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VO_x supported SBA-15 catalysts for the oxidative dehydrogenation of ethylbenzene to styrene in the presence of N_2O

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Abstract

The molecular designed dispersion (MDD) method was used for the modification of SBA-15 with vanadium oxide. Vanadyl acetylacetonate was grafted on the support surface at different $VO(acac)_2$ concentrations in a toluene solution, and then converted into the VO_x/SBA-15 catalysts at elevated temperatures. The thermal transformation of surface species was studied by FTIR-PAS spectroscopy. The obtained materials were characterized with respect to their texture (BET), metal dispersion (FT-Raman and UV–vis-DR) and reducibility (H_2-TPR). It was found that only isolated V^{5+} species were present in the samples with a low V loading. The catalyst with the highest V content showed the presence of polymeric V^{5+} species, which appeared to be easier reducible compared to the isolated form of V. The VO_x/SBA-15 samples were tested as catalysts in the oxidative dehydrogenation of ethylbenzene to styrene in the presence of N_2O. An increase in the catalytic activity with raising the V content was observed. It was however prove that monomeric V^{5+} species were considerably more active and selective in the styrene formation than oligomeric ones.

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1. Introduction

The catalytic dehydrogenation of ethylbenzene (EB) is nowadays the main method of styrene production. The process is performed at elevated temperatures (550–650 °C) in the presence of potassium doped hematite catalysts [1]. Additional promoters (e.g. Cr_2O_3, Ce_2O_3, MgO, MoO_3) are used in order to enhance the activity and selectivity, as well as stability of the catalytic system. The EB dehydrogenation process is endothermic and limited by thermodynamic equilibrium. An excess of superheated steam is therefore used to supply the heat of reaction and shift the equilibrium to higher styrene yields by a decrease in the partial pressures of reactants [2].

The thermodynamic limitation and high endothermic effect of the EB dehydrogenation cause that alternative routes for the styrene production are still searched. The oxidative dehydrogenation of ethylbenzene, based on an introduction of oxidant to the EB feed, seems to be one of the promising methods. The oxidative dehydrogenation process is exothermic [3,4], so that it can be carried out at a lower temperature compared to that used in the classical EB dehydrogenation, and additionally is not equilibrium-limited. At the beginning of 1970s, Al_2O_3 was used as a catalyst of the oxidative dehydrogenation of EB performed in the presence of oxygen [5]. The high activity of this catalyst, which increased with raising time-on-stream in a initial period of the reaction, was found. The similar effect of increasing catalytic performance was also observed for different materials characterized by the presence of surface acidic sites. It was proposed that an oxygen-rich coke, which is formed in the first hours of reaction and reaches a stationary amount on the catalyst surface, is the active phase in the oxidative EB dehydrogenation [6,7]. Furthermore, redox-type catalysts were studied in the oxydehydrogenation of EB with O_2. However, only differently promoted V containing materials showed a reasonable activity. It was found [8,9] that $Mg_3(VO_4)_2$

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and Mg_2VO_4 phases, which possess similarities in structure, can undergo interconversion via reduction–oxidation and play a catalytically active role in the process.

Apart from oxygen, which was the most frequently studied oxidizing agent, other oxidants were also tested in the dehydrogenation of EB. Recently, several attempts were carried out to utilize CO_2 [10–14]. However, carbon dioxide introduced to the EB stream acts both as an oxidizing agent and as a diluent similar to water vapour. An effectiveness of CO_2 as the oxidant is therefore limited. On the other hand, it was found that the presence of CO_2 could favour a fast deactivation of a catalyst by the formation of catalytically inactive coke [15]. Nitrous oxide (N_2O) seems to be a more promising oxidizing agent than carbon dioxide. The utilization of N_2O is of additional interest as nitrous oxide has been recognized to be one of greenhouse gases causing global warning. Coupling the N_2O decomposition with the ethylbenzene dehydrogenation over γ-Al_2O_3-supported transition metal (Fe, Cr and Cu) oxide catalysts led to high conversions of EB and N_2O [16]. Furthermore, a replacement of the alumina support by mesoporous silicas (SBA-15, MCF, MCM-48 and MSU) characterized by high surface area gave the Fe-, Cr- and Cu-containing catalysts, which were active in the oxidative dehydrogenation of EB in the presence of N_2O [17].

