Catalysis Today 142 (2009) 329–334

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Vanadium, niobium and tantalum modified mesoporous molecular sieves as catalysts for propene epoxidation

A. Held [*], P. Florczak

Department of Chemistry, A. Mickiewicz University, Poznań, Poland

ARTICLE INFO

Article history:
Available online 10 September 2008

Keywords:
Nitrous oxide (N_2O)
Epoxidation
Propylene oxide
SBA-3
Transition metals

ABSTRACT

SBA-3 mesoporous molecular sieves doped with transition metal ions (Fe, V, Nb and Ta) have been applied for selective oxidation of propene towards propylene oxide in the presence of N_2O as an oxidant. The kind and amount of applied modifiers significantly affected the catalytic activity. V/SBA-3 was found to be the most active among the catalyst under study. In spite of relatively high selectivity towards propylene oxide (reaching up to 23%), the main oxidation product was still propionaldehyde. Surprisingly, CO_x was not formed over V, Nb and Ta modified SBA-3 catalysts. Additional modification of V containing samples (V/SBA-3) with iron complexes resulted in the further increase in the catalysts activity for epoxidation reaction. A PO selectivity of about 20% could be achieved at a propylene conversion of 17% over mixed Fe/V/SBA-3 catalytic system.

1. Introduction

World production of propylene oxide (PO), one of the most important chemical intermediates, amounts to approximately 5×10^6 tons per year. Currently, the most widely used industrial routes to PO are based on chlorohydrin process or hydroperoxide methods. Considering, that both processes suffer from serious drawbacks, new technologies, based on direct propene to PO oxidation have been elaborated. Much attention has been directed to propylene epoxidation performed in the presence of hydrogen peroxide in liquid phase with TS-1 molecular sieve as catalyst [1,2]. The technology based on this idea, called HPPO (hydrogen peroxide to propylene oxide), was developed and it would be commercialised by Dow and BASF in cooperation with Solvay Company. The new installation according to this route is localised in the Netherlands (Antwerp) and the next one is under construction in Thailand [3,4]. Searching for application of molecular oxygen as an oxidant brought to elaboration of gas/solid catalytic system, employing hydrogen and oxygen as precursors of hydrogen peroxide, which was produced *in situ*, with simultaneous propene to propylene oxide oxidation in the presence of mixed metal system containing gold (Me-Au)/TiO_2 [5–9]. Exceptional oxidative activity of gold-titania catalysts applied with the mixture of oxygen and hydrogen (hydrogen peroxide precursors), used for the propene epoxidation reaction, was discovered and reported by Haruta and co-workers in 1998 [10,11]. Since then, gold containing catalysts attract attention as a potential catalyst for specific oxidation reaction such as a low temperature transformation of CO to CO_2 and the formation of propylene oxide by propene oxidation. Both propene conversion and selectivity towards propylene oxide were influenced by the nature of the support and the size of gold clusters, generated on oxide matrices [12]. Mesoporous molecular sieves of SBA-15 have been successfully used as Au/TiO_2 active system support [13]. Ti-MCM-41 catalyst, containing a high number of accessible and isolated titanium in tetrahedral coordination, has appeared a beneficial gold support, resulting in the rise of propylene oxide productivity [14].

The earlier successful application of N_2O-Fe-ZSM-5 system for benzene to phenol oxidation [15] as well as for light paraffins oxydehydrogenation [16] was the direct inspiration for the use of this catalytic system for propylene epoxidation. The activity of Fe-ZSM-5 catalyst for propene epoxidation was, however, low and acroleine was the main oxidation product [17]. Fe-ZSM-5 catalyst modified with alkaline ions (incorporated into the catalyst in order to eliminate the surface acidity, thereby preventing isomerization of PO) showed increase in selectivity to PO, however, propene conversion was even lower. Considering the above, iron complexes were accommodated in amorphous silica as well as in all silica molecular sieves (SBA-15 and MCM-41). Further modification of Fe-SBA-15 or Fe-MCM-41 with alkaline metal salts (especially with KCl) resulted both in higher propene conversion and also in higher selectivity to PO [17–20].

---

[*] Corresponding author. Tel.: +48 61 8291472; fax: +48 61 8291505.
E-mail address: awaclaw@amu.edu.pl (A. Held).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.07.030

Iron complexes accommodated in molecular sieves, especially in the channels of high silica zeolite ZSM-5, show a specific ability to decompose nitrous oxide with the formation of active oxygen species. Decomposition of N_2O, as a result of contact with Fe-ZSM-5, leads to the formation of α-oxygen and O^- oxygen species. α-Oxygen was found to be active in benzene hydroxylation, whereas, O^- species were responsible for oxidative dehydrogenation reaction [15]. O^- species were also suggested to play a crucial role in ethene to ethylene oxide epoxidation over silver catalysts [21]. Iron modified zeolite ZSM-5 is not the only one, which shows the ability to generate α-oxygen and O^- species. Iwamoto et al. [22] have applied N_2O as an oxidant for benzene to phenol hydroxylation in the presence of vanadium oxide. Even though, the vanadium containing catalyst was not commercialised for benzene hydroxylation, it indicated very promising oxidative features of N_2O/V_2O_5/support catalytic system.In the presented study all silica SBA-3 mesoporous material was used as a support. SBA-3 molecular sieve, synthesised similarly as SBA-15 (crystallisation at RT under acidic pH), using, however, different templating agent (alkyl quaternary ammonium salt, as for MCM-41 synthesis) is characterised with hexagonal mesoporous structure, very high surface area with significant contribution of microporosity [23]. As it was indicated earlier [24], the presence of micropores influences significantly the activity of iron complexes, accommodated in solid matrices, for N_2O decomposition. Considering the above, one can assume, that SBA-3 may combine the feature of neutral, all silica mesoporous material with the presence of micropores, establishing the favorable structure for the formation of complexes, active in N_2O decomposition with following formation of specific oxygen species. Considering the above, in the presented paper, we have not only used vanadium, but also niobium and tantalum supported on all silica mesoporous material of SBA-3 structure as catalysts for direct propene epoxidation in the presence of N_2O as an oxidant. Additionally, mesoporous SBA-3 materials were modified with iron complexes to compare the oxidative activity of vanadium, niobium and tantalum containing catalysts with iron comprising catalysts, reported in numerous papers [17–20,25,26] as active for propene epoxidation. The mixed Fe/Me/SBA-3 (where Me = V, Nb or Ta) systems were also applied for the reaction under study.

