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Effect of Ce–Fe oxides additives on performance of VPO catalyst for *n*-butane oxidation to maleic anhydride in the absence of gas-phase oxygen

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Abstract

Study on the increase of available lattice oxygen of VPO catalyst by adding Ce–Fe complex oxides was carried out using XRD, TPR and pulse reaction technique. For the oxidation of butane to maleic anhydride (MA) in the absence of gas-phase oxygen, the Ce–Fe promoted VPO catalysts have more available lattice oxygen and possess higher conversion and selectivity than that of the unpromoted one as well. It is supposed that the introduction of Ce–Fe complex oxides improves redox performance of VPO catalyst and increases the activity of lattice oxygen. However, the catalytic role of Ce–Fe complex oxides is still not clear.

Keywords: Selective oxidation; Lattice oxygen; Vanadium–phosphorus complex; *n*-Butane; Maleic anhydride

1. Introduction

For the past three decades, the feedstock for worldwide production of maleic anhydride (MA), an industrially important chemical, has changed from benzene to C_4 fractions and then to *n*-butane. Conversion of *n*-butane to MA is one of the few commercially successful selective oxidation processes, while vanadium–phosphorus complex oxides system is the only effective catalyst used for this reaction so far. Selective oxidation of *n*-butane to MA is a strongly exothermal reaction, including the subtraction of eight hydrogen atoms and insertion of three oxygen atoms into the C_4 molecule. Multitubular fixed-bed and fluid bed reactors are commonly used in industry. Very low inlet *n*-butane concentration (about 1.5–1.8%) is usually used to avoid the flammability of process streams, and the selectivity to MA is also not satisfactory (around 60–65 mol%) under the traditional industrial conditions.

Recently, using lattice oxygen of VPO catalyst instead of molecular oxygen to participate in butane oxidation DuPont developed a solid recirculating reactor technology for MA production, which separates the redox steps [1]. In Dupont process VPO catalyst is circulated between two reactors; in one reactor, butane is oxidized by vanadium phosphate; and in the other, vanadium is reoxidized. Since reaction occurs between *n*-butane and lattice oxygen in the absence of gas-phase oxygen, deep oxidation can be prevented and the selectivity of MA can be improved dramatically, so that the utilization of raw material is increased and the environmental pollution is reduced [2].

Seven oxygen atoms are required to convert a *n*-butane molecule to MA. Study with $^{18}O_2$ isotope revealed that only about four surface layers of lattice oxygen are involved in the redox cycle, so circulation

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of large amount of VPO catalyst is required, which not only increases the energy consumption but also requires the improvement of the strength of the catalyst [3]. In order to satisfy the requirement of Dupont process, Contractor et al. discovered a novel method in the preparation of an attrition resistant VPO catalyst by depositing a thin layer of silica at the periphery of the spray dried particles [4].

However, the catalytic performance of VPO catalyst plays an important role in this process. If the available lattice oxygen in VPO catalyst can be increased, the amount of circulating catalyst between the two reactors can be reduced. Most of the research on promoted VPO catalysts were published in patents and were focused on the improvement of the activity and selectivity. Hodnett [5] and Hutchings [6] summarized the performances of VPO catalysts with different promoters. A great number of promoters were used in VPO catalysts, but the understanding of their effects is scarce.

CeO_2, because of its high oxygen storage capacity, has been widely used in many fields, such as in catalytic conversion of light hydrocarbons [7], in oxidation reaction in liquid phase [8], and in treatment of exhaust gas [9]. It was reported that VPO catalyst with CeO_2 as the promoter increases the conversion of butane [10], while Fe_2O_3 promoted VPO catalyst results in the increase of MA selectivity [11,12]. As far as we know, method of increasing the reactivity of the available lattice oxygen of VPO catalyst used in the redox cycle process has not been reported yet. The aim of our present work is to increase the efficiency of the available lattice oxygen of VPO catalyst by adding Ce–Fe complex oxides for *n*-butane oxidation to MA in the absence of gas-phase oxygen. A comparative study is also carried out between pure VPO catalyst and catalysts promoted by cerium and iron as the oxygen carrier. The effects of atomic ratio of Ce to Fe on the activity of catalyst are discussed as well.

2. Experimental

2.1. Catalyst preparation

The Ce–Fe complex oxide was prepared by coprecipitation, i.e. 10% ammonia in water was added dropwise to 0.2 M aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ with a given composition until pH = 10, the precipitate was filtered, washed, dried at 373 K for approximately 15 h, then calcined at 1373 K for 2 h.

The VPO catalysts used in our study were prepared by organic synthesis method. V_2O_5 was suspended in a 2:1 (v/v) mixture of isobutyl alcohol and benzyl alcohol. The suspension was stirred under reflux at 383 K for 3 h for the reduction of V(V) to V(IV), followed by the addition of 5 wt.% Ce–Fe complex oxide prepared by coprecipitation. The solution was maintained under reflux at the same temperature with constant stirring for 6 h, then a proper amount of 85% phosphoric acid was added to adjust the P:V atomic ratio to approximately 1.1 and the reaction was continued for another 3 h. Then the slurry was filtered and washed using isobutyl alcohol for 3–4 times. The filtrate was first dried at 353 K for 5 h, and then at 393 K for 6 h to give a catalyst precursor. The catalyst was calcined in air at 673 K for 1 h, and then at 773 K for 5–9 h. Finally the VPO catalysts were ground, pressed into pellets, and crushed to 20–40 mesh particles.

Pure VPO catalyst used in our study was prepared using the same procedure as above except without Ce–Fe complex oxide.