In the present work the catalytic activity of the VO_x/SBA-15 catalysts in the oxidative dehydrogenation of EB with N_2O was studied. Recently, it has been shown [18,19] that mesoporous silicas modified with vanadium effectively catalyze the oxidative dehydrogenation of light paraffins. The molecular designed dispersion (MDD) method was chosen to the preparation of V-containing catalysts in this study. This technique is based on the reaction of the metal acetylacetonate complex with the surface hydroxyls of the silica support. The thermal decomposition of surface organometallic species results in the formation of highly dispersed metal oxides [20]. Four different VO_x contents were deposited on the SBA-15 support. The obtained catalysts were characterized by photoacoustic infrared spectroscopy (PAS), BET surface area, FT-Raman, UV–vis-DR spectroscopy and temperature-programmed reduction (H_2-TPR).

2. Experimental

2.1. Catalysts preparation

Mesoporous silica SBA-15 was prepared according to the procedure described earlier by Van Bavel et al. [21] using triblock copolymer poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (Pluronic 123) as a template. Four grams amount of Pluronic 123 copolymer was dissolved in 1.6 M HCl (150 ml) under stirring, followed by the addition of 9.14 ml of tetraethyl orthosilicate (TEOS). The resulting mixture was stirred for 8 h at 45 °C and then aged at 80 °C for 15 h. The solid product was filtered and washed with deionised water. The sample was subsequently dried at room temperature (RT).

Prior to the modification with vanadyl acetylacetonate, the templated sample was calcined at 550 °C with a heating rate of 1 °C min^{-1} and an isothermal period of 6 h in air, yielding the final mesoporous SBA-15 material. Deposition of $VO(acac)_2$ was performed by the liquid-phase molecular designed dispersion (MDD) method inside a dry nitrogen glovebox. The freshly calcined SBA-15 support (1.0 g) was added to 100 ml zeolite dried toluene containing a calculated amount of $VO(acac)_2$. The obtained suspension was stirred for 1 h. All depositions were performed in absence of air at RT with the exception of the $0.77VO_x$/SBA-15 sample, which was modified by a temperature gradient method. This catalyst precursor was obtained by deposition of vanadyl acetylacetonate complex starting at 45 °C and decreasing the temperature to RT during the stirring process in order to achieve high metal loading on the support [22]. After the deposition, the modified support was filtered off, washed few times with dry toluene and dried at RT under vacuum. Finally, the material was calcined in a programmable oven at 550 °C for 6 h in air atmosphere.

2.2. Characterization techniques

The FT-photoacoustic IR spectroscopy (PAS) was performed on a Nexus spectrometer bench placed in an ultra-dry air box and equipped with a MTEC 300 PA detection cell flushed with zeolite dried helium. One thousand scans were usually taken with a resolution of 4 cm^{-1}.

Vanadium loadings were colorimetrically determined by UV–vis technique (UNICAM 8700 instrument).

Textural parameters of the calcined samples were determined by N_2 sorption at −196 °C using an ASAP 2010 (Micromeritics) after outgassing the materials under vacuum at 200 °C for 16 h.

UV–vis-diffuse reflectance spectra were recorded on a Unicam 8700 UV–vis spectrometer equipped with a Thermo-Electron RSA-UCA Diffuse Reflectance cell. The average of three scanning cycles was taken with a scanning speed of 120 nm/min and a band width of 2 nm.

FT-Raman spectra were recorded on a Nicolet Nexus FT-Raman spectrometer with a Ge detector. All the measurements were performed at RT in a 180° reflective sampling configuration, with a 1064 nm Nd-YAG excitation laser. Two thousands scans were averaged for each spectrum and the laser power was set between 1 and 2.0 W.

Temperature-programmed reduction (TPR) of the catalysts was carried out in the temperature range of 100–1000 °C in a fix bed continuous flow quartz microreactor. The flow of the reduction mixture was controlled by a mass flow controller (Brooks 5850^E). The hydrogen consumption was monitored on-line by a thermal conductivity detector (TCD) connected to the reactor outlet by a heated line. Prior to the TPR experiments a sample (with mass normalized to contain 12 μmol V) was outgassed at 200 °C for 30 min in the flow of pure helium (grade 5). The TPR runs were carried out with the linear heating rate (β = 10 °C/min) in the flow of 2.0 vol.% of H_2 in Ar (20 ml/min).

