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Rate-determining stage in NO SCR with propane on low-exchanged Cu-ZSM-5 catalyst

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The kinetics of the NO SCR with propane has been studied on a low-exchanged Cu-ZSM-5 catalyst. The study of the kinetics of individual reaction stages (2-nitrosopropane isomerization to acetone oxime and reaction of adsorbed acetone oxime with gaseous NO) has shown that the NO reaction with acetone oxime is the rate-determining stage in the whole chain of transformations leading to the formation of molecular nitrogen in the low-temperature region below 300 °C. The kinetic analysis of the reaction has revealed that at the temperatures above 300 °C propane plays a more important role.

Keywords: Cu-ZSM-5, NO reduction, adsorbed acetone oxime, isomerization of 2-nitrosopropane, FTIR spectra, kinetics of reaction with NO, kinetics of the separate steps of the reaction, TPD, pulse method

1. Introduction

The investigation of the mechanism of selective catalytic reduction (SCR) of nitrogen oxides with propane on zeolite catalysts, especially, on Cu-ZSM-5, is of great interest for researchers [1,2]. A great number of studies in this field have been devoted to the investigation of the composition of intermediates formed in the reaction of NO with propane, their thermal stability and reactivity [3–7]. The scheme of successive transformations of these intermediates suggested by Sachtler et al. [6,7] seems to be the most reasonable. For instance, in [7] propyl radicals formed during the interaction of propane with nitrite–nitrate complexes were supposed to react with NO to yield, first, 2-nitrosopropane and, then, acetone oxime. Reacting with gaseous NO, the latter gives N_2 and N_2O. Using the isotope method, the authors have demonstrated that during the formation of nitrogen molecules in the reaction of adsorbed acetone oxime with gaseous NO one nitrogen atom comes from NO, while the second one comes from acetone oxime. However, they failed to observe the formation of 2-nitrosopropane and acetone oxime in the course of reaction. The formation of these intermediates during the reaction between NO and propane on a low-exchanged Cu-ZSM-5 catalyst was shown experimentally in our works [8,9].

To determine the actual role of observed surface complexes in the reaction, it is necessary to compare the rates of their consumption and formation of desired products with the application of *in situ* methods [10,11]. If the observed rates are close, then it is possible to claim that they take part in the desired reaction pathway. However, in order to find out the nature of the rate-determining stage, it is necessary to compare the activation energies of the stage and the whole reaction, the dependence of their rates on the concentrations of the reagents or perform isotope experiments. For example, the detachment of a hydrogen atom from the hydrocarbon molecule is the rate-determining stage in the NO SCR with methane on Co-ZSM-5, as the primary isotope effect was observed when CH_4 was substituted with CD_4 [12]. Naturally, another stage can become rate determining when a different catalyst and/or reducing agent are used or under different conditions. The nature of the rate-determining stage in the NO SCR with propane on Cu-ZSM-5 is still unknown. Although in [13] it has been suggested that the hydrocarbon activation on the nitrite complex can determine the reaction rate, experiments performed in [13] are not full and are not sufficient to make the final conclusion on the nature of the rate-determining stage. The observed match of the rates of this stage and the reaction itself only indicates [11] that this stage is one of intermediate stages in the transformations.

In the present work we have studied the kinetics of the NO SCR with propane on a low-exchanged Cu-ZSM-5 catalyst. The use of a catalyst with a low exchange degree made it possible to observe the transformations of key intermediates [8,9] on its surface and estimate the contribution of individual stages to the total rate of the NO SCR with propane. Kinetics parameters of the stages of nitrosopropane isomerization to acetone oxime and reaction of adsorbed acetone oxime with gaseous NO have been determined. The nature of the stage determining the reaction rate has been established.

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2. Experimental

2.1. Catalyst preparation

Cu-ZSM-5 was prepared by ion exchange at 20 °C. A 0.07 M water solution of copper acetate complex was added dropwise to a H-ZSM-5 slurry at pH value of about 7. The slurry was stirred for 24 h before being vacuum filtered. The product was washed with deionized water. The sample obtained was air-dried at 110 °C overnight and then calcined at 500 °C in air for 4 h. The elemental analysis gave the following data: Cu/Al = 0.28 and Si/Al = 19.5. The BET surface area was 412 $m^2\,g^{-1}$. Prior to the experiments the catalyst was treated in a flow of oxygen for 1 h, followed by treatment in a helium flow for 1 h at 500 °C repeatedly (about ten cycles).

