nm).

2.3. Catalytic tests at different contact times

Catalytic tests for NO decomposition at different contact times were performed at 673 K using a feed containing 4% NO/He (Messer Griesheim) in a tubular fixed-bed stainless-steel reactor. Contact times were changed by varying total flow rate of the reactant gas (2–80 $cm^3\,min^{-1}$) at constant amount of the catalyst (0.5 g). Corresponding contact times were in the range from 15 to 0.375 g s cm^{-3}. The reaction temperature was measured using an Ni–CrNi thermocouple. All the measurements were taken after the reaction had reached a steady state. The reactor effluent was analysed by GC (Varian 3300) using a molecular sieve 5A column, thermal conductivity detector and helium as carrier gas.

Catalyst durability was examined by its prolonged exposure to the reaction gas mixture and repeated use in new experiments. No change in catalytic performance was observed after prolonged exposure to the feed.

3. Results and discussion

Fig. 1 presents a composition of the gas effluent from the reactor as a function of the normalised contact time—τ/τ_{max}. The molar fraction of NO_2 in the gas leaving the reactor is

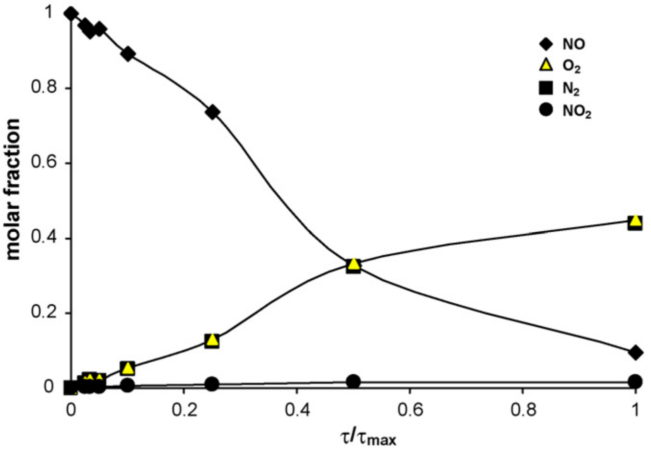

Fig. 1. The relationship between molar fractions of the reactants and normalised contact time for NO decomposition at 673 K over V-O-W/$Ti(Sn)O_2$ catalyst pretreated at 673 K in He (m = 0.5 g).

0.017. As can be seen, the molar fraction of O_2 and N_2 are almost the same and small differences can be explained by the secondary oxidation of undecomposed NO to NO_2 by the oxygen produced in the main reaction. The NO conversion to N_2 increases with the increase of the contact time, and reaches ca. 90% at τ/τ_{max} equal to 1.

This result is opposite to what Iwamoto et al. obtained for CuNaY [9] and Cu-ZSM-5 [10] catalysts. They found that over CuNaY [9] NO is converted at approximately the same rate to N_2 and to NO_2 and therefore the amount of oxygen formed is negligible. They claimed nitrogen dioxide is formed in a gas phase reaction between NO and O_2 resulting from NO decomposition. Iwamoto et al. [10] also did not observe oxygen in the products of NO decomposition at 673 K over Cu-ZSM-5 for contact time equal to 4 g s cm^{-3}.

In Fig. 2 the NO conversions to N_2 at 673 K as a function of the relative contact time (τ/τ_{max}) over V-O-W/Ti(Sn)O_2 (c) and Cu-ZSM-5 (a) are compared. The results obtained by Iwamoto et al. at 773 K over a CuNaY catalyst are also demonstrated (b) and the activity obtained by Iwamoto [10] over Cu-ZSM-5 with the degree of ion exchange equal to 73% at a contact time of 4.0 g s cm^{-3} is also shown (as a dark circle). As seen, NO conversion over Iwamoto Cu-ZSM-5 catalyst is similar to that over Cu-ZSM-5 used in the present investigation. In the whole range of contact times, V-O-W/T(Sn)O_2 activity is higher than that of Cu-ZSM-5. For the normalised contact time equal or longer than 0.25 it is also higher than the activity of CuNaY at 773 K.

