Broensted Acidity of Fibreglass Materials

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Abstract

The results are presented for the studies on acidic properties of fibreglass materials carried out using the methods based on adsorbed ammonia IR spectroscopy, deuterium-hydrogen exchange and the reaction rate for isopropanol dehydration. It has been demonstrated that these catalysts contain a considerable amount of Broensted acid centres (BAC) those are comparable to the BAC of HZSM-5 zeolite in strength. The concentration of BAC is proportional to Al content in fibre glass. It has been revealed that BAC are located in the bulk of glass fibres. It has been demonstrated that the centres located at the depth up to 100 nm are available for the molecules of isopropanol.

Key words: fibreglass materials, Broensted acidity, H/D exchange

INTRODUCTION

It has been recently demonstrated [1] that the catalysts based on fibreglass materials could be used for the processes of purifying diesel engine exhaust gases from the emissions of hazardous substances such as carbon monoxide (CO), hydrocarbons, soot particles and nitrogen oxides (NO_x) . These catalysts represent woven fibreglass silica/alumina materials with applied precious metals (the mass fraction of metal applied ranging within 0.01-0.1 %). As compared to the traditional types of catalytic neutralizers they provide a considerable depreciation of the catalyst, since the content of precious metals therein is several hundred times lower. Moreover, these catalysts provide a high overall efficiency due to high conversion level for NO_x reduction, an efficient, long and stable operation within a wide temperature range as well as a stable long-term operation in the presence of SO₂ without any noticeable decrease in activity [1].

As it is known, the activity of catalysts in the processes of nitrogen oxides reduction correlates with the acidity of catalysts [2-4]. The

authors of [3] demonstrated that the activity of ion-exchange zeolites in the process of NO reduction within propylene medium is proportional to the concentration Broensted acid centres (BAC). One could expect that the acidity of fibre glasses also influences the activity of fibreglass catalysts, too. However, now there is almost no information available in the literature concerning acidic properties of fibreglass materials as well as techniques to study them.

In this paper the results of the studies on Broensted acidity of fibreglass materials are presented taking into account the features of their structure [5]. The methods developed for acidity determination are based on data obtained by means of diffuse reflection IR spectroscopy for chemisorbed ammonia, from the measurement of a model catalytic reaction rate (isopropyl alcohol dehydration) and the parameters of deuterium-hydrogen exchange.

EXPERIMENTAL

For the preparation of catalysts we used an industrial silica-based fibre glass fabric (75–80 % SiO₂, 16–20 % Na₂O, 0.1–4 % Al₂O₃; Po-

lotsk-Steklovolokno JSC, Belarus) leached under the conditions described in [5] up to residual Na content less than 0.1 mass %. We investigated the samples of initial fibreglass materials (Table 1. samples SVK-1-SVK-3) and the samples of the materials modified by aluminium compounds (see Table 1, samples SVK-1M-SVK-3M). The modification procedure was carried out through the impregnation of fibreglass materials using $Al_2(SO_4)_3$ solution with the concentration of 0.25-0.50 g Al/100 mL (pH 2.2). The fabric was then separated from the impregnating solution, washed out with 4% solution of NH_4OH and deionised water, dried at 110 °C and calcinated in air at 350 °C during 4 h. The content of Al in the samples was determined by means of an ICP atomic emission spectrometer (Baird Corp.).

The techniques for the investigation of acidic properties of fibreglass materials with the help of chemisorbed ammonia IR spectroscopy as well as basing on the reaction rate of isopropyl alcohol dehydration are described in detail in [6].

The experiments on the deuterium-hydrogen exchange were carried out using a flowthrough set-up with a tubular quartz reactor operating close to the ideal displacement mode. The investigation of the deuterium-hydrogen exchange kinetics was carried out by means of an isotope dynamic method (Steady-State Isotopic Transient Kinetic Analysis, SSITKA) for two samples of fibreglass catalysts such as SVK-3 and SVK-3M. A mixture of 1.2 vol. % $H_2 + N_2$ was passed through a catalyst layer of 0.2 g in mass with the flow rate amounting to 1 mL/s. The samples were preliminary held in the $\rm H_2$ + $\rm N_2$ mixture at 500 °C during 30 min. Then the system was switched to a mixture of 1.2 vol. $\% D_2 + N_2 + Ar$, with a reverse switch-