2.2. Kinetic measurements

A flow method with the use of a reactor with a vibrofluidized catalyst bed (RVCB) [14] suggested by Schukin and Veniaminov for pulse measurements [15] has been used for investigation of the kinetics of the NO SCR with propane and adsorption properties of the catalyst by TPD. Full mixing conditions are realized due to the vibrofluidization of the catalyst bed. The pulse technique in combination with RVCB has all advantages of a flow method [16] and the possibility of direct determination of the reaction rate in each pulse.

To avoid the inner diffusion slowdown, the reaction activation energy and kinetic reaction orders with respect to NO and C_3H_8 were determined from the experimental data obtained on a Cu-ZSM-5 catalyst with the grain size of 0.38 mm [17].

Prior to the kinetic experiments, the catalyst sample (0.5 g) was subjected to a standard treatment in the He flow at 500 °C for 1 h. After the treatment, the temperature of the reactor was decreased to the desired value and the reaction mixture was introduced at the rate of 10000 h^{-1}. The feed composition was varied within C_3H_8/NO = 0.5–2.0; O_2 = 0–5.5%. The procedures of kinetic experiments and product analysis have been described in more detail in [8,9].

2.3. Adsorption of acetone oxime. Pulse experiments

Prior to the adsorption the sample (0.3 g) was subjected to the standard treatment and cooled down to the temperature at which the acetone oxime adsorption was performed (100–200 °C). In contrast to [7], where acetone oxime was deposited by catalyst impregnation with the aqueous solutions of acetone oxime of variable concentration, we adsorbed acetone oxime from the vapor phase. A sample of acetone oxime (∼5 mg) was placed into a 2 ml metal loop located in front of the reactor on a six-way valve. For introduction of acetone oxime to the catalyst the loop was purged with helium for 5 s with the rate 100 $ml\,min^{-1}$. The loop and all the tubes on the way of acetone oxime to the reactor were heated to 90 °C. After the treatment of the catalyst surface with the acetone oxime vapor the reactor was purged with helium for 5 min to remove acetone oxime from the gas phase.

The interaction of acetone oxime with NO was estimated from the nitrogen formation in each pulse of NO diluted with He (pulse volume 19.8 Ncm^3, NO concentration within 660–7500 ppm, pulse interval 15 min, carrier gas flow 100 $cm^3\,min^{-1}$) and change of the surface coverage of acetone oxime revealed in TPD spectra (TPD spectra will be described below). A flame-ionization detector (FID) was used for registration of the TPD spectra of acetone oxime and 2-nitrosopropane. A converter for conversion of the its oxidation products (CO and CO_2) to methane [8] was located in front of the detector. The procedures of TPD experiments have been described in more detail in [8,9].

2.4. In situ FTIR measurements

IR spectra were recorded on a BOMEM-102 FTIR spectrometer in the frequency range of 1300–4000 cm^{-1}. An IR cell was used to record spectra in the temperature range of 20–250 °C. Self-supporting wafers of ca. 10–12 $mg\,cm^{-2}$ thickness were pressed and positioned on a support between NaCl windows of the cell. All procedures of the FTIR measurements have been described in more detail in [9].

3. Results and discussion

3.1. Kinetic parameters of the reaction

The investigation of the activity and selectivity of the low-exchanged Cu-ZSM-5 catalyst has shown that at temperatures above 185 °C the selectivity of the nitrogen formation at the C_3H_8/NO ratio above 1.4 is close to 100%, i.e., nitrogen is the principal product of the NO reduction.

The dependence of the reaction rate on the oxygen concentration is similar to the one observed in [2]. The reaction rate is equal to zero in the absence of oxygen and sharply grows with the introduction of small quantities of O_2 reaching its maximum at $[O_2] = 0.4\%$. In the range of oxygen concentrations between 0.4 and 0.6% the reaction rate is approximately constant. Further increase of the oxygen concentration results in the decrease of the reaction rate. The character of this decrease depends on temperature. At low temperatures (150–250 °C) the reaction rate ceases to depend on the oxygen concentration in the gas-phase starting with the concentration of 0.4 vol%, i.e., zero reaction order with respect to oxygen is observed. The presence of a small amount of oxygen in the gas phase seems to be necessary for nitrite–nitrate surface complexes formation which are responsible for the initiation of further intermediates transformation into acetone oxime. It should be noted that nitrite–nitrate complexes are formed easily at room temperature [9].

