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Oxidative dehydrogenation of propane on VSiβ catalysts

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Abstract

VSiβ catalysts of V content varying between 0.14 and 4.0 V atoms/u.c., and containing VO_x species of different coordination as shown by UV–vis spectroscopy, have been tested in oxidative dehydrogenation of propane. The catalytic performance depends on the V content, which controls the type of the VO_x species. The catalyst of the lowest V content (0.14 V atoms/u.c.), in which isolated VO_4 tetrahedra are observed, is active but not selective, the only reaction product being CO_2. At higher V content up to 1.22 V atoms/u.c., propene appears in the reaction products, its selectivity increasing with the V content, i.e. with the increase in the amount of tetrahedral species up to 1.22 V atoms/u.c. At still higher V content, at which octahedral V species appear, the selectivity to propene decreases. C_3H_8 TPR measurements have shown that ODH of propane to propene may take place with the participation of the catalyst lattice oxygen, whereas this form of oxygen is not active in total combustion of the alkane.

Keywords: VSiβ catalysts; Oxidative dehydrogenation; Propane

1. Introduction

Porous materials, in particular zeolites, were for many years discarded as catalysts or supports for transition metal ions, TMI or TMI oxides in selective oxidation reactions with gaseous oxygen. This was due on one hand to their high acidity, unfavourable for selectivity to partial oxidation products, and, on the other hand, to the diffusion effects in pores of small diameter, which caused consecutive oxidation of desirable products to carbon oxides. With the discovery of new zeolithic materials of lower acidity (high Si/Al ratio) and/or of higher pore diameters, the interest in application of such materials in oxidation reactions has been renewed [1].

In the present work, oxidative dehydrogenation, ODH of propane on VSiβ zeolite catalysts of different V content has been studied. Beside practical aspect of finding a good catalyst, the studies aimed at identification of active and selective species in vanadia-based catalysts in particular in V–Si–O system.

Silica supported vanadia catalysts have been found recently active in ODH of low parafins, ethane [2], propane [3,4] and *n*-butane [5], V-silicalite was found to be one of the most selective system for the propane ODH [6], but propene productivity was low. V-containing microporous materials have been considered as alternative catalysts for ODH of paraffins [7–10]. The presence of isolated tetrahedral V^V species on/in an inert matrix has been proposed as responsible of high selectivity to olefins. It was shown, that this selectivity drastically decreased for vanadium loading above 2 wt.% in V_2O_5/SiO_2 catalysts, at which polyvanadates and even crystalline V_2O_5 species are formed [11]. The V–O–V–O groups, present in the latter species are according to ref. [11] responsible for the over-oxidation of propene into carbon oxides. The view that isolated tetrahedral VO_x species are active and selective in ODH reactions [8,10,11] is not shared by other authors [12], who claim that clusters V–O–V containing two to four V atoms are required for good activity and selectivity.

The problem of the number of V atoms in an active centre for ODH reactions is rather important, both for rational selection of the catalysts and for description of the molecular mechanism of ODH reactions. Assumption of a single M–O active site on/in an inert, hardly reducible matrix (such as for instance SiO_2), is not compatible with the present concepts on oxidation reactions [13,14]. These concepts claim: (a) redox mechanism with participation of the catalyst lattice oxygen, (b) separation of the centres of reduction and reoxidation and (c) easy diffusion of the catalyst oxygen, as conditions necessary for selective

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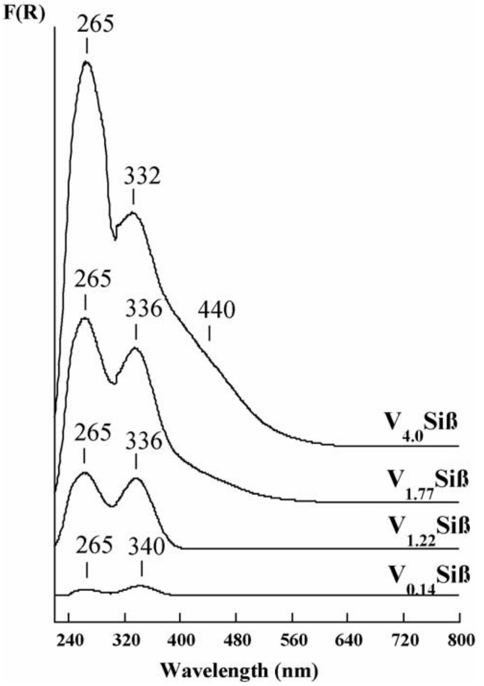

Fig. 1. UV–vis spectra of VSiβ samples.

oxidation. Studies of the VSiβ samples with well-defined structure of V centres can contribute to solving the problem of the active V centres and, moreover to formulating mechanism of oxidation in porous materials.

