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Additional Information

Influence of ZSM-5 porosity and type of deposited iron species on its catalytic activity in the process of selective ammonia oxidation

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Abstract

In the presented studies an influence of different parameters, such as zeolite sample porosity, form of used iron source ($[Fe_3(OAc)_6O(H_2O)_3]^+$ oligocations or $FeSO_4$ solutions) and method of iron species deposition (ion-exchange, impregnation), on the catalytic activity in the process of the selective catalytic oxidation of ammonia (NH_3-SCO) was studied. Conventional and mesoporous ZSM-5 zeolites, obtained by desilication and modified with iron species, were analysed with respect to their textural, surface and crystalline properties (N_2-sorption, HRTEM, XRD) as well as the form of introduced Fe species (UV-vis-DRS). Ion-exchange with $[Fe_3(OAc)_6O(H_2O)_3]^+$ oligocations and impregnation with these

oligocations and $FeSO_4$ solutions were found as the most effective methods of the zeolite samples activation for NH_3-SCO.

1. Introduction

Zeolites, materials characterized by microporous, crystalline structure have been extensively examined for applications in various industries, including catalytic and sorption processes [1]. The success of zeolites and their wide application is related to their exceptional features, which play an important role in catalysis. In addition to the properties that allow them to be relatively easily modified, zeolitic materials exhibit extraordinary attribute, which is shape selectivity for the guest molecules [1, 2]. However, the reason of this phenomenon, the location of active sites within the narrow and uniform micropores, may also result in internal diffusion limitations of bulkier reactant molecules during catalytic process. Hence, the reduction of the intracrystalline diffusion limitations usually leads to the improvement of the activity and selectivity of the catalysts [3]. The mentioned restrictions can be minimized e.g. by creation of additional pores with larger diameter in the structure of conventional zeolites. One of the most popular, effective and cheap methods of mesoporosity generation in zeolites is based on the desilication process (treatment in basic solution) [3, 4].

Modification of the porous materials (e.g. zeolites, mesoporous silica sieves) with transition metals (e.g. Cu, Fe, Co) is an effective way to increase their activity in the selected reactions of the environmental catalysis [5-12]. One of the processes from the environment protection sector, which proceeds on the red-ox active sites, is selective catalytic oxidation of ammonia to dinitrogen (NH_3-SCO, AMOX). The emission of toxic ammonia from various industrial processes (e.g. nitric acid and nitrogen fertiliser production plants, urea manufacturing or the $DeNO_x$ process) into the atmosphere can be limited by the application of heterogeneous catalysis [13].

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Two methods are the most often used for the introduction of transition metals into zeolites - ion-exchange (IE) and incipient wetness impregnation (IM). These two approaches allow to effectively introduce metallic active phase in various forms, from monomeric cations to more aggregated species. It is worth to mention, that good dispersion of metal (in the form of uniform species and without blocking of narrow pores) is important issue in synthesis of active and highly selective catalysts. Less aggregated metal species, like mononuclear cations or small metal oxide oligomers, have been found to be active in various catalytic processes. An introduction of transition metals in the desired form can be facilitated by the modification of the zeolite porous structure (generation of mesoporosity) [5-7].

The aim of research was examination of the physicochemical properties of parent and desilicated ZSM-5 modified with monomeric iron cations (Fe) and ($[Fe_3(OAc)_6O(H_2O)_3]^+$, oligocations Fe3) by ion-exchange and impregnation methods. The obtained samples (containing different form and content of iron) were examined in the selective catalytic oxidation of ammonia to dinitrogen.

2. Experimental methods

2.1. Catalysts preparation

Desilication

The detailed procedure used for desilication of ZSM-5 zeolite with the Si/Al molar ratio of 45 (Clariant Company, Germany) in the H-form and denoted as HMFI, was presented in our previous paper [14]. Desilication method was based on the treatment of the parent HMFI material in 90 mL of base solution containing sodium hydroxide and tetrapropylammonium hydroxide (TPAOH), with the molar TPA^+/OH^- ratio of 0.4 and total concentration of OH^- equal to 0.2 M. 3 g of powdered parent zeolite was stirred with the alkaline solution under reflux at 65ºC for 4 h.