The complex character of the reaction rate dependence on temperature is revealed also in the dynamics of changes of other kinetic parameters. Data presented in figure 1 indicate that there are two temperature regions with different reaction characteristics. The reaction orders with respect to NO and propane change with the temperature rise between 215 and 500 °C. Below 300 °C the NO reaction order is close to first order. The temperature rise to 400 °C results in the decrease of the NO kinetic order to a constant value of 0.4. Note that the decrease of the NO reaction order with the temperature rise had been observed earlier on a Cu-MOR catalyst with the exchange degree of 23% [18].

The temperature dependence of the C_3H_8 reaction order (figure 1) is opposite to that of NO. A fractional propane reaction order equal to 0.52 is observed at low temperature. The temperature rise leads to its increase up to 0.90. Values of the apparent activation energy obtained in the low-temperature and high-temperature regions are close to each other. Below 250 °C the activation energy in NO SCR with propane is 19.8 ± 0.4 kcal mol^{-1}. This value is in good agreement with the corresponding value obtained for an excessively exchanged Cu-ZSM-5 catalyst (20 kcal mol^{-1}) [18]. Meanwhile, in the temperature range of 400–500 °C it is equal to 21.0 ± 0.4 kcal mol^{-1}. The change of the reaction orders with the transition to a different temperature region can lead to a change of the reaction activation energy as well. However, we cannot claim that the activation energies are really different in the two temperature regions because the difference of the obtained values is very small.

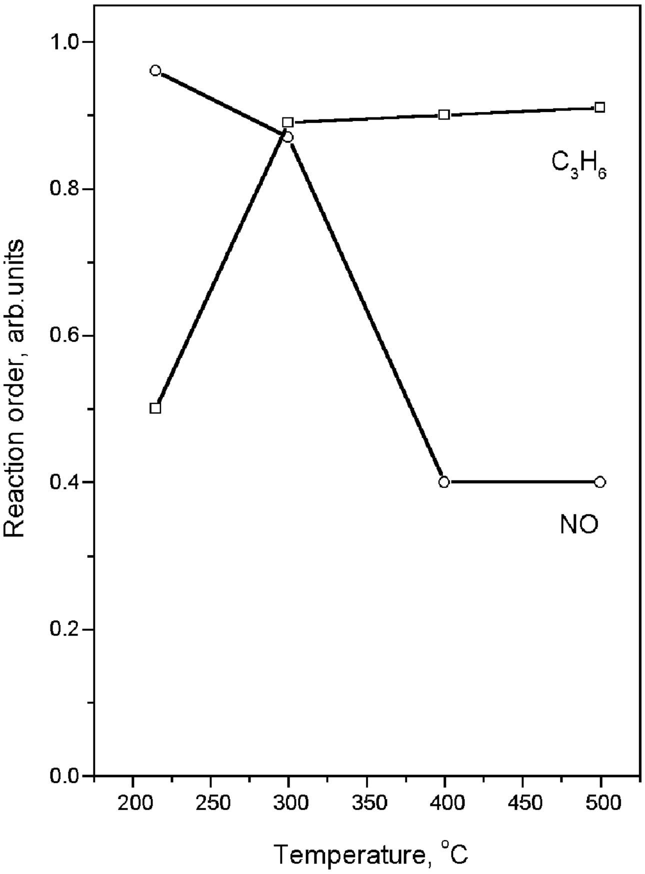

Figure 1. Effect of temperature on kinetic orders with respect to NO and C_3H_8 in NO SCR with propane.

3.2. Kinetics of individual stages

The existence of two temperature regions with different reaction orders with respect to NO and propane could be caused by change of the rate-determining stage of the process with the temperature increase. Among stages that can determine the overall rate of the NO SCR with propane, propane activation with the formation of propyl radicals [7,11] and transformation of key intermediates (2-nitrosopropane and acetone oxime) [7] are usually mentioned. The character of changes of the propane reaction order (figure 1) makes it possible to suppose that the stage of the propane interaction with nitrite complexes can be rate determining at temperatures above 300 °C, when the propane reaction order is close to first order. Other stages can be expected to play a more significant role in the low-temperature region (below 300 °C).