2.3. Catalytic measurements

The synthesized catalysts were tested in the oxidative dehydrogenation of EB in the presence of nitrous oxide. The catalytic runs were performed in a plug flow microreactor (i.d., 6.0 mm; length, 240 mm). Fifty milligrams of the catalyst was loaded at the central position of the reactor onto a quartz wool plug. The flow of the gaseous reactants was controlled by mass flow controllers (Brooks 5850^E). EB was fed into the system with a syringe pump (Cole-Parmer). The reaction products were monitored by a gas chromatograph (Varian CP-3800) equipped with three capillary columns—CP-8 (for separation of aromatic compounds), Poraplot Q (for CO_2, H_2O, N_2O), Molsieve 5A (for N_2, O_2, CO) – and two detectors – TCD and mass spectrometer Saturn 2000 (Varian). A sample of reactants was always collected directly from the outlet of the reactor using a six-port valve (Valco).

Prior to the catalytic run the sample was outgassed at 450 °C for 30 min in a flow of N_2O (0.4 ml/min) diluted with He (up to a total flow of 49.6 ml/min). Then, dosing of EB (130 μl of liquid EB per hour) started. The first GC analysis was performed after 25 min. The temperature of the catalyst bed was increased from 450 to 550 °C in steps of 50 °C with three analyses of the obtained products (at 35 min intervals) at each step.

3. Results and discussion

The MDD method was used for the deposition of vanadyl acetylacetonate complex on the SBA-15 support. Fig. 1A and B shows the photoacoustic infrared spectra of the nonmodified SBA-15 support and this sample after the modification with $VO(acac)_2$. An appearance of bands in the region of 1300–1600 cm^{-1}, which are characteristic of the vibrations of acetylacetonate complex, can be observed for the samples after the deposition. Moreover, an intensity of band at 3745 cm^{-1}, attributed to isolated silanol groups, decreased after the modification of SBA-15. This suggests that a part of surface hydroxyls was bonded to the metal acac complex. The broadening of band between 3000 and 3600 cm^{-1} reveals the presence of hydrogen bonding interaction between the acac ligands of the complex and the silanol groups. The PAS spectrum of the sample after calcination at 550 °C is presented in Fig. 1C. A decrease in the intensity of broad band at 3000–3600 cm^{-1} suggests that the thermal treatment of the $VO(acac)_2$ deposited on the SBA-15 support resulted in the decomposition of the acac complex. On the other hand, the bands at 3660 cm^{-1}, attributed to V–OH surface species, and at 930 cm^{-1}, assigned to the Si–O–V stretching vibrations [23], found for the calcined samples, demonstrate the formation of VO_x species anchored to the support surface.

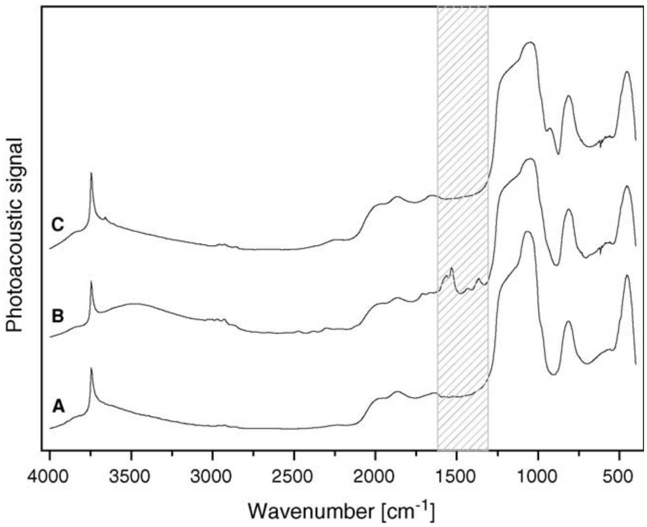

Fig. 1. Infrared photoacoustic spectra of nonmodified SBA-15 support (A), SBA-15 after deposition of $VO(acac)_2$ (B), and SBA-15 after deposition of $VO(acac)_2$ followed by thermal treatment at 550 °C (C).