2. Experimental

2.1. Catalysts and their structure

The VSiβ catalysts were prepared by a two-step post synthesis method, which consists of first creating vacant T-sites by dealumination of the TEAβ zeolite, Si/Al = 11 (provided in its templated form by RIPP China) with nitric acid, and then impregnation of as-prepared Siβ zeolite with an aqueous solution at pH 2 of ammonium metavanadate (NH_4VO_3), used as V^V precursor [15,16]. The vanadium content varied between 0.14 and 4.0 V atoms/u.c. (0.17–4.72 wt.% V). Upon impregnation, V ions are incorporated in the framework of Siβ zeolite as isolated tetrahedral V^V species [16,17]. The bands at 265 and 340 cm^{-1}, observed in UV–vis spectra of the samples (Fig. 1), correspond to tetrahedral V species. They are attributed to $\pi(t_2) \rightarrow d(e)$ and $\pi(t_1) \rightarrow d(e)$ oxygen–tetrahedral V^V charge transfer transitions in bridging (V–O–Si) and (V═O) oxygen, respectively. The ratio of the two bands increases with the V content. In the VSiβ samples with higher V content, octahedral V species occur, which is revealed by the pale yellow or bright orange colours of the samples, and a broad absorption band around 400–480 nm. The latter band is attributed to a charge transfer transition occurring between six oxygen ligands and a central V ion in a distorted octahedral coordination, in line with previously published data [18,19]. ESR technique did not show the presence of V^{4+} ions. Table 1 gives the list of the samples and their characterization.

2.2. Propane TPR

The propane TPR measurements were carried out in a microreactor coupled to a mass spectrometer VG/Fisons Quartz-200D. About 0.2 g of a sample was heated from 30 to 550 °C (10 °C/min) in a stream of mixture of He and propane (30 ml/min; propane content 20%). The mass peaks registered were as follows: CO_2 = 44, CO = 28, H_2O = 18, propane = 29 and propene = 41 and 42.

2.3. Isopropanol decomposition

The decomposition of IPrOH to propene and acetone was studied at 200 °C using a pulse method with the GC analysis. Dried helium was the carrier gas. 0.05 g of the sample and 1 μl of isopropanol were used and the total flow-rate of helium was 100 ml/min. Prior to the test the samples were treated in situ in a stream of dried helium for 1 h at 200 °C to purify them from the adsorbed water and physisorbed oxygen. The isopropanol pulses were injected successively until constant values of conversion and yield of products (propene and acetone) were attained. The conversion and the yield of products decreased slightly (~5–10%) with the number of pulses up to three to five pulses and then remained constant. The values given in Table 1 are the mean values of three pulses after the constant value of the activity was reached.

Table 1
List of the samples in VSi zeolite system and their characterization

Symbol	V atoms/u.c.	V coordination	$I_{265(V–O–Si)}/I_{340(V═O)}$[a]	Activity[b] (mmol C_3H_8 g V^{-1} min^{-1})	IsPrOH (μmol m^{-2} s^{-1})	
					Propene	Acetone
$V_{0.14}$Siβ	0.14	Tetrahedral	0.5	10.2–5[c]	0.008	0.00
$V_{0.9}$Siβ	0.90	Tetrahedral	–	3.8	–	–
$V_{1.22}$Siβ	1.22	Tetrahedral	1.1	1.1	8.7	0.03
$V_{1.77}$Siβ	1.77	Tetrahedral octahedral	1.2	3.3	–	–
$V_{4.0}$Siβ	4.00	Tetrahedral octahedral	1.6	2.8	15.5	0.006

[a] From UV–vis; I_x, intensity of band at x nm.

[b] Reaction temperature 470 °C.

[c] Activity of support taken into account: activity of Siβ support (mmol g^{-1} min^{-1}) was subtracted from the activity of the $V_{0.14}$Siβ sample (mmol g^{-1} min^{-1}) and the difference referred to amount of V g^{-1}.