2. Experimental

SBA-3 mesoporous molecular sieves were prepared by hydrothermal synthesis performed under acidic conditions, according to the procedure described elsewhere [27]. The initial mole ratio of the reaction mixture was the following: 0.11 TEOS: 0.025 CTMABr: 1.94 HCl: 9.17 H_2O. Aging of the gel was carried out at room temperature for 8 days. The resulting solid was filtered, washed, dried and calcined in nitrogen stream at 500 °C for 2 h with following calcination in air at 500 °C for 4 h.

After calcination, SBA-3 support was modified with transition metal ions (Fe, V, Nb and Ta) by means of incipient wetness impregnation, using the aqueous solutions of iron(III)nitrate, ammonium vanadate or ammonium niobium(V) oxalate and *n*-hexane solution of tantalum butoxide, respectively. The Fe-SBA-3 and Me/SBA-3 samples (where Me = V, Nb or Ta) were tested in propene epoxidation reaction. Additionally, Me/SBA-3 samples were modified with iron ions (in amount related to 1 wt.% of Fe) by incipient wetness impregnation and subsequently calcined at 500 °C for 1 h.

The correctness of mesostructure of as-synthesised and transition metals modified SBA-3 samples was checked by powder X-ray diffraction (XRD) pattern, which was recorded on Bruker AXS D8 Advance diffractometer. The N_2 adsorption/desorption isotherms were collected at 77 K on ASAP 2000 from Micromeritics.

The catalytic tests in propene oxidation were performed in continuous flow reactor. Catalytic experiments were carried out in the range of temperature from 300 °C to 400 °C, under atmospheric pressure, with WHSV = 3420 ml/h/g_{cat}, related to contact time of 1.1 S. Substrates: propene and N_2O were diluted with helium (molar ratio of propene: nitrous oxide: helium = 1:15:12.5). The products were analyzed using on-line GC, equipped with FID and TCD detectors.

The coke content over studied catalysts (after 3 h on stream) was determined on the grounds of elemental analysis (carbon and hydrogen) using Americas Elementar Analyser Vario EL III.

Acidity of applied samples was estimated on the base of their activity for propan-2-ol decomposition. The reaction was conducted in a puls-microreactor at 250 °C.

Interaction of reagents (propene and N_2O) with the surface of catalysts was searched by means of FT-IR spectroscopy. IR measurements were performed *in situ* with a BRUKER – VECTOR 22 spectrometer. After evacuation at 300 °C for 2 h, reagents were contacted with catalysts at different temperatures (from RT to 450 °C). FT-IR spectra were recorded at room temperature.

ESR spectrometer of Radiopan equipped with X band was used for the recording of ESR spectra of vanadium and iron modified SBA-3 samples. Reflectance UV–vis spectra were recorded using Carry 100 Varian spectrometer.

3. Results and discussion

The X-ray diffraction patterns of as synthesised SBA-3 and transition metals modified mesoporous materials are shown in Fig. 1. All the studied samples exhibit the reflection peaks in the low angle region, characteristic for mesostructure. Impregnation of transition metal ions on SBA-3 support resulted in decrease in the intensity of the reflections characteristic for mesostructure. Nevertheless, XRD patterns indicate that the hexagonally ordered structure of SBA-3 was sustained after modification procedure.

The maintenance of SBA-3 structure upon introduction of transition metals has also been supported by nitrogen adsorption/desorption measurements. BET surface area and pore distribution were calculated on the grounds of nitrogen adsorption/desorption isotherms recorded at 77 K. It was found that the plain SBA-3, crystallised at room temperature, showed very high surface area (1642 $m^2\,g^{-1}$). The average pore diameter for this sample was about 1.7 nm (Table 1). The adsorption/desorption isotherm of

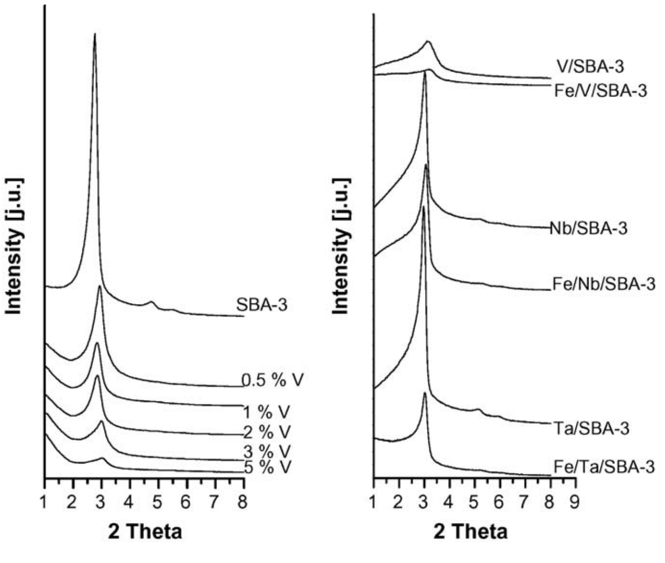

Fig. 1. XRD patterns of plain and transition metals modified SBA-3.