The reaction of the SBA-15 support with the toluene solution of vanadyl acetylacetonate at different concentrations of $VO(acac)_2$ followed by the thermal treatment enabled to obtain the catalysts with a various V loading. The chemical composition and textural properties of the obtained materials are collected in Table 1. The presented data show that the modification of the SBA-15 support with VO_x species resulted in changes of textural parameters of the samples. The grafting of high amount of vanadium caused a significant decrease in the BET surface area observed for the $0.40VO_x$/SBA-15 and $0.77VO_x$/SBA-15 samples. On the other hand, the deposited VO_x considerably reduced the micropore volume in the case of these both catalysts. Due to migration effects at temperatures above 300 °C, it should be concluded that the presence of V-containing active phase decreases slightly the microporosity so that part of the total pore volume becomes inaccessible.

The coordination of VO_x species grafted on the SBA-15 support was studied by FT-Raman and UV–vis-DR spectroscopy. As shown in Fig. 2, the only Raman band at about 460 cm^{-1}, which is attributed to the vibration of the siloxane rings present in the mesoporous silica, is observed for the sample with the lowest V content. It is most likely that the V loading is below a detection level in this case. An increase in the V concentration resulted in an appearance of the band at 1042 cm^{-1}, which is found for the $0.25VO_x$/SBA-15, $0.40VO_x$/SBA-15 and $0.77VO_x$/SBA-15 samples. This band is characteristic of the symmetric stretching mode of the V=O bond of the isolated VO_x species grafted on the SBA-15 support. The absence of bands at 994 and 697 cm^{-1} in the recorded FT-Raman spectra reveals that no V_2O_5 crystals were formed during the calcination at 550 °C.

The room temperature UV–vis-DR spectra of the calcined VO_x/SBA-15 samples, additionally dried at 200 °C directly before the measurement, are presented in Fig. 3. The wide band between 270 and 300 nm observed for the $0.11VO_x$/SBA-15, $0.25VO_x$/SBA-15 and $0.40VO_x$/SBA-15 samples could be assigned to the VO_x species highly dispersed on the support surface, which were also detected by FT-Raman measurements. For the catalyst with the highest V loading ($0.77VO_x$/SBA-15), an additional peak in the range of 350–400 nm appeared. This band corresponds to low polymerized V chains or/and domains with vanadium in tetrahedral and square pyramidal configuration. However, even at the highest V loading, absorption above 470 nm was not observed. It should be therefore concluded that no microcrystalline V_2O_5 is present in the studied catalysts.

Table 1
Vanadium loadings and textural parameters of the calcined samples

Catalyst	V loading (mmol/g)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
$0.11VO_x$/SBA-15	0.11	740	0.89	0.14
$0.25VO_x$/SBA-15	0.25	733	0.82	0.14
$0.40VO_x$/SBA-15	0.40	650	0.74	0.10
$0.77VO_x$/SBA-15	0.77	630	0.81	0.08

The temperature-programmed reduction (TPR) profiles of the SBA-15-based catalysts modified with various amount of vanadium are presented in Fig. 4. The samples with V loading ranging from 0.11 to 0.40 mmol/g exhibit only one reduction peak, which is attributed to the reduction of highly dispersed monomeric VO_x species. The reduction temperature maximum shifts to slightly higher temperatures with raising the V content, and can be found at 625, 638 and 646 °C for the $0.11VO_x$/SBA-15, $0.25VO_x$/SBA-15 and $0.40VO_x$/SBA-15 samples, respectively. It should be however noticed that the VO_x species introduced on the SBA-15 support by grafting are significantly less reducible compared to V-containing SBA-15-based catalysts obtained by the impregnation method [24,25]. The total amount of hydrogen consumed during the reduction process reveals that reduction of V^{5+} to V^{4+} occurs in the studied temperature range.

For the $0.77VO_x$/SBA-15 catalyst, two overlapping peaks are observed in the TPR profile. The deconvolution performed showed that the first maximum is found at 580 °C, whereas the second one at 710 °C. An appearance of easily reducible VO_x species in this sample should be correlated to the results of UV–vis-DR study, which revealed the presence of polymeric V^{5+} species. $O_{lattice}$ existing in such V-containing agglomerates is weaker bounded and can be easier detached by H_2 with the formation of H_2O molecule than oxygen present in the isolated VO_x species. It should be therefore concluded that in the case of the $0.77VO_x$/SBA-15 sample polymeric species of V^{5+} are reduced at lower temperatures, and reduction of isolated V^{5+} species demands somewhat higher temperatures.