In the next step, the obtained material was transformed into H-form by a triple ion-exchange procedure with NH_4NO_3. Desilicated zeolite in H-form was denoted as HMFI/des.

The parent HMFI and HMFI/des materials were modified with iron salt solutions by two methods - ion-exchange and incipient wetness impregnation. Iron was introduced using Fe^{2+} cations ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich) and tri-nuclear iron oligocations ($[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$, F3) (preparation details presented in [8-10]).

Ion-exchange

The zeolitic materials (HMFI and HMFI/des) were subjected to ion-exchange procedure with $FeSO_4 \cdot 7H_2O$ solution (3 g of zeolite per 250 ml of solution), after drying at 110ºC overnight. The modification was performed by stirring with the prepared iron solution at 500 rpm under reflux at 85ºC for 6h. The concentration of the salt was adjusted to the theoretically determined ion-exchange capacity of each sample. The mixture was stirred under Ar atmosphere to prevent iron species against oxidation. Finally, the obtained materials were cooled down in an ice bath, centrifuged (3500 rpm, 15 min), washed with distillated water and calcined at 600ºC for 6 h.

The resulting Fe-samples modified with $FeSO_4 \cdot 7H_2O$ solution by ion-exchange were denoted as Fe(IE)MFI and Fe(IE)MFI/des.

The same procedure was applied in the case of modification of the samples with iron oligocations ($[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$), which are denoted as Fe3(IE)MFI and Fe3(IE)MFI/des.

Incipient wetness impregnation

Both the samples, parent and micro-mesoporous (previously dried overnight at 110ºC), were modified with iron by incipient wetness impregnation (with adequate volume of iron solution, basing on determined sorption capacity) with the solutions of $FeSO_4 \cdot 7H_2O$ and $[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$. The concentration of the metal precursors was adjusted to obtain 5 wt.% of Fe in the samples. After impregnation the samples were dried overnight at 60ºC and calcined at 600ºC for 6 h. The obtained samples are denoted as Fe(IM)MFI, Fe(IM)MFI/des, Fe3(IM)MFI and Fe3(IM)MFI/des.

All the sample codes and the parameters of their modification procedures are presented in Tab. 1.

Tab. 1. Sample codes, description of the modification procedures and textural parameters of the studied

Sample code	Desilication	Fe introduction method	Fe source	S_{BET} /m²/g	S_{EXT} /m²/g	V_{MIC} /cm³/g	V_{MES} /cm³/g
HMFI	-----	-----	-----	462	72	0,178	0,233
HMFI/des	65ºC for 4 h	-----	-----	571	266	0,130	0,491
Fe(IE)MFI	-----	ion-exchange	$FeSO_4 \cdot 7H_2O$	467	71	0,176	0,210
Fe(IE)MFI/des	65ºC for 4 h	ion-exchange	$FeSO_4 \cdot 7H_2O$	548	274	0,113	0,485
Fe3(IE)MFI	-----	ion-exchange	$[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$	449	78	0,167	0,247
Fe3(IE)MFI/des	65ºC for 4 h	ion-exchange	$[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$	520	276	0,102	0,509
Fe(IM)MFI	-----	impregnation	$FeSO_4 \cdot 7H_2O$	389	61	0,148	0,191
Fe(IM)MFI/des	65ºC for 4 h	impregnation	$FeSO_4 \cdot 7H_2O$	460	213	0,103	0,377
Fe3(IM)MFI	-----	impregnation	$[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$	408	79	0,149	0,188
Fe3(IM)MFI/des	65ºC for 4 h	impregnation	$[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$	485	247	0,101	0,432

2.2. Catalysts characterization

The powder X-ray diffractograms of the samples were obtained with a Bruker D2 Phaser instrument. The diffractograms were recorded in the 2Ө range of 5 – 50° with a step of 0.02° and a counting time of 1 s per step.