Table 1
Textural properties of the modified SBA-3 materials

Sample	S_{BET} ($m^2 g^{-1}$)	Average pore diameter (nm)
SBA-3	1642	1.7
V/SBA-3	958	1.8
Fe/V/SBA-3	584	2.2
Fe/Nb/SBA-3	1184	1.8
Fe/Ta/SBA-3	917	1.9

nitrogen for plain SBA-3 shows the adsorption step between 0.20 and 0.30 of p/p_o ratio, which is due to capillary condensation in mesopores. However, the initial part shows a high "knee" which implies the presence of micropores in SBA-3. In combination with both observations, the registered isotherm represents a superposition of type I and type IV isotherms [23]. BET surface area significantly decreased after introduction of transition metals into SBA-3 material.

All the samples prepared by impregnation of transition metal compounds on all silica mesoporous SBA-3 material were used as catalysts for propene epoxidation in the presence of N_2O as an oxidant. The catalytic tests have shown that activity of the samples (propene conversion and selectivity towards PO) was affected both by the kind and number of transition metal ions introduced into the system (Fig. 2). Among the catalysts doped with transition metals of group V, the highest activity was observed over vanadium-modified sample (propene conversion achieved up to 10%, whereas on Nb/SBA-3 and Ta/SBA-3 samples propene conversion did not exceed 2%). The comparison of the oxidative activity of vanadium, niobium and tantalum containing SBA-3 with commonly studied iron catalyst indicates the best activity of V/SBA-3 sample (Fig. 2). Selectivity towards PO achieved almost 17% for vanadium containing catalyst (V/SBA-3), whereas for Fe/SBA-3 it did not exceeded 10%. However, the main product of propene oxidation still remained propanal (selectivity towards propanal was in the range of 50–75%). Niobium and tantalum oxide-like compounds supported on SBA-3 showed catalytic activity even worse then iron containing catalyst. However, what is worthwhile to underline, the catalysts under study (containing vanadium, niobium or tantalum) did not catalyse the total oxidation reaction and CO_x was not detected in the products (only for the highest vanadium concentration a small amount of CO_2 has appeared at temperature above 380 °C.

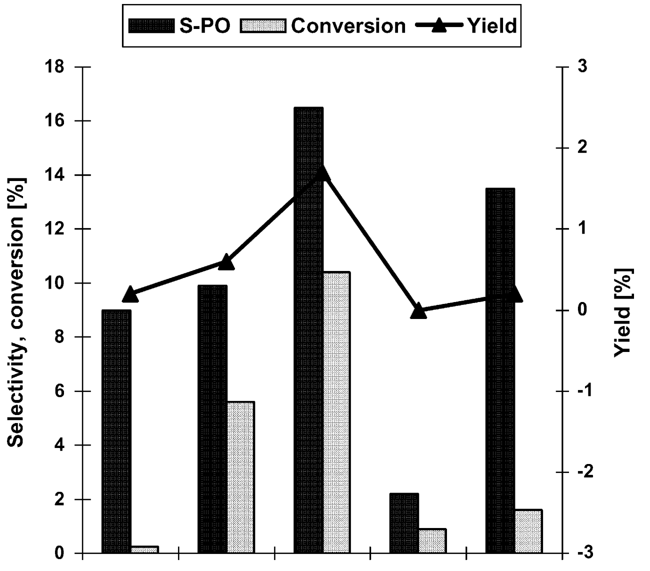

Fig. 2. Catalytic activity of blank SBA-3 and SBA-3 modified with iron, vanadium, niobium and tantalum (introduced with amount of 1 wt.%) in direct propene epoxidation performed at 380 °C.

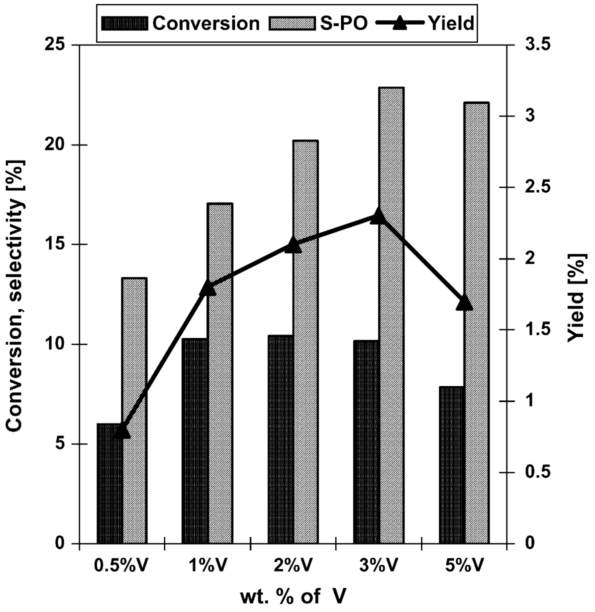

Fig. 3. Influence of vanadium concentration on the activity of V_x/SBA-3 (x wt.% of V; $x = 0.5, 1, 2, 3, 5$) catalysts in direct propene epoxidation (reaction temperature 380 °C).