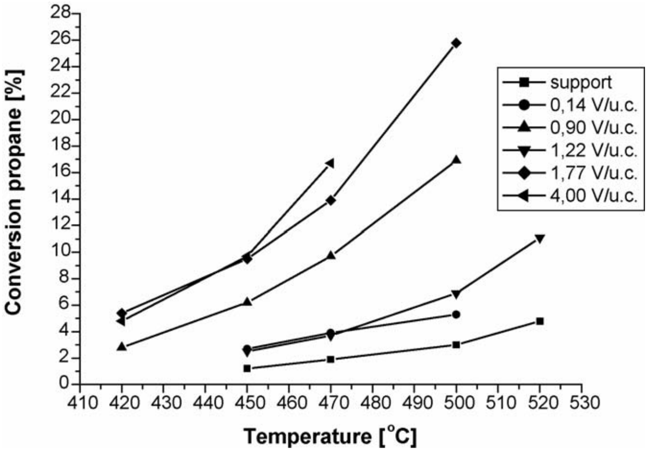

Fig. 2. Changes of the propane conversion (at $\tau = 1$ s) with the reaction temperature for VSiβ catalysts.

2.4. Catalytic tests

ODH of propane was studied in a fixed bed reactor coupled to a gas chromatograph, described in detail in ref. [20]. The reaction conditions were as follows: temperature range 420–520 °C, amount of a catalyst 0.5 or 1 ml (0.22–0.45 g), grain diameter 0.63–1.0 mm, diluted with quartz beads, reaction mixture: 7.1 vol.% of propane in air, contact time $\tau = 0.33$–2 s. Propene, CO and CO_2 were the only reaction products.

3. Results and discussion

Formation of propene in the ODH reaction was observed for all the samples with the exception of that of the lowest V content ($V_{0.14}$Siβ), for which CO_2 was the only product of oxidation. Figs. 2 and 3 show, respectively, the changes of propane conversion and selectivity to propene with the reaction temperature. The increase in the conversion and decrease in the selectivity to propene with temperature, are typical of ODH reactions.

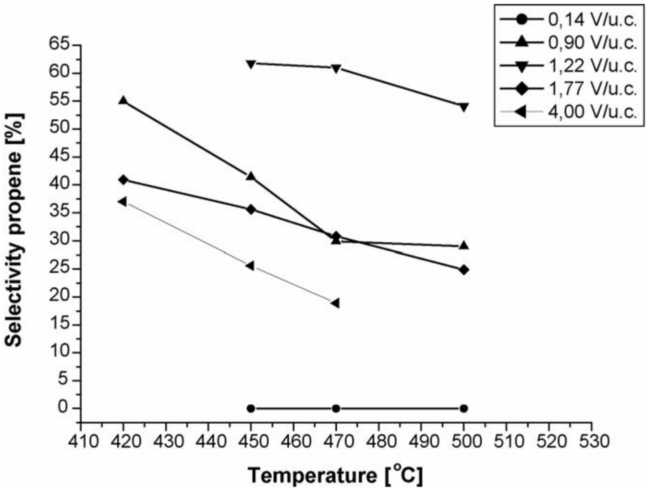

Fig. 3. Changes of the selectivity to propene (at $\tau = 1$ s) with the reaction temperature for VSiβ catalysts.

As seen, conversions of propane and selectivities to propene vary with the V content in a complex manner. Pure Siβ zeolite was found to be slightly active (conversion 1–3% in the studied temperature range) and quite selective (selectivity to propene of ∼60%). Introduction of small amounts (0.14 V atoms/u.c.) of V leads to the increase in the activity, but a dramatic decrease of the selectivity to propene to 0. The only product of the propane oxidation on this sample is CO_2. The conversions are considerably higher for the samples with higher V content and containing V also in octahedral coordination, whereas selectivities to propene for these catalysts are generally lower. The total activity of the samples calculated per amount of V (column 5 of Table 1) is not constant, which suggests different intrinsic activity of vanadium in different samples. The activity of the samples exhibiting both tetra and octahedral V species is higher than that of the sample containing high concentration of only tetrahedral V. It is striking, however, that the highest activity is shown by a sample with the lowest V content (tetrahedral, isolated V), even if we subtract the activity of the pure support. Still, as mentioned above, this sample is active only in total combustion of propane. Fig. 4 presents selectivities to propene and the ratio CO/CO_2 at 450 and 470 °C plotted versus the V content in the samples. In view of the consecutive mechanism of ODH reactions, the selectivities in Fig. 4 are compared for the same conversion values.