At normalised contact time up to 0.25 the activity of V-O-W/T(Sn)O_2 and Cu-ZSM-5 at 673 K of CuNaY at 773 K does not differ very much. Above $\tau/\tau_{max} = 0.25$ the NO conversion over zeolitic catalysts steadily increases with the contact time while over V-O-W/T(Sn)O_2 it initially increases suddenly and later occurs more slowly. The activity was measured in the direction from higher to lower contact times. It is therefore reasonable to conclude that the abrupt loss of activity at τ/τ_{max} equal to 0.25 is the result of catalyst surface reconstruction due to the decrease of oxygen partial pressure in the gas phase while reaching the steady state of catalyst in stream. This reconstruction results in a sudden decrease in the amount of the active sites on the surface.

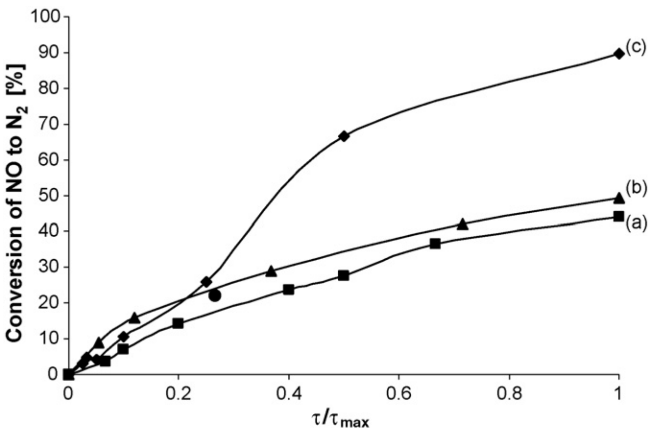

Fig. 2. The relationship between the conversion of NO to N_2 and normalised contact time over the Cu-ZSM-5 at 673 K (a), CuNaY at 773 K (b) and over V-O-W/Ti(Sn)O_2 at 673 K (c) catalysts ($m = 0.5$ g, 0.375–15 g s cm^{-3} range of contact time), as well as over Cu-ZSM-5 [10] at a contact time of 4.0 g s cm^{-3} (a dark circle).

To further study the surface reconstruction induced by redox processes, NO decomposition at 423 K in the absence and in the presence of 10% O_2 was investigated over the catalyst pretreated in the feed and in the oxygen flow.

NO conversion at 423 K in 200 ppm NO/He and 200 ppm NO + 10% O_2/He feeds with $\tau/\tau_{max} = 0.5$ over V-O-W/Ti(Sn)O_2 catalyst pretreated at 723 K in a 200 ppm NO/He stream and next in flowing oxygen (40 cm^3 min^{-1}) is illustrated in Fig. 3. As shown, the NO conversion achieves higher values over the catalyst pretreated in an oxygen stream than over the one pretreated in the 200 ppm NO/He stream. This explains why the NO conversion over the catalyst pretreated in the oxygen-free (or almost free) stream increases with time. The catalyst undergoes oxidation by oxygen formed in NO decomposition. The further increase of NO conversion after introducing oxygen into the feed can be attributed to further surface oxidation. Only a slight decrease in NO conversion in the 200 ppm NO/He stream over the catalyst pretreated in oxygen reveals that after reaching the steady state the surface does not undergo any distinct reconstruction in these conditions. However, the increase in NO conversion with time in stream after the addition of 10% oxygen illustrates that reaching the initial steady state in oxygen-free feed caused some reduction of the catalyst surface.

Further information about oxidation-induced surface reconstruction was determined from Raman spectra of the freshly prepared catalyst and that used in NO decomposition at different contact times as well as of the catalysts pretreated in different atmospheres.

In Fig. 4 the spectra of the catalyst freshly prepared and stored in ambient conditions as well as used in NO decomposition at 673 K are presented.