Modification of SBA-3 support with different amount of vanadium (Fig. 3) revealed that vanadium content in the range of 1–3 wt.% resulted practically in the same propane conversion (about 10% at the temperature reaction of 380 °C), whereas selectivity to PO increased along with vanadium concentration. Increase in selectivity to PO with growing vanadium concentration (for propene conversion equal to 5%) is also presented in the Fig. 4. The yield of propylene oxide was the highest over SBA-3 doped with 3 wt.% of vanadium and it reached almost 2.5% (Fig. 3). Vanadium concentration influenced clearly the products distribution (Fig. 5). Along with vanadium concentration increase in catalysts, selectivity towards propionaldehyde decreases (from nearly 65% to 34%), while the presence of acetone became higher.

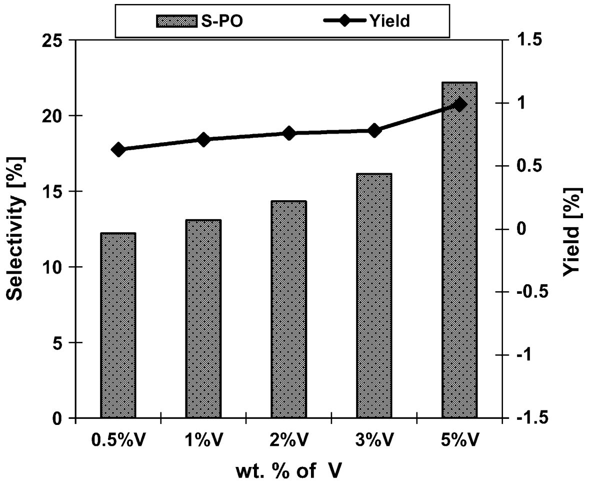

Fig. 4. Influence of vanadium concentration on selectivity to PO of V_x/SBA-3 (x wt.% of V; $x = 0.5, 1, 2, 3, 5$) catalysts in direct propene epoxidation (at propene conversion equal to 5%).

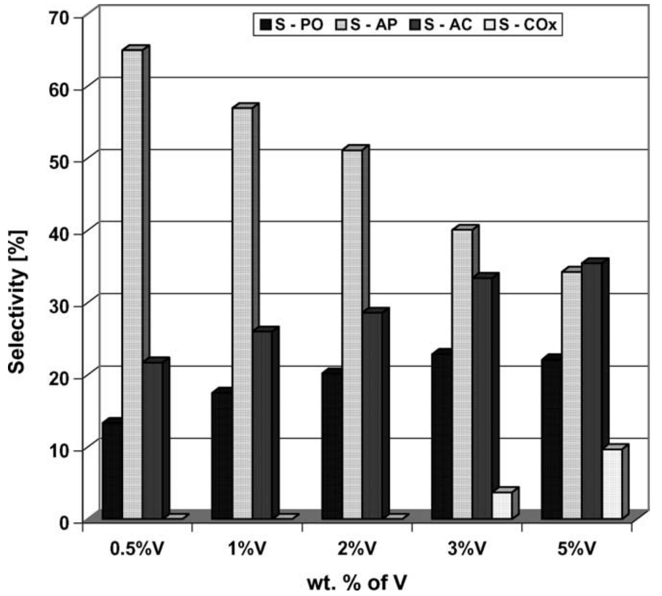

Fig. 5. Products distribution in direct propene epoxidation performed over V_x/SBA-3 (x wt.% of V; x = 0.5, 1, 2, 3, 5); (reaction temperature 380 °C).

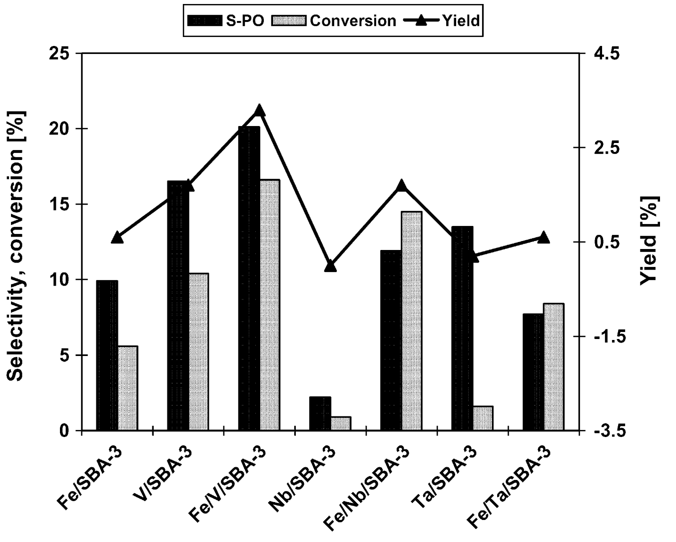

Fig. 6. Catalytic activity of Fe/SBA-3 (1 wt.% of Fe), Me/SBA-3 (1 wt.% of V, Nb or Ta) and mixed Fe/Me/SBA-3 (1 wt.% of Fe and 1 wt.% of Me) catalysts in direct propene epoxidation performed at 380 °C.

Starting from vanadium concentration equal to 3 wt.%, small amount of total oxidation product was also detected.