The calcined V-containing samples were tested as catalysts in the oxidative dehydrogenation of EB to styrene in the presence of nitrous oxide. The conversions of reactants (EB and

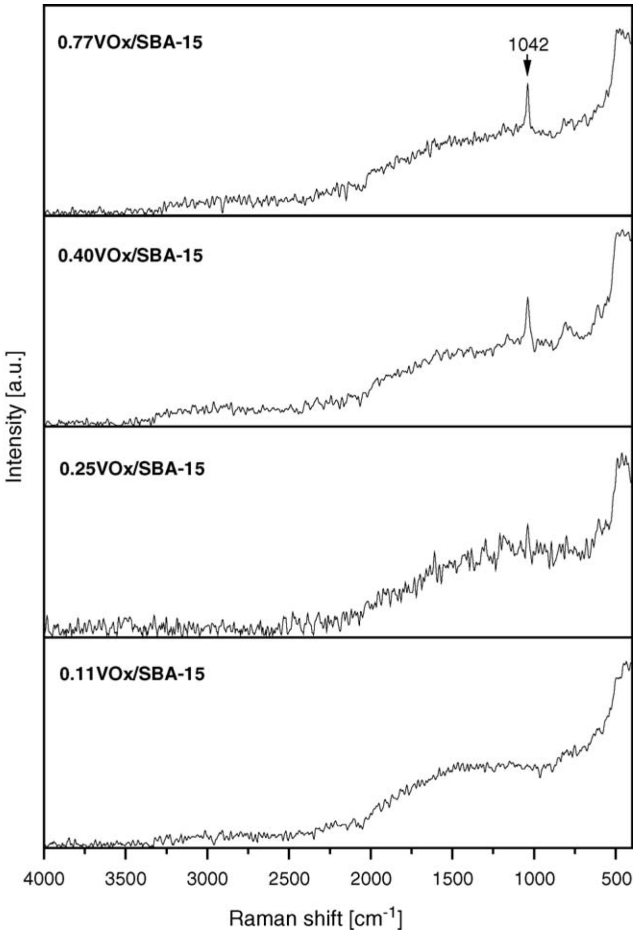

Fig. 2. FT-Raman spectra of VO_x/SBA-15 samples with different vanadium loading.

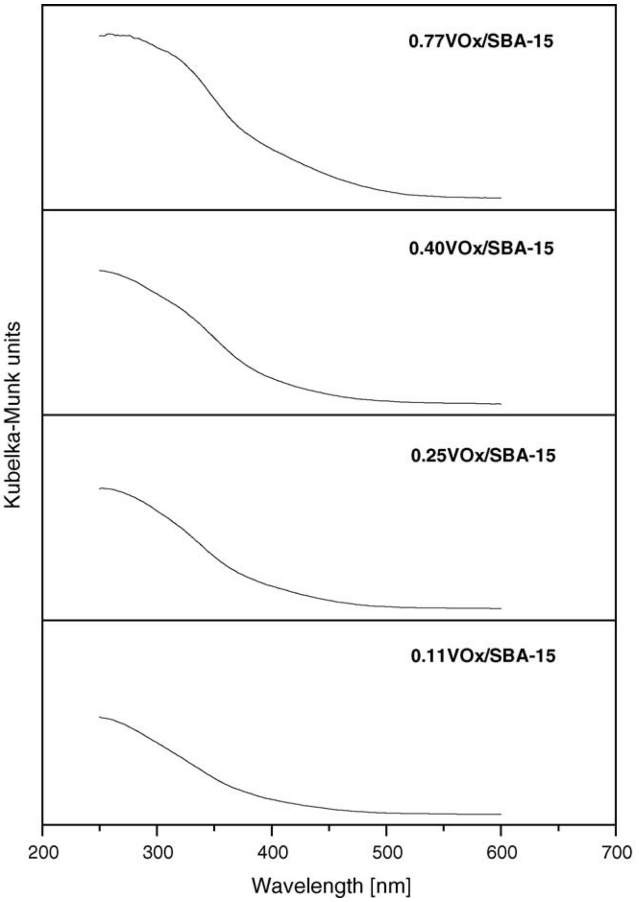

Fig. 3. UV–vis-DR spectra of VO_x/SBA-15 samples with different vanadium loading.