3.3. Kinetics of 2-nitrosopropane isomerization

Earlier we have shown that a significant amount of 2-nitrosopropane is present on the surface of Cu-ZSM-5 after the coadsorption of NO and propane at 50 °C [8,9]. 2-nitrosopropane is also known to isomerize to acetone oxime, the isomerization rate of nitrocompounds to oximes significantly decreasing after their adsorption on the surface [19].

Let us discuss the effect of temperature on the surface coverage with 2-nitrosopropane and acetone oxime. Changes of the surface concentration of the isomers were registered by two independent methods: TPD and IR. As NO is not formed during the decomposition of acetone oxime, whereas the decomposition of 2-nitrosopropane results in the evolution of both NO and CO_2 with a constant ratio 1 : 3 [8,9], it is possible to evaluate the ratio of the isomers by analyzing the NO/CO_2 ratio in TPD spectra. As an example, figure 2 presents a fragment of the TPD spectrum corresponding to the evolution of CO_2 and NO resulting from the desorption of acetone oxime (A) and nitrosopropane (B). Individual peaks were discriminated using a procedure described in [8]. Solid lines present simulated peaks both for CO_2 and NO evolution corresponding to the desorption of acetone oxime and 2-nitrosopropane. Kinetic parameters employed for peaks simulation were the same as in [8]. The surface concentrations were evaluated by numerical integration of these peaks. In the IR spectra the ratio of 2-nitrosopropane to acetone oxime can be determined from the ratio of the intensity of the line of the C=N bond stretching vibrations, which is proportional to the surface coverage with acetone oxime, to the intensity of the line of one of the bending vibrations of CH_3 groups, which seems to be proportional to the summary surface concentration of both isomers.

Table 1 presents TPD data and the ratios of the intensities of the bands of C=N stretching vibrations (I_{1661}) and bending vibrations of methyl groups (I_{1374}) 1 h after the coadsorption of NO and propane at different temperatures. The I_{1661}/I_{1374} ratio appeared to be proportional to the fraction of acetone oxime (α_{ox}^{a}) on the surface obtained from the TPD experiments (figure 3). This indicates that there is a good correlation between the results obtained by two independent methods ($R_{corr} = 0.99903$) and one can conclude that the extinction coefficients of CH_3 bending vibrations in 2-nitrosopropane and acetone oxime are practically the same.

These data make it possible to calculate the activation energy of the isomerization stage, which is equal to 10.1 ± 0.6 kcal mol^{-1}. The obtained value is lower than the value of apparent activation energy of the reaction.

To obtain information on the surface concentrations of 2-nitrosopropane and acetone oxime under conditions close