The spectrum of the catalyst freshly prepared and stored in ambient conditions shows: (i) distinct peaks of rutile (at 240, 425 and 602 cm^{-1}); (ii) a large band centered at ca. 800, a weak one at ca. 690, peaks at 133 and 115 cm^{-1} from tungsta [17,18] and V-W oxide bronze [17], respectively; (iii) a broad band at ca. 985 cm^{-1} from $V{=}O$ stretching vibration in vanadia-like species with water adsorbed on Lewis acid sites [19]; (iv) a weak and broad band at ca. 1095 cm^{-1} from the adsorbed O_2^- species [20]. The lack of the peaks at 144 and 995 cm^{-1} from crystalline V_2O_5 shows that vanadia-like species occur mainly in monolayer form.

The peaks at ca. 700 and 800 cm^{-1} and the lack of the peak at 133 cm^{-1} from crystalline monoclinic tungsta in the spectrum of the catalyst used in NO reduction at different contact times show the presence of the tungsta monolayer. The peak at 144 cm^{-1} from vanadia lattice vibrations reveals the presence of the vanadia-like crystalline species. The simultaneous occurrence of the peaks at 980, 913 and 876 cm^{-1} illustrates, in accordance with DFT data [19], the presence of the tungsten atoms on the surface of V_2O_5 crystallites. Thus, the feed at $\tau/\tau_{max} = 0.025$ interacts with the catalyst surface containing crystalline vanadia-like species with high tungsten atom content on their surfaces as

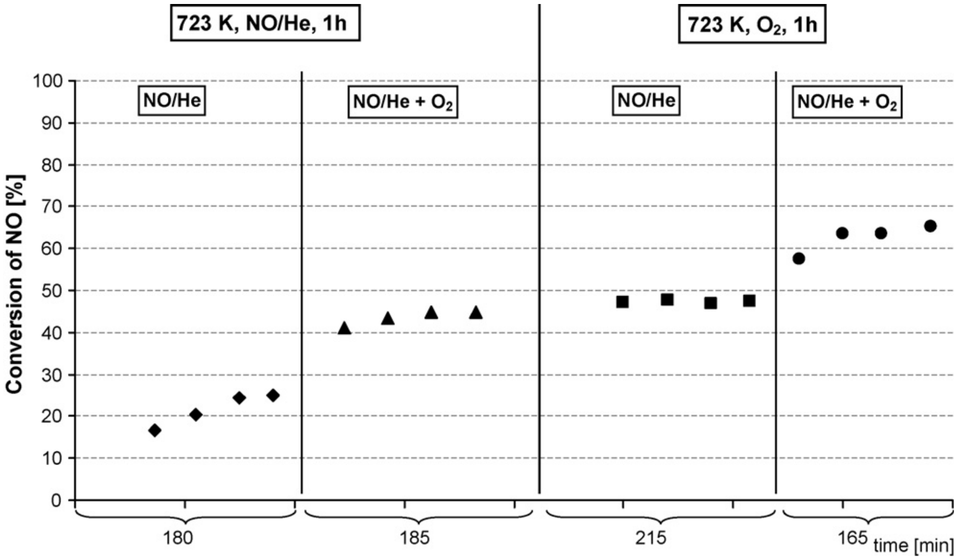

Fig. 3. NO conversion at 423 K over the V-O-W/Ti(Sn)O_2 catalyst in (200 ppm NO/He) and (200 ppm NO + 10% O_2/He) streams over the catalyst pretreated in 200 ppm NO/He stream or in oxygen ($m = 0.2$ g, $\tau/\tau_{max} = 0.5$).

well as monolayer tungsta-like ones. It may be concluded that during the catalyst pretreatment at 673 K in helium the monolayer vanadia-like species (Fig. 4(a)) dissolves in the top layers of the V-W oxide bronze structure, which can result in the formation of vanadia structure in these areas. The next inward diffusion of vanadium from such layers may result in the formation first of bronze and next of tungsta in them. The formation of the tungsta top layer may be responsible for the sudden drop of catalyst activity in NO decomposition. It should be stressed here that the freshly prepared catalyst with monolayer vanadia-like species practically not containing tungsten (lack of the distinct peak at ca. 880 cm^{-1}) shows NO conversion equal to ca. 15%. One may thus think that the enhanced activity of the catalyst pretreated in helium and next used in the NO decomposition at the highest contact time results from vanadia-like surface layers with pronounced tungsten atom content.