The activity of V/SBA-3 catalysts, after initial, inconsiderable lowering of propene conversion, remained relatively stable and only very slight decrease of propene conversion was observed with time on stream. However, the catalysts turned black after reaction and they were covered with coke deposit. It indicated that part of reagent was transformed into polymeric, heavy products. To estimate the C balance, amount of propene converted to heavy product was estimated on the grounds of elemental analysis of coke deposit cumulated during three hours of the reaction. On the grounds of GC analysis, it was estimated that besides PO, acetone and propionaldehyde only traces of the others products such as acroleine, acrylic acid were detected. Considering the amount of coke deposit and the presence of C_3 unsaturated compounds the C balance was kept within 7% or below.

Regarding the earlier reports concerning the activity of iron modified molecular sieves for propene epoxidation [28,29], and also on the ground of our experiments, the V, Nb and Ta modified SBA-3 were additionally doped with iron ions introduced in amount of 1 wt.% (Fig. 6). Introduction of iron ions into Me/SBA-3 catalysts resulted in a clear increase in propene conversion and in selectivity towards PO, which was observed for all catalysts under study. However, contrary to Me/SBA-3 materials, iron doped Me/SBA-3 catalysts catalysed also the total oxidation process and CO_x was observed in the reaction products. Nevertheless, PO yield reached 3.3% over Fe/V/SBA-3. Since no total oxidation products were observed over V, Nb and Ta modified SBA-3 samples, the CO_x formation could be stimulated by the presence of iron ions in Fe/Me/SBA-3 materials.

Interaction of reagents (propene and N_2O) with the surface of V/SBA-3 catalyst and iron modified Fe/V/SBA-3 sample was searched by means of IR spectroscopy (Fig. 7). Starting from 300 °C, propene and nitrous oxide adsorption on transition metals modified SBA-3 resulted in the appearance of the bands at about 1720, 1690 and 1620 cm^{-1}. The first two bands (1720, 1690 cm^{-1}) can be assigned to carbonyl C=O stretching vibration [28], whereas the last one (1620 cm^{-1}) may indicate the formation of water as a result of total oxidation reaction. According to Busca et al. [29], the band at 1620 cm^{-1} can also be due to the formation of surface carbonates. Increase in the temperature of interaction results in significant increase in the intensity of all those bands. The band at about 1620 cm^{-1} was clearly more intensive over Fe/V/SBA-3 when compared with V/SBA-3 sample. Those results are consistent with experimental data obtained from continuous flow reactor, where high selectivity to CO_x was noted over iron containing catalysts. Evacuation at RT resulted in decrease in the intensity of all the bands, however, they were still present. The following evacuation at 300 °C remained only the bands attributed to different forms of carbonates.

Starting from 300 °C we have also noticed the formation of a shoulder at about 1590 cm^{-1} and new, low intensive bands at about 1420, 1395 and 1365 cm^{-1}, that can be assigned to the mixture of acetate and formate asymmetric and symmetric stretching vibrations [30,31]. The bands of carboxylate species became even more pronounced after evacuation at RT and they were still visible after evacuation at 300 °C for 1 h. According to [32], acetate groups are

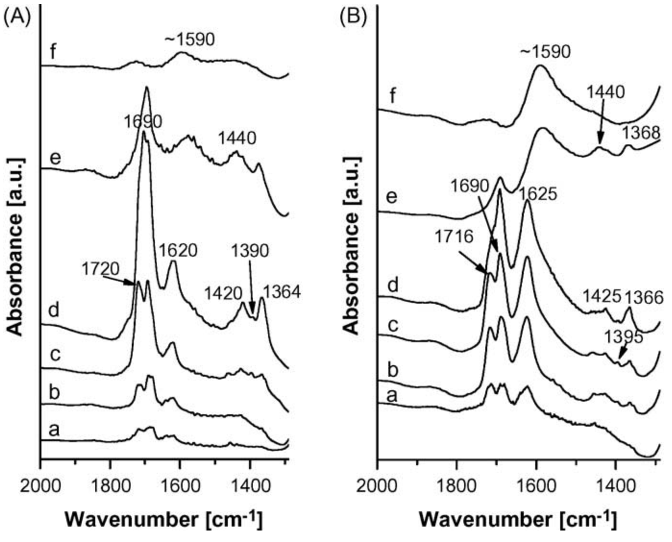

Fig. 7. FT-IR spectra of (A) V/SBA-3 (1 wt.% of V) and (B) Fe/V-SBA-3 (1 wt.% of Fe, 1 wt.% of V) recorded after contact with reagents (propene and N_2O) at different temperatures: (a–d) catalyst after contact with reagents at: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) evacuation at RT and (f) evacuation at 300 °C.

strongly adsorbed on catalysts surface and can be hardly removed even after evacuation at higher temperature.

The IR spectra resulting from interaction of propene and N_2O with catalysts surface indicated the formation of the carbonyl compounds. These results are consistent with experimental data, obtained from the oxidation reaction performed in continuous flow reactor, where among the products of propene oxidation, besides PO, also propanal, acetone and acroleine were recorded. According to Ananieva and Reitzmann [18], PO is an initial product of propene oxidation, performed over supported iron complexes in the presence of N_2O as an oxidant. Aldehyde and ketone are the products of PO isomerization occurring over acidic and basic sites [33]. The acidity of the studied catalysts was estimated on the grounds of their activity for propan-2-ol decomposition. The results of these measurements confirmed the presence of weak acidic centres in the catalysts under study.

Both vanadium and iron modified mesoporous materials have already been studied as catalysts for oxidation reactions [32], however, there are very few reports concerning the use of the mixed systems [34,35]. Vanadium and iron modified SBA-3 as well as the mixed samples, prepared by impregnation method and applied as catalysts for propene epoxidation, were characterised by UV–vis and ESR spectroscopy.