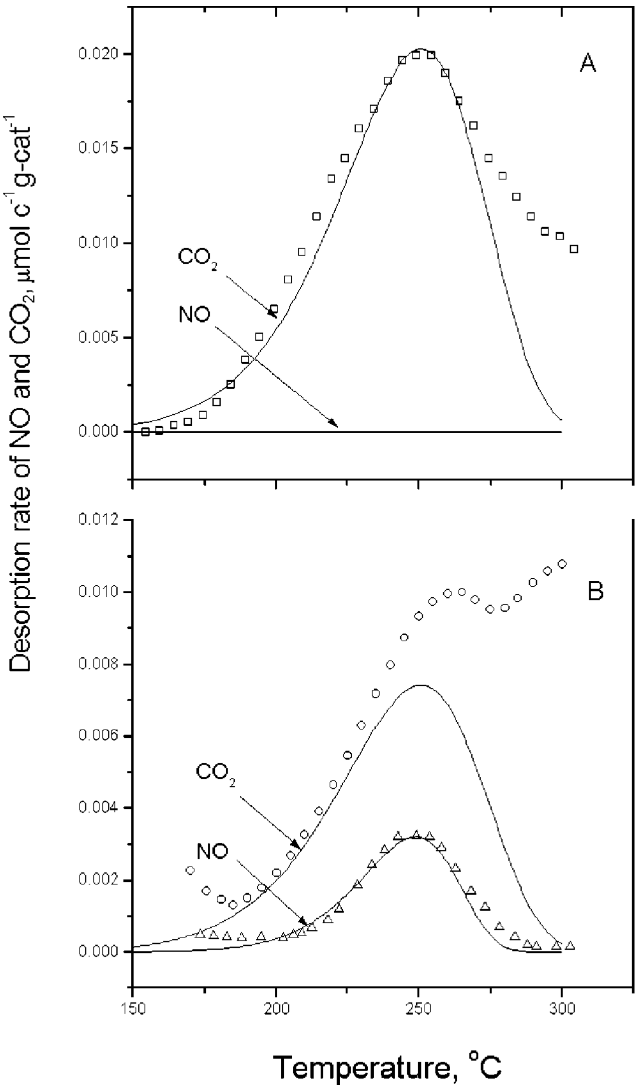

Figure 2. Fragments of TPD spectra corresponding to the evolution of CO_2 and NO formed during desorption of acetone oxime (A) (T_{ads} = 170 °C) and 2-nitrosopropane (B) from [8] (T_{ads} = 50 °C). Solid lines present individual peaks discriminated and simulated using a procedure described in [8]. Points correspond to experimental data. Heating rate: 10 °C min^{-1}.

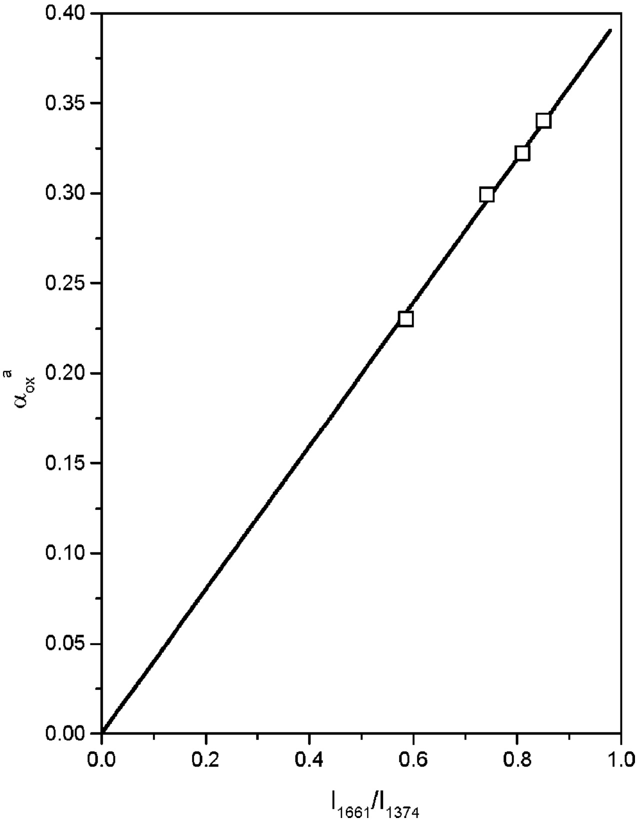

Figure 3. Dependence of acetone oxime fraction (α_{ox}^{a}) obtained by TPD analysis on ratio of I_{1661}/I_{1374}.

Table 1

TPD data and the ratios of the intensities of the bands of C=N stretching vibrations (I_{1661}) and bending vibrations of methyl groups (I_{1374}) 1 h after the coadsorption of NO and propane at different temperatures (NO = 666 ppm, C_3H_8 = 3000 ppm).

Temperature (°C)	TPD data			FTIR data	
	Amount (μmol g-cat^{-1})		α_{ox}^{a} [a]	I_{1661}	I_{1661}/I_{1374}
	2-nitrosopropane	acetone oxime			
120	0.0599	0.085	0.586	0.0713	0.230
140	0.0372	0.108	0.743	0.0926	0.299
150	0.0279	0.119	0.810	0.0998	0.322
160	0.0218	0.125	0.851	0.105	0.340

[a] $\alpha_{ox}^{a} = \frac{[(CH_3)_2CNOH]}{[(CH_3)_2NOH]+[(CH_3)_2CHNO]}$.