The effect of the oxygen content in the feed on the surface structure is additionally illustrated in Fig. 5, which shows Raman spectra of the catalyst pretreated at 723 K in 200 ppm NO/He stream (a) and at 723 K in the oxygen stream (b); and next stored in ambient conditions for several days.

Comparison of the spectrum of the catalyst pretreated in 200 ppm NO/He stream (Fig. 5(a)) and the spectrum of the freshly prepared one (Fig. 4(a)) reveals that pretreatment causes the population of O_2^- species on the surface (peak at 1092 cm^{-1}) to increase, as well as the appearance of the crystalline V_2O_5

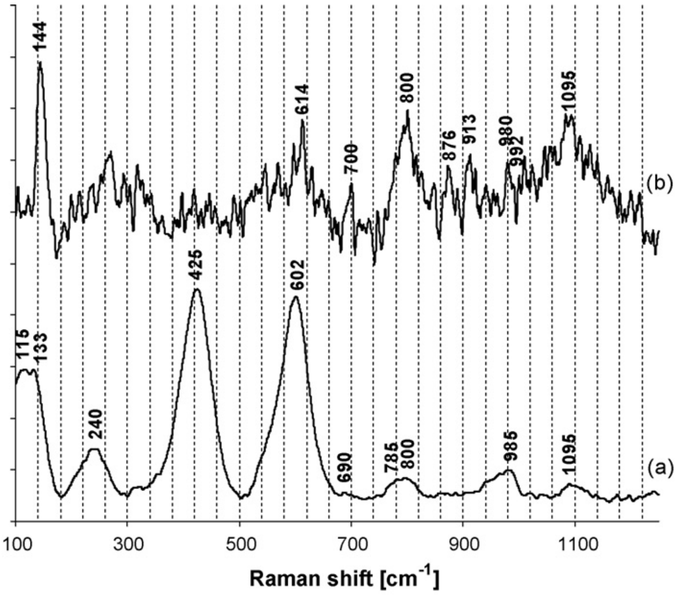

Fig. 4. FT-Raman spectra of V-O-W/Ti(Sn)O_2 catalysts: (a) freshly prepared and (b) used in catalytic test in NO decomposition at 673 K in the feed containing 4% NO/He in the (0.375–15 g s cm^{-3}) range of contact times.

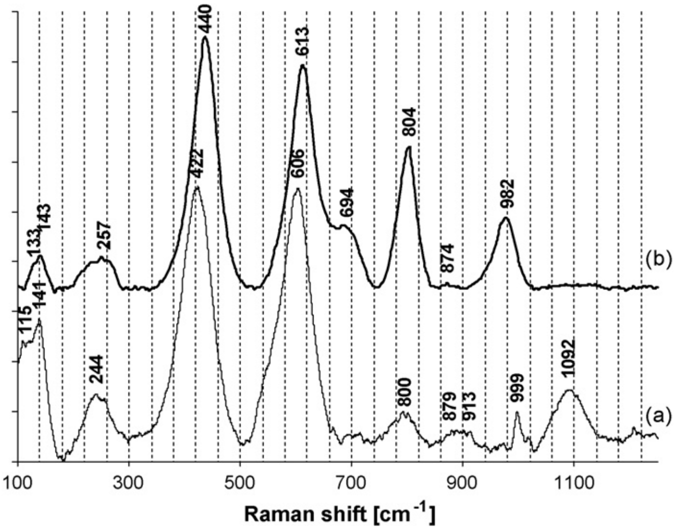

Fig. 5. FT-Raman spectra of V-O-W/Ti(Sn)O_2 catalysts: (a) pretreated at 723 K in 200 ppm NO/He for 1 h and (b) pretreated at 723 K in O_2 for 1 h.