The textural parameters of all the studied samples were determined by N_2 adsorption at -196 °C using a 3Flex v1.00 (Micromeritics) automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 350 °C for 24 h.

High resolution electron micrographs (HRTEM) were collected by a JEOL JEM2100F electron microscope operating at 200 kV.

The UV–vis–DRS was applied to determine coordination and aggregation of transition metal species introduced into the obtained samples. The spectra were recorded using an Evolution 600 (Thermo) spectrophotometer in the range of 200 – 900 nm with a resolution of 2 nm.

2.3. Catalytic tests

Catalytic studies of selective catalytic oxidation of ammonia (NH_3-SCO) were performed in a fixed-bed flow microreactor system in the temperature range 100 to 600 °C under atmospheric pressure. During the catalytic run, the reactant's concentration was continuously measured using a quadrupole mass spectrometer (Prevac) connected directly to the reactor outlet. Prior to the reaction, each sample (0.100 g) of the catalyst, with a particle size in the range of 160 - 315 μm, was outgassed in a flow of pure He (20 mL/min) at 600 °C for 1 h. The following composition of the gas mixture: [NH_3] = 5000 ppm, [O_2] = 25000 ppm diluted in pure helium (total flow rate of 40 mL/min) was used.

Results and discussion

2.4. Physicochemical characterization of the catalysts

The analysis of nitrogen adsorption-desorption isotherms of the samples before and after alkaline treatment (results shown in supplementary materials, Fig. S1) proves the generation of mesoporosity in HMFI/des (change in the isotherm shape type from Ia to IVa) [15]. In the case of N_2 isotherms recorded for the samples modified with iron (results not shown), the

shape did not change significantly in comparison to the parent and desilicated samples, respectively.

Textural parameters of the studied samples, determined by N_2 sorption measurements are presented in Tab. 1. The base treatment of the MFI sample resulted in a slight decrease in micropore volume, although an increase of BET and external surface areas as well as volume of mesopores was observed after desilication. Analysis of this phenomenon leads to the conclusion that the applied desilication procedure allowed to generate significant mesoporosity in the structure of preserved microporous zeolite. Moreover, the presence of regularly distributed 'meso-holes' created on the catalyst surface after desilication was confirmed by high resolution transmission electron microscopy (HRTEM) measurements (HRTEM micrographs are shown in the supplement materials, Fig. S2 A and B). The diameters of the generated meso-cavities (basing on the HRTEM images) are about 10 nm.

Modification of the samples with iron did not change significantly the textural parameters of the samples. A decrease in the surface development can be connected with the surface coverage by the metal species. This effect is especially significant in the case of the impregnated samples with higher metal loadings.

Fig. 1 shows the XRD powder patterns of the studied samples. The reflections characteristic of the MFI structure type are present in all diffractograms, hence zeolitic character of the samples after modifications was maintained. Lower intensity of the reflections in diffractograms of the desilicated samples is probably related to the partial destruction of the zeolitic structure occurred during alkaline treatment. Furthermore, it can be seen, that no reflections connected with the presence of α-Fe_2O_3 clusters were found [16]. The lack of these reflections indicates a good degree of dispersion of the introduced metallic phase. Deposition

of iron in the form of highly dispersed species was also confirmed by HRTEM and EDS analysis (results discussed in [14]).
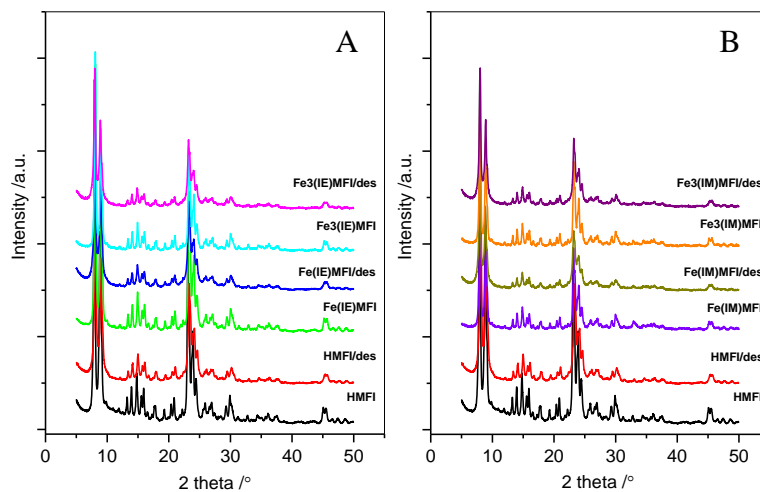