Table 2

Surface coverage with 2-nitrosopropane and acetone oxime in dependence of the reaction temperature in the steady state of the catalyst (NO = 666 ppm, C_3H_8 = 3000 ppm, O_2 = 2.2 vol%, flow rate 100 ml min^{-1}, catalyst loading 0.3 g).

Temperature (°C)	Surface coverage (μmol g-cat^{-1}) With 2-nitrosopropane	Surface coverage (μmol g-cat^{-1}) With acetone oxime	Current NO content (ppm)
150	1.19	4.80	663
160	0.98	5.01	660
170	0.69	5.30	659
182	0.57	5.42	645
190	0.44	5.55	627

to those realized during the NO SCR with propane, we have performed experiments on the NO and CO_2 TPD immediately after the reaction. In this case the feed was changed to helium and the reaction temperature was decreased to 50 °C in several seconds. Then, thermal desorption of NO and CO_2 was conducted by heating the reactor to 500 °C with the rate of 10 °C min^{-1}. The results of these experiments are presented in table 2. They indicate that both 2-nitrosopropane and acetone oxime are present on the surface under reaction conditions. The dependence of the ratio between the isomers on temperature can be satisfactorily described by the isomerization kinetics. This means that the decrease of the acetone oxime concentration due to its reaction with NO is compensated by the isomerization under the reaction conditions, so that the equilibrium between the isomers is not altered. Therefore, it is possible to conclude that isomerization in these conditions is significantly faster than the acetone oxime reaction with NO and cannot determine the rate of the SCR process. Indeed, the activation energy of this stage is significantly lower than that of the NO SCR with propane.

3.4. Interaction of acetone oxime with NO

Let us now discuss the stage of acetone oxime interaction with NO. In the whole temperature range studied (100–200 °C) nitrogen was the principal product of the NO reaction with acetone oxime adsorbed on Cu-ZSM-5. The concentration of nitrous oxide was lower by two orders of magnitude than those of N_2, most likely due to the reduction of nitrous oxide to nitrogen on the catalyst surface, which was reduced more in this case than in [20].

Figure 4 presents a typical dependence of the nitrogen formation and changes of the surface concentration of acetone oxime on the number of NO pulses. One can see that the amount of nitrogen formed is directly proportional to the surface coverage of acetone oxime. From another side the amount of nitrogen formed in the first pulse is proportional to the concentration of NO in the feed meaning first order on NO in this stage (e.g., 0.04, 0.21 and 0.34 μmol N_2 g-cat^{-1} at 666, 4700 and 7500 ppm NO content in pulse at 200 °C, respectively). The rate constant and the activation energy of the reaction of gaseous NO with acetone oxime adsorbed on Cu-ZSM-5 are equal to $(4.44 \pm 0.16) \times 10^{10}$ l mol^{-1} s^{-1} and 20.2 ± 0.6 kcal mol^{-1} (within 100–200 °C), respectively. One can see that the obtained value of apparent energy activation for this step is close to that for the reaction.