UV–vis spectra (shown in the Fig. 8) were recorded for the samples containing different amount of vanadium modifier (from 1 to 5 wt.%). For comparison, Fe/SBA-3 with 1 wt.% of iron and mixed, iron and vanadium containing samples (1 wt.% of V and 1 wt.% of Fe) were also searched by UV–vis spectroscopy. UV–vis spectra of the samples under study showed three distinctive bands, located at 218, 265 and 295 nm. The band at 218 nm has also appeared on unmodified silica support. The two others bands can be assigned to low-energy ligand (O^{2-}) to metal (Fe^{3+} or V^{5+}) charge-transfer (LMCT) transitions occurring between isolated tetrahedral vanadium or iron species, coordinated to the mesoporous silica surface [36–41]. The intensity of the band at 295 nm was affected by the kind and the concentration of the introduced modifier (iron or vanadium). Its intensity increased along with vanadium loading and it was higher for vanadium-modified samples when compared with Fe/SBA-3. Broadening of the band at 295 nm samples indicate for the presence of the band centred at about 350 nm, which corresponds to oligomeric iron or vanadium chains, formed in internal/external surface of porous SBA-3 samples [37,40,41]. The oligomeric species are formed by means of connection of isolated tetrahedral vanadium species with the formation of V–O–V bridges. Intensity of that band increased with growing content of vanadium. UV–vis band, in the region of lower energy (higher wavelength), was noted for the samples with higher content of vanadium. The appearance of the broad absorption band in the range of 400–550 nm indicates for the presence of "bulk-like" V_2O_5 species. However, UV–vis band in the region of 400–800 nm may also originate from V^{4+} or V^{3+} d–d transitions located in agglomerated phase [42]. The assumption of the presence of V^{4+} ions in the condensed phase is consistent with ESR spectrum of V/SBA-3 sample. In the ESR (Fig. 9) spectrum of V/SBA-3, besides well-dissolved lines of hyperfine splitting, originating from isolated V^{4+} ions, also broad line, attributed to V^{4+} species in condensed phase, characterised with dipol–dipol interaction, has appeared.

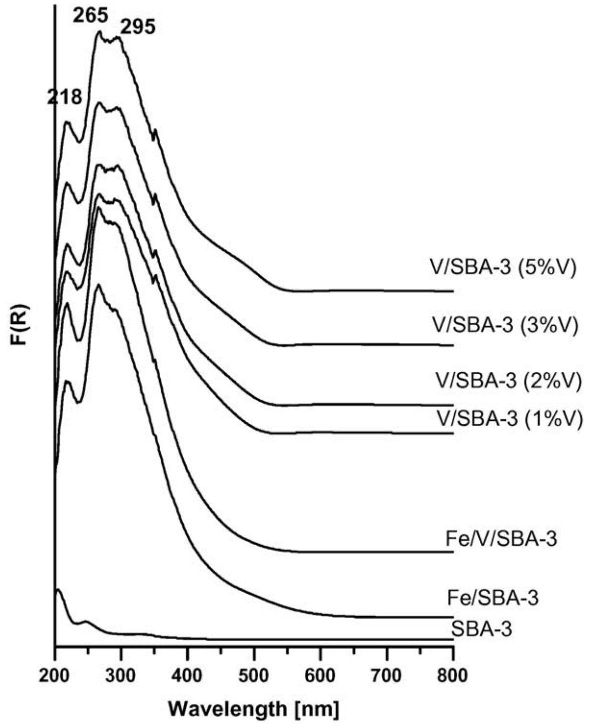

Fig. 8. UV–vis reflectance spectra of plain and vanadium and/or iron modified SBA-3.

ESR spectra were recorded at RT and at 77 K for Fe/SBA-3 (1%), V/SBA-3 (1%) and for mixed Fe/V/SBA-3 sample (Fig. 9). ESR spectra of iron containing complexes, recorded at RT, indicate the presence of broad signal with *g*-factor equal to about 2 and relatively sharp signal at $g = \sim 4.3$. Lowering the temperature of measurement to 77 K resulted in appearance of both signals of much higher intensity and additionally, a broad band characterised with g factor about 3, which can be attributed to extraframework iron species. The signal of $g = 4.3$ was ascribed to iron (III) ions in tetrahedral coordination located either in framework [43] or in extraframework positions [44–48]. Considering that the modification of mesoporous matrix was performed by means of impregnation and that iron species should be located in the mesoporous material channels, the signal should be due to extraframework, tetrahedral iron species. The assignment of iron ESR signal with g factor about 2 is also equivocal. Commonly, this signal is assigned to iron oxide clusters. However, if it was the case, the lowering of temperature of ESR measurement should result in diminishes of the signal intensity. If, at lower temperature, intensity of signal with $g = \sim 2$ increases, it indicates that the signal originates from highly symmetric, isolated Fe (III) species [43]. Indeed, this is the case, nevertheless, it seems that the narrow signal of $g = \sim 2$ is overlapped with the broad one. Therefore, not only isolated iron (III) species but also some iron (III) forms, which interact with each other, should be present in the iron-modified samples under study.

ESR spectra of V/SBA-3 (1%) with well-dissolved lines of hyperfine splitting indicate the presence of isolated vanadium (IV) species in octahedral coordination. Such spectra are typical for tetravalent vanadium species with a d^1 configuration and a nuclear spin I of $^7/_2$, resulting in a spectrum characterised with a high number of hyperfine lines [41,49,50]. The detailed analysis of ESR spectrum of V/SBA-3 sample brings to the conclusion that, besides well-dissolved lines of hyperfine splitting, also broad line attributed to V^{4+} characterised with dipol–dipol interaction is also present. This conclusion is consistent with UV–vis spectrum indicating for the presence of V^{4+} ions in condensed phase [49].