TABLE 1 Properties of fibreglass catalysts in comparison with zeolite HZSM-5

ing to the H_2 + N_2 mixture in 15 min. At the outlet from the reactor a temporal variation was registered for m/e = 2, 3, 4, 28 and 40 signal intensities the with the help of a VG Sensorlab V6 mass spectrometer for determining H₂, HD, D₂, N₂ и Ar concentrations, respectively. In order to estimate the purging time for the reactor and supplying pipes we added 0.1 vol. % Ar to the $D_2 + N_2$ mixture. All the experiments were carried out at the reactor temperature amounting to 500 °C. The D₂ enrichment level was equal to 96 %. The analysis of isotope response curves was carried out within the framework of the mathematical model described in [7]. This model takes into account a direct isotope exchange of gaseous hydrogen with OH groups of a catalyst, as well as the diffusion of labelled hydrogen atoms into the bulk of fibre glass.

RESULTS AND DISCUSSION

Table 1 demonstrates data concerning the specific surface and the content of Al in the fibreglass materials under investigation, as well as data concerning HZSM-5 zeolite used as a reference.

It has been established that the concentration of BAC in fibreglass materials (see Table 1), determined according to IR spectroscopic data for chemisorbed ammonia is proportion al to the content of Al. With modifying fibreglass materials using aluminium sulphate the number of BAC increases by a factor of 3 to 5 (see Table 1). The BAC/Al ratio reaches the value equal to 0.5 (for the zeolite under investigation this ratio amounts to 0.2). Since the method of glass fibre preparation provides the uniform distribution of Al over all the volume of fibre glass,

Sample	Mass fraction	$S_{\rm sp},$	BAC,	W _{prop} ,	$W_{\rm acet}$,
	of Al, %	m^2/g	µmol/g	$mol/(g \cdot h)$	$mol/(g \cdot h)$
SVK-1	0.15	0.7	13	0.069	0.01
SVK-2	0.53	0.6	36	0.049	0.0178
SVK-3	1.25	1.0	48	0.21	0.022
SVK-1M	0.39	0.7	67	0.55	0.025
SVK-2M	0.70	0.6	110	0.70	0.025
SVK-3M	1.53	1.0	240	0.67	0.027
HZSM-5	2.30	600	165	4.2	1.2

we believe that the molecules of ammonia diffuse into the bulk of fibre glass and the acid centres measured basing on the chemisorption of ammonia are distributed over all the fibre volume.

The studies on the transformation of isopropyl alcohol have shown that fibreglass materials provide the reaction of dehydration mainly to occur, since the rate of propylene formation is 3 to 30 times higher than the rate of acetone formation. The comparison of dehydration reaction rates allows one to conclude that the BAC of fibreglass catalysts and BAC of HZSM-5 zeolite are at least comparable with respect to strength (see Table 1).

The specific catalytic activity of fibreglass materials $(0.08-1.17 \text{ mol}/(\text{m}^2 \cdot \text{h}))$ and the number of BAC per unit surface area (10.8 to 144 centres/100 Å), measured basing on ammonia chemisorption is to a considerable extent higher than corresponding values for HZSM-5 zeolite $(0.007 \text{ mol}/(\text{m}^2 \cdot \text{h}) \text{ and } 0.17 \text{ centres}/$ 100 Å, respectively). At the same time for fibreglass materials the rate of isopropanol dehydration normalized to the concentration of BAC is much lower than that for zeolite. This fact is possible in two cases: either the BAC of fibreglass materials being weaker, or the reaction occurring only within near-surface layers of fibres, *i.e.* not all the centres measured basing on ammonia chemisorption are involved in the reaction.

In order to determine the acidity of the centres those take a real part in the reaction we used the technique of SSITKA for H_2-D_2 isotope exchange. In paper [7] we demonstrated that the reaction rate of deuterium-hydrogen exchange at the BAC of HZSM-5 zeolite amounts to $(1.3-1.7) \cdot 10^{-3} \text{ s}^{-1}$, whereas for OH groups of aerosil those represent weak acid centres the rate of deuterium-hydrogen exchange is at least two order of magnitude lower than for zeolite.