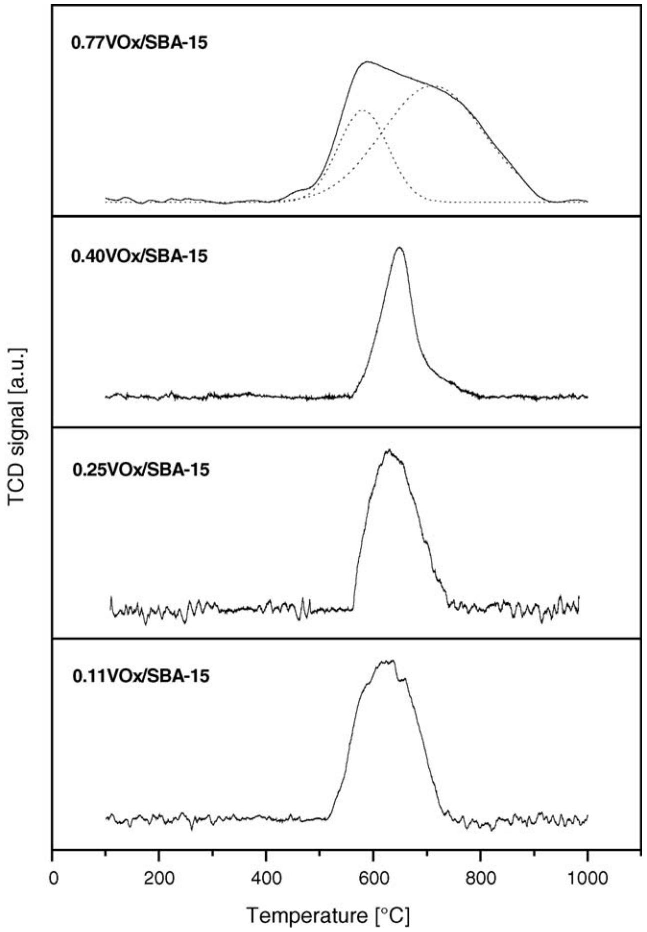

Fig. 4. H_2-TPR reduction profiles of VO_x/SBA-15 samples with different vanadium loading.

N_2O) observed at different reaction temperatures in the presence of V-doped catalysts are presented in Fig. 5. It was found that the conversion of both EB and nitrous oxide increased with raising the reaction temperature and V loading. It should be however noticed that even at the highest reaction temperature of 550 °C the total conversion of N_2O was not detected. Simultaneously, the relatively high amount of EB consumed reveals that VO_x species are more active centers in the oxidative dehydrogenation of EB compared to that formed by Fe, Cu or Cr oxides [17]. No significant decrease in the activity was observed during the catalytic runs. It should be therefore assumed that nitrous oxide, used as an oxidizing agent, protects the catalyst against the formation of inactive carbonaceous deposit.

Styrene and CO_2 were found to be the main carbon-containing products formed in the studied reaction. The formation of only traces of other aromatic hydrocarbons (like benzene and toluene) as well as CO was detected. The influence of the reaction temperature on the yields of styrene and carbon dioxide is illustrated in Fig. 6. As it was expected the rates of styrene and CO_2 production increased with the reaction temperatures and the content of V in the sample. In the case of the most active samples (0.40VO_x/SBA-15 and 0.77VO_x/SBA-15), the styrene yield of 38.3–38.4% was achieved at 550 °C.