ESR spectra of mixed system differ from the spectra of Fe/SBA-3 and V/SBA-3 samples significantly. Distinct signal from V (IV) species present in ESR spectrum of V/SBA-3 disappeared and low field signal characteristic of iron (III) became weaker and broadened, while this one with *g* about 2 got even stronger when compared with the spectrum of Fe/SBA-3. Additionally, the weak, not very well developed band of factor g equal to about 2.3 became

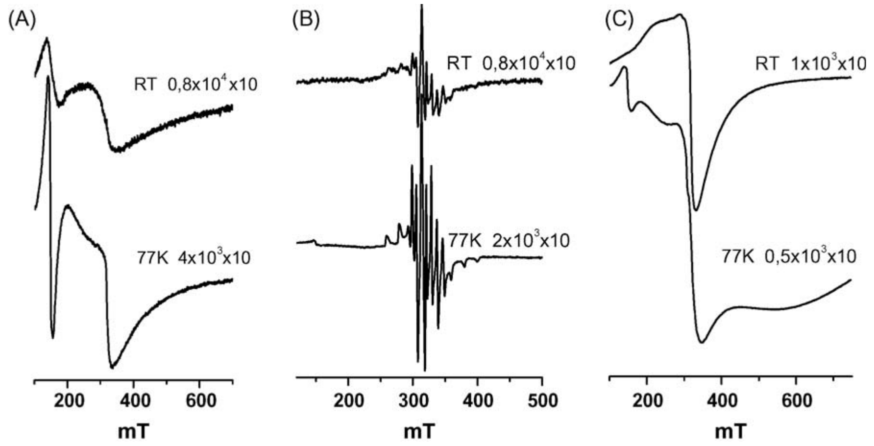

Fig. 9. ESR spectra of (A) Fe/SBA-3 (1 wt.% of Fe), (B) V/SBA-3 (1 wt.% of V) and (C) Fe/V/SBA-3 (1 wt.% of Fe and 1 wt.% of V) recorded at RT and 77 K.

visible. Disappearance of ESR signals originating from V (IV) in octahedral environment may indicate the transformation of V^{4+} to V^{5+}. One can suppose the formation of $FeVO_4$, which may stabilize vanadium (V) and it is easily synthesised by solid interaction of both components (Fe and V) [51]. However, it is not clear, whether the oxidative activity of Fe/V/SBA-3 system should be attributed to the presence of $FeVO_4$ or to the mixed system of other composition. The further investigation is indispensable to explain the interaction between iron and vanadium complexes.

4. Conclusions

1. SBA-3 mesoporous materials modified with vanadium ions show significant activity in propene epoxidation in the presence of N_2O as an oxidant.
2. Among the products, besides propylene oxide also propanal and acetone were observed, whereas CO_x formation was not noticed.
3. The addition of iron ions into Me/SBA-3 (Me = V, Nb and Ta) enhances both propene conversion and selectivity towards propylene oxide.
4. The mixed Fe/V/SBA-3 catalyst showed the best oxidative activity among the catalysts under study.
5. Interaction of both components of active phase (iron and vanadium) was assumed on the grounds of ESR spectroscopy.
6. IR bands resulting from the interaction of substrates (propene and N_2O) with vanadium-modified SBA-3 materials indicated the formation of carbonyl compounds, which should result from PO isomerization.

Acknowledgements

We thank the Polish Ministry of Scientific Research and Information Technology for financial support under the project N N204 246335.