Taking into account the structure of fibreglass catalysts [5], we suppose that there is a direct isotope exchange on the surface and nearsurface layers of a glass fibre occurring between molecular hydrogen (H₂, HD, D₂) and OH groups of the near-surface layer of fibre glass (OH₁). Labelled hydrogen atoms then distribute over all the bulk of fibre glass (OH_{bulk}) through isotope exchange between neighbouring OH groups (Fig. 1).

The observed deuterium exchange rate on the surface of modified sample such as SVK-3M decreases to a considerable extent as the isotopic substitution of catalyst's OH groups by OD groups proceeds. It is connected with the fact that the isotope label has no time to completely diffuse into the bulk of the catalyst and the isotopic fraction of deuterium-substituted hydrogen atoms in the structure of OH₁ groups gradually increases. Basing on the observed values for the concentration of isotopic molecules (H₂, HD μ D₂), we have calculated time dependences for the atomic isotope fraction of labelled hydrogen atoms in the gas phase (α_D) as well as for molecular fraction of mixed hydrogen ($f_{\rm HD}$). The calculated $\alpha_{\rm D}(t)$ and $f_{\rm HD}(t)$ dependences obtained are presented in Fig. 2 in comparison with the normalized curve the response to argon



Fig. 1. Pattern of deuterium-hydrogen exchange for fibreglass materials modified with aluminium sulphate.



Fig. 2. Dependence of D atomic isotope fraction and HD fraction on time when switching from $H_2 + N_2$ to $D_2 + N_2 + Ar$ and back observed for the sample SVK-3M: 1 - calculation according to the model taking into account only OH_1 ; 2 - calculation according to the model taking into account both OH₁ and OH₂.

 $C_{\rm Ar}^{\rm norm} = \alpha_{\rm D}^{\rm ini} (C_{\rm Ar}^{\rm exp}(t) / C_{\rm Ar}^{\rm ini})$ where $C_{\rm Ar}^{\rm ini}$ and $\alpha_{\rm D}^{\rm ini}$ are the concentration of argon and the atomic fraction of deuterated hydrogen in the initial mixture, respectively. The numerical analysis of isotopic response curves carried out within the framework of the model presented in [7] has demonstrated that in this case the rate of $D_2 \leftrightarrow OH_1$ isotopic exchange and the rate of isotopic label diffusion into the bulk of fibre glass are comparable. The calculated curves of the response are also presented in Fig. 2 (curve 1). One can see that the observed dynamics of the response is described quite adequately, with the exception of the initial part of isotopic response curves, where the calculated rate of exchange is lower than that observed in the experiment.

One can assume that there could be different BAC occurring within fibre glasses (as well as within zeolites), thus we have considered a pattern for the exchange taking into account the deuterium-hydrogen exchange reaction occurring on two types of BAC with the subsequent diffusion of labelled hydrogen atoms into the bulk of fibre glass. The numerical modelling has demonstrated that the centres of the second type (OH₂) almost do not participate in the exchange with OH groups located in the bulk of fibre glass (OH_{bulk}). In this connection we suppose that OH₁ groups are located within a near-surface layer of fibre glass, whereas OH_2 groups are on the external surface (see Fig. 1). The corresponding variant of the description is presented in Fig. 2 (curve 2). One can see that the accuracy of the description in this case is much higher. The calculated values for the kinetic parameters of deuterium exchange on SVK-3M catalyst are presented in Table 2.

TABLE 2

Calculated values for the parameters of deuterium-hydrogen exchange on BAC for catalysts SVK-3M and SVK-3

Sample	$OH_1,$ 10^{20} atoms/g	R_1, s^{-1}	$\overline{R_1}$, atoms/(g · s)	${ m OH}_2,$ $10^{20}~{ m atoms/g}$	$R_2, { m s}^{-1}$	$\overline{R}_2,$ atoms/(g · s)	$ m OH_{bulk}, \ 10^{20} atoms/g$
SVK-3M	0.06	$5\cdot 10^{-3}$	$30\cdot 10^{15}$	0.045	$4.4\cdot 10^{-3}$	$20\cdot 10^{15}$	6
SVK-3	0.018	$5 \cdot 10^{-3}$ (prescribed)	$9\cdot 10^{15}$	0	-	0	5 (±2)