At both temperatures the maximum of the selectivity to propene is observed for the $V_{1.22}$Siβ catalyst exhibiting only tetrahedral V species. The value of ∼50% at conversion of ∼8% are comparable to those observed for vanadia dispersed in low quantities on SiO_2. The decrease in the selectivity is seen at higher V content at which, beside tetrahedral, also octahedral vanadium was found. It is worth observing that at the same time the CO/CO_2 ratio increases steadily with the increase in the V content. In ODH of propane on conventional vanadia-based catalysts with high amounts of vanadia (e.g. V_2O_5/TiO_2 and V_2O_5/SiO_2), CO, formed by consecutive oxidation of propene, is the main product of total combustion [4,20]. Only small amounts of CO_2, formed mainly in the parallel propane

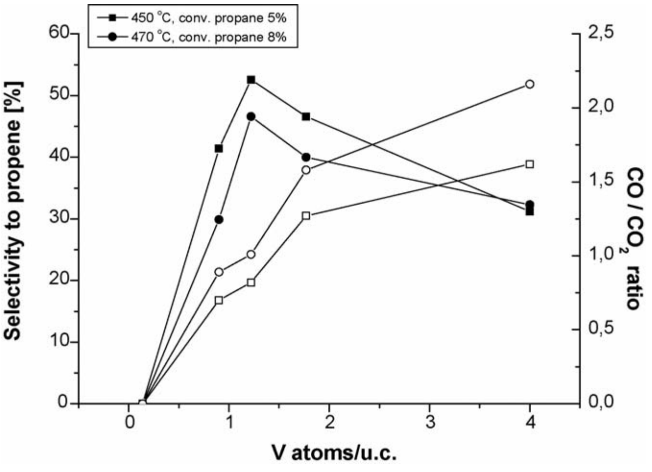

Fig. 4. Selectivity to propene (■ and ●) and the ratio CO/CO_2 (□ and ○) at reaction temperatures: 450 and 470 °C as a function of the V content in the samples.

oxidation and with participation of electrophilic, chemisorbed oxygen, are observed. The high amounts of CO_2 (low CO/CO_2 ratio), observed in this study for VSiβ catalysts of low V content (tetrahedral species), suggest, that the mechanism of ODH for these samples may be different, involving participation of chemisorbed oxygen species.

C_3H_8 TPR have shown appearance of propene with the onset temperature at ∼400 °C, accompanied by the peak of water at the the same temperature. Practically neither CO nor CO_2 were oberved. Fig. 5 presents the TPR curve for $V_{1.22}Si\beta$ sample. A peak at 100 °C corresponds to desorption of physisorbed water. Similar TPR curves were obtained for samples with other V content, the intensity of the signal increasing with the V content. The above results indicate that propane may undergo oxidative dehydrogenation to propene and water on VSiβ catalysts at the expense of the catalyst oxygen. This implies, that the redox mechanism may operate in the ODH reactions on modified porous silica-like materials. The formation of total combustion products for these catalysts, however, does not involve the lattice oxygen.

In the isopropanol decomposition the sample of the lowest V content is practically inactive, giving only traces of propene. The amount of propene (a measure of acidity) increases considerably at higher V content, indicating that V provides acidic centres. Amounts of acetone (a product of dehydrogenation) are very small.