Fig. 1. PXRD patterns of the HMFI and HMFI/des materials and samples modified with iron solutions by ion-exchange (A) and impregnation (B) method

The UV-vis-DR spectra recorded for the materials modified with iron solutions are presented in Fig. 2. The spectra of the Fe-modified samples consist of 3 bands located below 300 nm, in the range of 300-400 nm and above 400 nm. The absorption < 300 nm is characteristic of monomeric Fe^{3+} cations, while the band located at 300-400 nm is attributed to small oligonuclear Fe_xO_y clusters. The presence of absorption band above 400 nm is connected with the presence of bulky Fe_2O_3 particles [17]. The analysis of the spectra recorded for the materials modified with iron by ion-exchange (Fig. 2 A) was presented in details in our previous work [14]. However it is worth to notice that the intensity of the absorption bands corresponds to the iron content in the samples (Fe(IE)MFI - 0.6 wt.%, Fe(IE)MFI/des - 0.4 wt.%, Fe3(IE)MFI - 6.2 wt.%, Fe3(IE)MFI/des - 5.1 wt.%, details in [14]). In the case of the samples modified by impregnation method, iron was introduced in three possible forms (monomeric cations, oligomeric species and bulky metal oxide particles). High surface loading of iron observed for the IM series is related to the specificity of these modification

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method and resulted in the creation of more aggregated iron species in comparison the zeolites modified by ion-exchange. It is worth to notice that both the porosity of samples and the iron source used did not influence significantly the form of deposited iron species in the samples modified by impregnation method. Also the intensity of all the spectra is similar what corresponds with the same intended Fe content in the samples ≈ 5 wt.%.
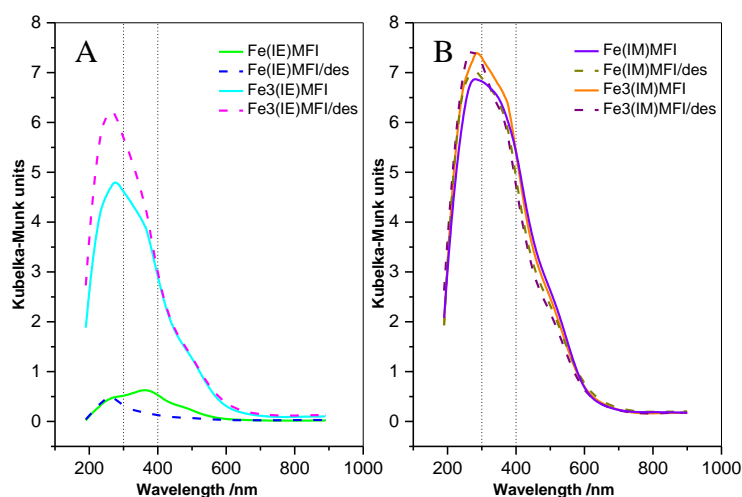

Fig. 2. UV-vis-DR spectra of the parent and desilicated samples modified with $FeSO_4$ and Fe3 oligocations by ion-exchange (A) and impregnation (B) methods

2.5. Catalytic study

The parent and desilicated materials modified with iron by different methods were tested as catalysts in the process of selective catalytic oxidation of ammonia to dinitrogen (NH_3-SCO). The results of the catalytic studies are shown in Fig. 3 A and B. In a series of the samples prepared by ion-exchange (Fig. 3 A), the influence of the applied modification method (desilication, ion-exchange with Fe3 oligocations) on the catalytic activation of the zeolitic samples can be clearly seen. The samples modified with Fe3 tri-nuclear iron oligocations presented significantly higher catalytic activity in comparison to the samples modified with $FeSO_4$.