The reaction rate observed for deuteriumhydrogen exchange on non-modified sample SVK-3 within all the time of switching from $H_2 + N_2$ mixture to $D_2 + N_2$ mixture remained almost constant, i.e. the level of isotopic substitution for the OH groups immediately participating in the exchange reaction with D_2 , is negligible. Since in this case the exchange reaction rate does not increase at the initial period of time one could conclude that the centres of OH₂ type are almost absent in the non-modified sample thus the deuterium-hydrogen exchange occurs only at the only type of the centres such as OH_1 . The numerical analysis of the dynamics for H/D exchange for the SVK-3 sample has demonstrated that the rate of labelled atoms transfer into the bulk of fibre glass (due to the diffusion in the bulk) is very high thus the concentration of OD groups within the nearsurface layer of a fibre is in equilibrium with the bulk, *i.e.* this value is close to zero. In this connection using the numerical analysis we cannot determine the quantity of OH₁ groups those interact directly with molecular hydrogen, whereas we can determine only the integrated deuterium exchange rate (\overline{R}_1) amounting to $9 \cdot 10^{15}$ atoms/(g · s). Taking into account the chemical composition of fibreglass catalysts (aluminium silicate) one may suppose that the strength of the acid centres formed as the result of modifying and the strength of the acid centres occurring in the initial catalyst are approximately identical and they could be characterized by the deuterium-hydrogen exchange rate R_1 equal to $5 \cdot 10^3$ s⁻¹. In this case the concentration of OH₁ groups for the non-modified catalyst calculated from the relationship $\overline{R}_1 = R_1 N_{
m OH,}$ amounts to $0.02 \cdot 10^{20}$ atoms/g. The values calculated for kinetic parameters of deuterium exchange on SVK-3 catalyst are presented in Table 2.

The exchange reaction rates for the centres located at the external surface of fibre glass $(4.4 \cdot 10^{-3} \text{ s}^{-1})$ and within near-surface layers of fibres $(5 \cdot 10^{-3} \text{ s}^{-1})$ are comparable with the deuterium exchange rate observed for HZSM-5 zeolite $((1.3-1.7) \cdot 10^{-3} \text{ s}^{-1})$ [7]. Therefore one could conclude that the Broensted centres of fibreglass materials are comparable to zeolite HZSM-5 centres in strength. However, only a

part of BAC from those determined basing on ammonia chemisorption participate in deuterium-hydrogen exchange and isopropanol dehydration. On the assumption of uniform BAC distribution measured basing on ammonia chemisorption inside fibre glass 9 μ m in diameter; the thickness of the layer wherein the deuterium-hydrogen exchange occurs was calculated according to the formula

$$\frac{N_{\rm NH_4^+}}{N_{\rm SSITKA}} = \frac{r_1^2}{r_1^2 - (r_1 - x)^2}$$

Here $N_{\rm NH_4^+}$, $N_{\rm SSITKA}$ are the concentration values for BAC according to the ammonia chemisorption and H/D exchange data, respectively; r_1 is glass fibre radius; x is the desired thickness of the layer (this value amounted to ~100 nm).

CONCLUSIONS

A methodology has been developed for measuring the strength and concentration of BAC, as well as the thickness of working layer for fibreglass materials based on simultaneous use of the three techniques such as chemisorbed ammonia diffuse reflection IR spectroscopy, isopropyl alcohol dehydration reaction rate measurement and SSITKA technique for deuterium-hydrogen (H_2/D_2) exchange. The combination of IR spectroscopy and SSITKA technique allows one to determine the working layer depth for glass fibres. The use of isopropyl alcohol catalytic dehydration reaction indicates that this layer is really available with respect to the molecules of reagents. It has been demonstrated that the Broensted centres of fibreglass materials are comparable in strength to the centres of zeolite HZSM-5. It has been revealed that as the result of modifying the fibreglass materials with aluminium sulphate the occurrence of additional acid centres is observed a part of those is located within near-surface layers of glass fibres. Moreover, a new type of the centres appear those are located on the external surface of a fibre, being completely absent in the non-modified sample.

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