References

[1] Q. Wang, L. Wang, J. Chen, Y. Wu, Z. Mi, J. Mol. Catal. A: Chem. 273 (2007) 73.
[2] V. Arca, A.B. Boscoletto, N. Fracasso, L. Meda, G. Ranghino, J. Mol. Catal. A: Chem. 243 (2006) 264.
[3] M.G. Clerici, G. Bellusi, U. Romano, J. Catal. 129 (1991) 159.
[4] T.A. Nijhuis, M. Makkee, J.A. Moulijn, B.M. Weckhuysen, Ind. Eng. Chem. Res. 45 (2006) 3447.
[5] J. Lu, X. Zhang, J.J. Bravo-Suárez, S. Tsubota, J. Gaudet, S.T. Oyama, Catal. Today 123 (2007) 189.
[6] J.J. Bravo-Suárez, K.K. Bando, T. Fujitani, S.T. Oyama, J. Catal. 257 (2008) 32.
[7] A.M. Joshi, W.N. Delgass, K.T. Thomson, Top. Catal. 44 (2007) 27.
[8] B.K. Min, C.M. Friend, Chem. Rev. 107 (207) 2709.
[9] R.M. Lambert, F.J. Williams, R.L. Croplez, A. Palermo, J. Mol. Catal. A 228 (2005) 27.
[10] T. Hayashi, K. Tanabe, M. Haruta, J. Catal. 178 (1998) 566.
[11] M. Haruta, Cattech 6 (2002) 102.
[12] B. Taylor, J. Lauterbach, W.N. Delgass, Catal. Today 123 (2007) 50.
[13] E. Sacaliuc, A.M. Beale, B.M. Weckhuysen, T.A. Nijhuis, J. Catal. 248 (2007) 235.
[14] A.K. Sinha, S. Seelan, T. Akita, S. Tsubota, M. Haruta, Appl. Catal. A: Gen. 240 (2003) 243.
[15] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[16] A. Held, J. Kowalska, K. Nowińska, Appl. Catal. B: Environ. 64 (2006) 201–208.
[17] Q. Zhang, Q. Guo, X. Wang, T. Shishido, Y. Wan, J. Catal. 239 (2006) 105.
[18] E. Ananieva, A. Reitzmann, Chem. Eng. Sci. 59 (2004) 5509.
[19] V. Duma, D. Hönicke, J. Catal. 191 (2000) 93.
[20] A. Costine, T. O'Sullivan, B.K. Hodnett, Catal. Today 112 (2006) 103.
[21] E.L. Force, A.T. Bell, J. Catal. 44 (1976) 175.
[22] M. Iwamoto, K. Matsukami, S. Kagawa, J. Phys. Chem. 87 (1983) 903.
[23] F. Chen, X.-J. Xu, Sh. Shen, S. Kawi, K. Hidajat, Microporous Mesoporous Mater. 75 (2004) 231.
[24] M. Santhosh Kumar, J. Pérez-Ramírez, M.N. Debbagh, B. Smarsly, U. Bentrup, A. Brückner, Appl. Catal. B: Environ. 62 (2006) 244.
[25] B. Horváth, M. Hronec, R. Glaum, Top. Catal. 46 (2007) 129.
[26] B. Moens, H. De Winne, S. Corthals, H. Poelman, R. De Gryse, V. Meynen, P. Cool, B.F. Sels, P.A. Jacobs, J. Catal. 247 (2007) 86.
[27] K. Nowińska, R. Fórmaniak, W. Kaleta, A. Wącław, Appl. Catal. A: Gen. 256 (2003) 115.
[28] G. Mul, A. Zwijnenburg, B. Linden, M. Makkee, A. Moulijn, J. Catal. 201 (2001) 128.
[29] G. Busca, T. Zerlia, V. Lorenzello, A. Girelli, J. Catal. 88 (1984) 125.
[30] E. Heracleous, A.A. Lemonidou, J.A. Lercher, Appl. Catal. A: Gen. 264 (2004) 73.
[31] T.E. Hoost, K.A. Laframboise, K. Otto, Appl. Catal. B: Environ. 7 (1995) 79.
[32] Y. Moro-oka, Appl. Catal. A: Gen. 181 (1999) 323.
[33] Q. Zhang, W. Yang, X. Wang, Y. Wang, T. Shishido, K. Takchira, Microporous Mesoporous Mater. 77 (2005) 223.
[34] J. Radnik, A. Wahab, M. Schneider, M.M. Pohl, R. Schlögl, B. Kubias, Appl. Catal. A: Gen. 285 (2005) 139.
[35] A. Brückner, G.-U. Wolf, M. Meisel, R. Stösser, H. Mehner, F. Majunke, M. Baerns, J. Catal. 154 (1995) 11.
[36] M. Baltes, K. Cassiers, P. Van Der Voort, B.M. Weckhuysen, R.A. Schoonheydt, E.F. Vansant, J. Catal. 197 (2001) 160.
[37] T. Tsoncheva, L. Ivanova, R. Dimitrova, J. Rosenholm, J. Colloid Interface Sci. 321 (2008) 342.
[38] D.E. Keller, T. Visser, F. Soulimani, D.C. Koningsberger, B.M. Weckhuysen, Vibr. Spectr. 43 (2007) 140.
[39] T. Kawabata, Y. Ohishi, S. Itsuki, N. Fujisaki, T. Shishido, K. Takaki, Q. Zhang, Y. Wang, K. Takehira, J. Mol. Catal. A 236 (2005) 99.
[40] L. Li, Q. Shen, Z. Hao, Z.P. Xu, G.Q. Max Lu, Appl. Catal. A: Gen. 344 (2008) 131.
[41] F. Gao, Y. Zhang, H. Wan, Y. Kong, X. Wu, L. Dong, B. Li, Y. Chen, Microporous Mesoporous Mater. 110 (2008) 508.
[42] E.V. Kondratenko, M. Baerns, Appl. Catal. A: Gen. 222 (2001) 133.
[43] D. Goldfarb, M. Bernardo, K.G. Strohmaier, D.E.W. Vaughan, H. Thomann, J. Am. Chem. Soc. 116 (1994) 6344.
[44] M.N. Tomofeeva, S.Ts. Khankhasaeva, S.V. Badmaeva, A.L. Chuvilin, E.B. Burgina, A.B. Ayupov, V.N. Panchenko, A.V. Kulikova, Appl. Catal. B: Environ. 59 (2005) 243.
[45] P. Decyk, Catal. Today 114 (2006) 142.
[46] P. Decyk, M. Trejda, M. Ziółek, J. Kujawa, K. Głaszczka, M. Bettahar, S. Monteverdi, M. Mercy, J. Catal. 219 (2003) 146.
[47] H.-Y. Chen, El-M. El-Malaki, X. Wang, R.A. van Santen, W.M.H. Sachtler, J. Mol. Catal. A: Chem. 162 (2000) 159.
[48] G. Catana, J. Pelgrims, R.A. Schoonheydt, Zeolites 15 (1995) 475.
[49] G. Catana, R. Ranachandra Rao, B.M. Weckhuyswen, P. Van Der Voort, E. Vansant, R.A. Schoonheydt, J. Phys. Chem. B 102 (1998) 8005.
[50] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25.
[51] S. Ekambaram, K.C. Patil, J. Alloys Comp. 217 (1995) 104.