In the case of the samples modified by impregnation method (Fig. 3 B), the catalytic activity of the samples is similar and any dependency between the used iron source or sample porosity and NH$_3$ oxidation efficiency was not found. It could be connected with the high surface loading of metal obtained by impregnation method. It seems that both the use of ion-exchange with Fe3 oligocations or impregnation method (with Fe3 oligocations and FeSO$_4$) gives similar results in NH$_3$-SCO (temperature of 50% conversion T$_{50}$≈430°C). As it can be seen in the case of Fe3(IE)MFI and Fe3(IE)MFI/des generation of intercrystalline mesoporosity slightly increased their catalytic activity, what is possibly connected with the higher iron content introduced into the Fe3(IE)MFI/des sample. Higher iron content in desilicated sample can be connected with more open porous structure and better accessibility of ion-exchange positions. However in the case of other samples the positive effect of desilication was not observed.

It is worth to notice that in the case of all the studied catalysts high reaction selectivity to N$_2$ (above 90%) was obtained.
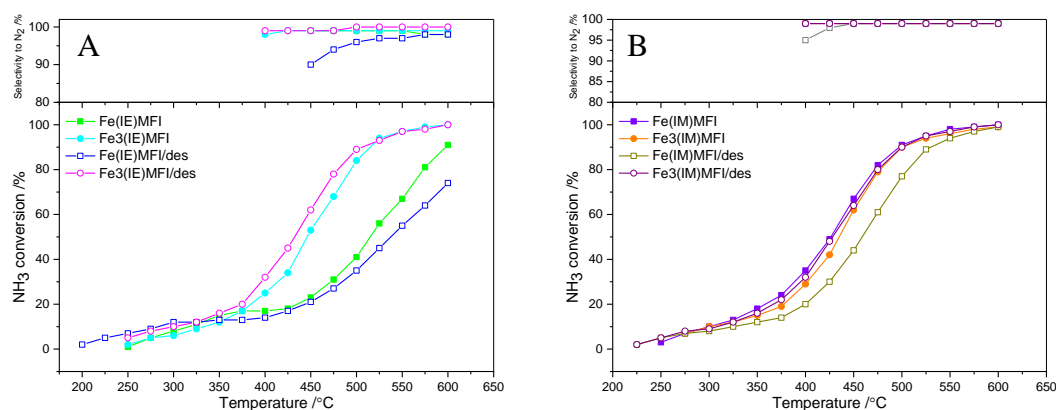

Fig. 3. Temperature dependence of NH$_3$ conversion and N$_2$ selectivity in SCO of NH$_3$ for parent and desilicated MFI modified with FeSO$_4$ and Fe$_3$ oligocations by ion-exchange (A) and impregnation (B)

3. Conclusions

MFI zeolites (conventional and desilicated) modified with iron by different methods were found to be active catalysts in the process of selective catalytic oxidation of ammonia to dinitrogen. The methods enabling introduction of the high iron amount into the samples such as ion-exchange with Fe3 oligocations and impregnation (both with Fe3 oligocations and $FeSO_4$) were found to be the most efficient. The influence of generated porosity in the MFI structure had a positive impact only in the case of ion-exchange with oligocations. This effect can be connected with the more open porous structure, which enable introduction of higher amount of iron into the sample. The dependency between the iron form (in the case of the samples modified by impregnation, iron was present in the form of more aggregated species) was not observed.

The obtained catalysts, especially modified with oligomeric iron species effectively operate in the high temperature region, with a very high selectivity of ammonia oxidation to dinitrogen. Thus, it seems that these catalysts could be optimized for possible application in ammonia oxidation process in hot flue gases.

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