species (peaks at 999 and 141 cm^{-1}) at the cost of the monolayer one (disappearance of the peak at 985 cm^{-1}). It can thus be concluded that pretreatment in 200 ppm NO/He results in the reduction of the catalyst surface, which leads to the dissolution of the vanadia-like species in the subsurface tungsta layers and crystalline vanadia-like layers (peaks at 141 and 999 cm^{-1}) with high tungsten content on the exposed surface (band between 879 and 913 cm^{-1}) as well as crystalline V-W oxide bronze layer formation connected with the disappearance of the monoclinic tungsta crystalline layers (disappearance of the peak at 133 cm^{-1} from tungsta lattice vibration).

However, the catalyst pretreatment in oxygen stream causes oxidation of the catalyst surface (disappearance of the peak of O_2^- at 1092 cm^{-1}) and advanced surface vanadium segregation from V-W oxide bronze (disappearance of the peak at 115 cm^{-1}) resulting in the formation of crystalline vanadia-like species (peak at 143 cm^{-1}) with low tungsten content in the exposed surface (982 cm^{-1}) on the monoclinic tungsta crystalline layers (804, 694 and 133 cm^{-1}).

At the highest contact time, content of O_2 formed due to NO decomposition in the gas phase above the catalyst is close to 2 vol.%, and it remains almost the same at twice lower contact time. It may therefore be concluded that the crystalline vanadia-like surface with high tungsten content became exposed as a result of the oxidation-induced vanadium diffusion to the tungsta monolayer. The O_2 content drop to ca. 0.07 vol.% at the lowest contact time may be caused by the partial covering of the vanadia-like layers by the tungsta monolayer formed in reducing conditions.

4. Conclusions

The activities of V-O-W/Ti(Sn)O_2 and Cu-ZSM-5 catalyst obtained in NO decomposition at different contact times were compared.

Catalytic tests were performed in a tubular stainless-steel reactor with 0.5 g of the catalyst fed by 4% NO/He stream in the range of flow rates 2–80 $cm^3\ min^{-1}$.

It was found that the rate of NO decomposition over V-O-W/Ti(Sn)O_2 is higher than over Cu-ZSM-5 in the whole range of contact times.

The NO conversion to N_2 increased with the increasing of the contact time over V-O-W/Ti(Sn)O_2 catalyst and reached ca. 90% at τ/τ_{max} equal to 1, while with Cu-ZSM-5 catalyst it was ca. 50%.

The surface species structure of the freshly prepared and used catalyst in NO decomposition was investigated by Raman spectroscopy.

It was shown that vanadium and tungsten oxides form hybrid crystallites containing V-W oxide bronze, monoclinic tungsten threeoxide with some vanadium atoms and pentoxide of divanadium with some tungsten atoms.

The structure of the surface layers of those hybrid crystallites exposed to the feed depends on the catalyst pretreatment and on the oxygen content in the feed.

The reducing catalyst pretreatment causes exposure of the WO_3 monolayer, laying on V_2O_5 ones with high W content, to the feed. While the oxidising pretreatment results in exposition of the V_2O_5 layers with a low W content.

To obtain the most active catalyst for NO decomposition in the presence of oxygen, mildly reduced pretreatment is needed, which results in the formation of the V_2O_5 layers with high W content in steady state conditions.

The results obtained in the present study reveal that V-O-W/Ti(Sn)O_2 is promising and stable catalyst with better activity then Cu-ZSM-5 zeolite, which was known as one of the most attractive catalyst for NO decomposition. The most important feature of the V-O-W/Ti(Sn)O_2 catalyst is high activity even in the presence of oxygen in the feed, which is not the case with Cu-ZSM-5. Therefore, it could find a practical application for NO decomposition.

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