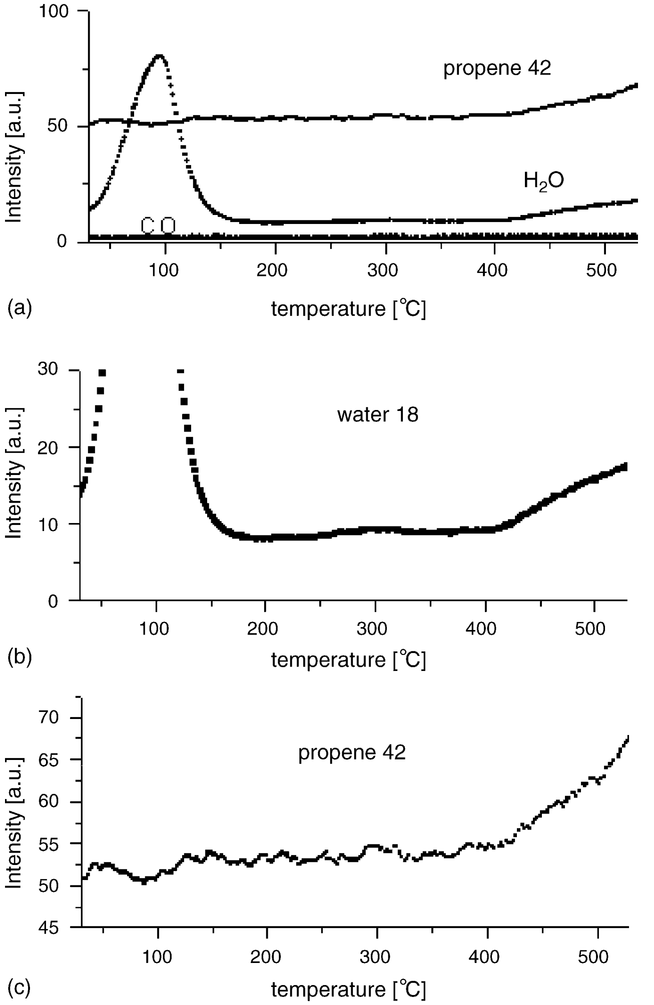

Fig. 5. C_3H_8 TPR for $V_{1.22}Si\beta$ sample (a) and (b and c) peaks of propene and water magnified.

In agreement with refs. [8,10,11], the obtained results show the lower selectivity of the octahedral vanadium species present in oxo-clusters or vanadia phase on the surface of the zeolite, as compared with tetrahedral species. No selectivity to propene for the catalyst with the lowest content of V (0.14 V atoms/u.c.), in which the active tetrahedral species may be isolated is, however, in contrast with the literature data [8–10], which claim isolated species as active and selective. The obtained results indicate, that the species active and selective in ODH should contain rather several V atoms, in keeping with ref. [12]. Indeed, the results for $V_{0.14}Si\beta$ suggest, that isolated VO_x species embedded in $SiAlO_x$ matrix are capable of activation of gaseous oxygen to form CO_2: they are, however, incapable of transferring chemisorbed oxygen into a selective nucleophilic form, necessary for formation of propene. At higher vanadium content some interaction between the tetrahedral forms in the silica matrix may occur, leading to modification of M–O bonds (higher reducibility) and making possible the electron transfer within the catalyst. The separation of the centres for catalyst reduction and reoxidation, leading to higher selectivity [13,14] may then occur, similarly like it is the case in the conventional selective oxidation catalysts.

As shown by UV–vis spectroscopy (Fig. 1), the V ions are incorporated as tetrahedral V species containing a V=O double bond and linked by two [$(SiO)_2(HO)V{=}O$ species] or three [$(SiO)_3V{=}O$ species] V–OSi bonds to the zeolitic walls [15,16]. The existence of hydroxylated $(SiO)_2(HO)V{=}O$ species, possessing a V–OH group interacting with a nearby SiOH silanol group is supported by IR measurements (Si–O vibrators at 950 and 980 cm^{-1}, O–H vibrators at 3620 and 3650 cm^{-1}) [15,16]. This interaction generates acidic Brønsted sites as shown by FT-IR in the presence of adsorbed pyridine [16]. Moreover, the increase of the V content leads to formation of Lewis acidic sites related to lattice tetrahedral (mononuclear) and extra-lattice octahedral (mononuclear and polynuclear) V species (the results will be published).

4. Conclusions

1. Activity and selectivity of VSiβ catalysts in oxidative dehydrogenation of propane depend on the content and structure of VO_x species.
   (a) Isolated tetrahedral vanadium species at the lowest V content are active only in total oxidation of propane, CO_2 being the only product.
   (b) Catalysts containing higher concentration of tetrahedral V species (at higher V content) are active and selective in oxidative dehydrogenation of propane to propene, the highest selectivity being observed at 1.22 V atoms/u.c.
   (c) The selectivity to propene decreases with the appearance of octahedral V species.
2. Different distribution of total oxidation products (CO and CO_2) for V (tetrahedral) Siβ catalysts as compared with

conventional, supported vanadia catalysts, implies different mechanism of the reaction for the catalysts of the two types.

3. Lattice oxygen in VSiβ zeolites is active in oxidative dehydrogenation of propane to propene and water, and inactive in formation of carbon oxides.

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