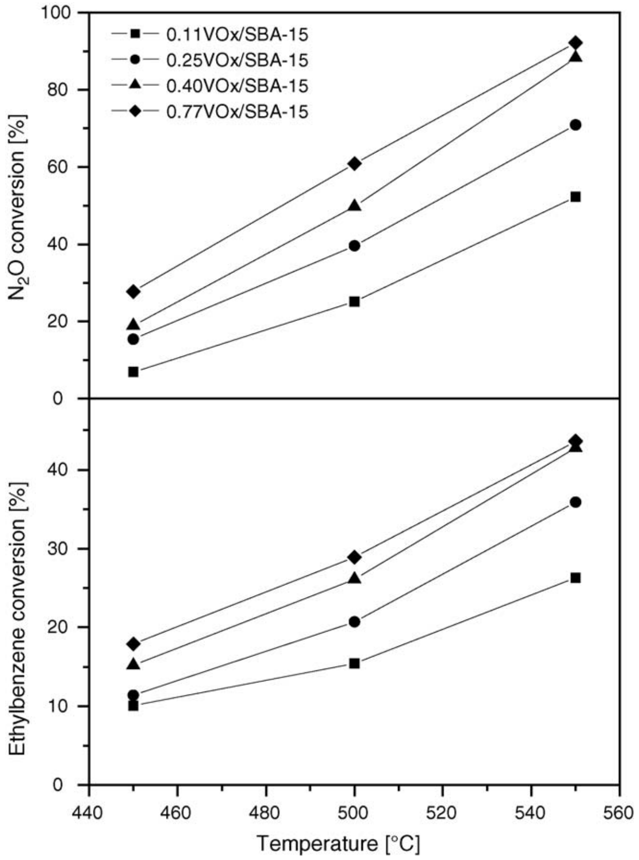

Fig. 5. Conversions of ethylbenzene and N_2O vs. reaction temperature over the V-modified SBA-15 catalysts.

The rate of styrene formation, expressed as a number of styrene moles produced over a 1 g amount of a catalyst per 1 h, was calculated to better understand the influence of the V content on the activity of the studied catalysts. The obtained results are presented in Fig. 7A. It is evident that the most distinct increase in the styrene production rate is observed for the catalysts with low V loadings. This effect should be correlated to the results of FT-Raman, UV–vis-DRS and TPR studies, which showed that the monomeric VO_x species are the entire form of V present at a low V concentration. It should be therefore assumed that the isolated VO_x species are the most active centers in the oxidative dehydrogenation of EB in the presence of N_2O. An increase in the V loading results in the formation of polyvanadate species, which show the worse catalytic performance in the selective oxidation of EB. The similar tendencies in the catalytic behaviour of various V-containing catalysts were previously observed in the oxidative dehydrogenation of light paraffins with oxygen. For example Argyle et al. [26] found that the rate of oxidative dehydrogenation of ethane and propane is much faster when the reaction is carried out in the presence of monovanadates highly dispersed on the Al_2O_3 support. On the other hand, the polymeric VO_x species existing in the SBA-15-based catalyst with the highest V concentration showed a high EB conversion. When the rate of styrene production is related to the rate of CO_2 production (cf. Fig. 7B), it appears to be obvious that the polyvanadate-type centers are more selective in the total oxidation of aromatic