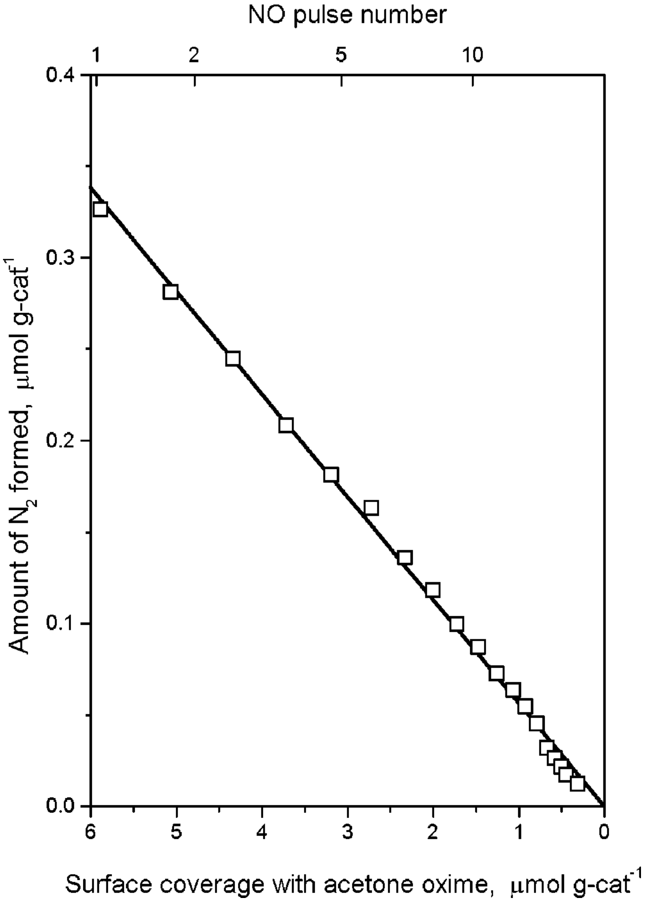

Figure 4. Dependence of the amount of nitrogen formed under interaction of gaseous NO with adsorbed acetone oxime at 200 °C on the surface coverage with acetone oxime. NO content 7500 ppm.

The obtained kinetic parameters of the acetone oxime interaction with NO make it possible to evaluate the contribution of this stage to the rate of the NO SCR with propane. The calculation of the nitrogen formation rate in the reaction of NO with acetone oxime with the use of the kinetic constant of this stage under the NO SCR conditions (i.e., with known NO concentration, steady-state surface concentration of acetone oxime and temperature) has shown that the calculated value is close to that measured experimentally for the NO SCR with propane in the low-temperature region (figure 5).

4. Conclusion

So, the study of the reaction kinetics has revealed that there are two temperature regions with significantly different reaction pathways. The transition from one region to the other one is accompanied with the change of the reaction orders with respect to NO and propane, which indicates that different reaction stages determine the process rate in these regions. Obtained kinetic parameters of individual

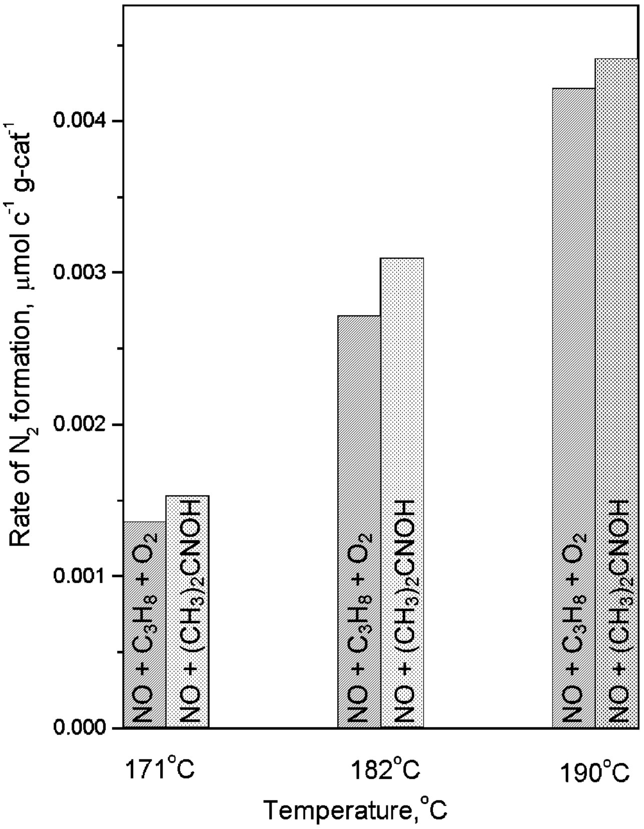

Figure 5. Comparison of the experimental reaction rate with the rate calculated on the basis of the kinetic parameters of the stage of acetone oxime interaction with NO at different temperatures.

reaction stages (2-nitrosopropane isomerization to acetone oxime and reaction of adsorbed acetone oxime with gaseous NO) supply us to conclude that the isomerization is faster than the acetone oxime reaction with NO, and, therefore, cannot be the rate-determining stage. An evaluation of the nitrogen formation rate from the rate of the NO reaction with acetone oxime in the SCR conditions has shown a relatively good match with the value experimentally measured in the NO SCR with propane in the low-temperature range. On the basis of this fact and match of the activation energies, it is reasonable to conclude that the NO reaction with acetone oxime is the rate-determining stage in the whole chain of transformations leading to the formation of molecular nitrogen in the low-temperature region, at least, on a low-exchanged Cu-ZSM-5 catalyst. The nature of the rate-limiting stage at high temperature is unclear now.

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