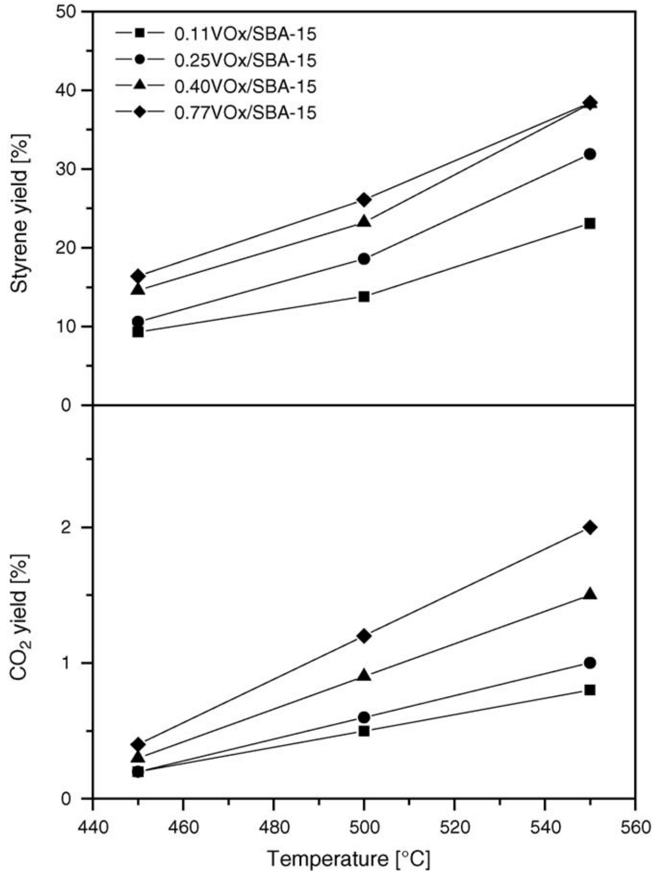

Fig. 6. Yields of the main carbon-containing products vs. reaction temperature over the V-modified SBA-15 catalysts.

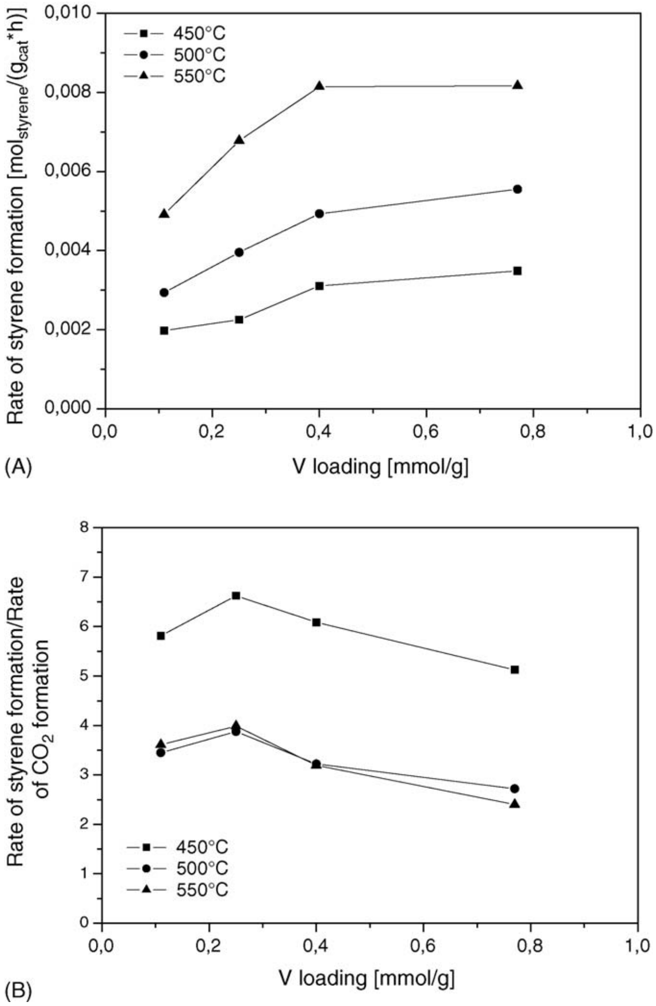

Fig. 7. Influence of V loading on the rate of styrene formation (A) and ratio of the rate of styrene formation to the rate of CO_2 formation (B) over the V-modified SBA-15 catalysts.

compounds to CO_2. This effect should be assigned to easier reducibility of polymeric form of V compared to that of isolated VO_x species.

4. Conclusions

The VO_x species were supported on the SBA-15 surface using the molecular designed dispersion method. This procedure of modification resulted in the high dispersion of vanadium. Only isolated forms of V^{5+} species were detected by FT-Raman and UV–vis-DR spectroscopy for the samples containing 0.11, 0.25 and 0.40 mmol V/g. An increase in the V loading to 0.77 mmol V/g caused the formation of polymeric VO_x species on the support surface, however the isolated form of vanadium was still dominant for this catalyst. The TPR study showed that the oligomeric V^{5+} species were easier reducible compared to the isolated ones.

The VO_x/SBA-15 catalysts were very active in the oxidative dehydrogenation of ethylbenzene in the presence of N_2O. In spite of the whole amount of nitrous oxide introduced was not converted over the studied catalysts in the temperature range of 450–550 °C, an effectiveness of N_2O, as an oxidizing agent, was very high. The catalytic activity increased with the V content in the catalyst. However, the samples with a high V loading appeared to be more selective in the total oxidation of aromatics. This effect was attributed to easier reducibility of polymeric V^{5+} species.

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