2.2. Characterization of the catalyst

BET surface area was measured on a COULTER OMNISORP 100CX. X-ray diffraction (XRD) measurements were taken on a Qingniao BDX3200 X-ray diffractometer using Ni-filtered Cu Kα radiation.

Temperature-programmed reduction (TPR) experiments were performed at a heating rate of 15 K/min and a flow rate of 5% hydrogen–helium of 30 ml/min.

2.3. Evaluation of the available lattice oxygen of the catalyst

2.3.1. Method 1

The available lattice oxygen of catalyst for *n*-butane oxidation to MA in the absence of gas-phase oxygen was evaluated by means of *n*-butane pulse reaction. Evaluation was carried out in a fixed-bed quartz micro-reactor of 5.5 mm i.d. and 400 mm long. Thereby, 200 mg catalyst was loaded in the middle of the reactor, which was sandwiched between quartz particles packed at the outlet and inlet sections. The

catalyst bed was uniformly heated in an electric furnace controlled by a temperature controller. A NiCr–NiAl type thermocouple was used to measure the temperature of the catalyst bed. All catalysts were oxidized in air at 673 K for 30 min and then purged in a flow of argon (purity of 99.999%) in order to obtain an oxidized surface free of adsorbed oxygen. Then six pulses of 1.0 ml 20% n-C_4H_{10}/He each were consecutively introduced into the reactor using a six-way valve under 0.12 MPa pressure at the same temperature. Helium flow (purity of 99.999%) of 20 cm^3/min was used as the carrier gas. The time intervals between adjacent pulses were about 20 min owing to the requirement of the gas chromatographic analysis. In order to avoid re-oxidation of the catalyst surface during the pulse experiments, an oxygen getter was used to remove the trace of oxygen in He. The effluent of the reactor, kept at 450 K to prevent condensation of the products, was analyzed on a gas chromatograph with a 1 m Propak Q column using in series with TCD and FID detectors to improve the precision. Conversion of n-C_4H_{10} ($X_{C_4H_{10}}$) and selectivity (S_{MA}) and yield (Y_{MA}) of MA were calculated based on the average of six pulses. In the pulse reaction experiments, the tolerable carbon mass balances were within 2%.

2.4. Method 2

In order to assess the nature of lattice oxygen of the catalysts, the consecutive pulse experiments with an on-line quadrupole mass spectrometer (AMTEK QuadLink 1000) to monitor the products were performed. There are eight mass channels for the simultaneous detection with minimum dwelling time of 3 ms in the quadrupole mass spectrometer. The time intervals between adjacent pulses were 20 s. In these experiments, 25 pulses of 0.39 ml 20% n-C_4H_{10}/Ar each were injected consecutively into the reactor using a six-way valve at 673 K and 0.1 MPa pressure. In order to avoid the harmful effects of MA on the mass spectrometer, MA was separated from the effluent by condensation before entering the mass spectrometer. In this study, the amount of MA was obtained through subtracting the amounts of CO_2 from the consumed n-butane. The basis of this method is that the carbon-containing products in the reaction are CO_2, CO and MA only, and the total amount of carbon atoms must be in balance. The results of quantitative mass spectrometric analysis were calibrated by the gas chromatographic method mentioned above.

3. Results and discussion

3.1. Catalyst characterization

BET surface areas of the VPO catalysts are in the range of 10–15 m^2/g.

H_2 temperature-programmed reduction (H_2-TPR) was carried out to investigate the oxygen species of pure VPO catalyst. It can be seen from Fig. 1 that TPR profile of pure VPO catalyst has two overlapped TPR peaks located at 1026 and 1073 K, respectively, which revealed that these two oxygen species have similar activity and are not easy to be reduced by hydrogen.

Fig. 2 shows that the resolution of the two TPR peaks of all VPO/Ce–Fe catalysts are better than that of pure VPO catalyst, and the first peak temperatures of all VPO/Ce–Fe catalysts are lower than that of pure VPO catalyst. Compared to pure VPO, the area ratios of the first peak to the second peak of all VPO/Ce–Fe catalysts are larger than that of pure VPO. TPR results show that the addition of Ce–Fe complex oxides to VPO catalyst leads to a decrease in the reduction temperature of lattice oxygen and an increase in the quantity of reducible lattice oxygen species at lower temperature.

It is well known that selective oxidation of n-butane to MA over VPO catalyst is a structure sensitive reaction. It is generally believed that $(VO)_2P_2O_7$ is the active phase of VPO catalyst and the active crystal plane for selective oxidation is the (2 0 0) plane of $(VO)_2P_2O_7$ [13]. In order to achieve high activity for MA production, it is necessary to possess not only active phase $(VO)_2P_2O_7$, but also $VOPO_4$. The XRD spectrum of pure VPO and VPO/Ce–Fe catalysts is shown in Fig. 3. The XRD patterns show that VPO/Ce–Fe (1:3) and VPO/Ce–Fe (4:1) catalysts contain a mixed phase of vanadyl pyrophosphate (2θ: 18.4, 21.4, 28.3, 29.9, 33.7°) and γ-VOPO4 (2θ: 14.0, 22.7, 28.3°) identified according to [14]. In VPO/Ce–Fe (1:3) catalyst the intensities of γ-$VOPO_4$ phase is obviously stronger than those of vanadyl pyrophosphate phase, while in VPO/Ce–Fe (4:1) catalyst both intensities of γ-$VOPO_4$ and vanadyl pyrophosphate phases are nearly the same. The XRD

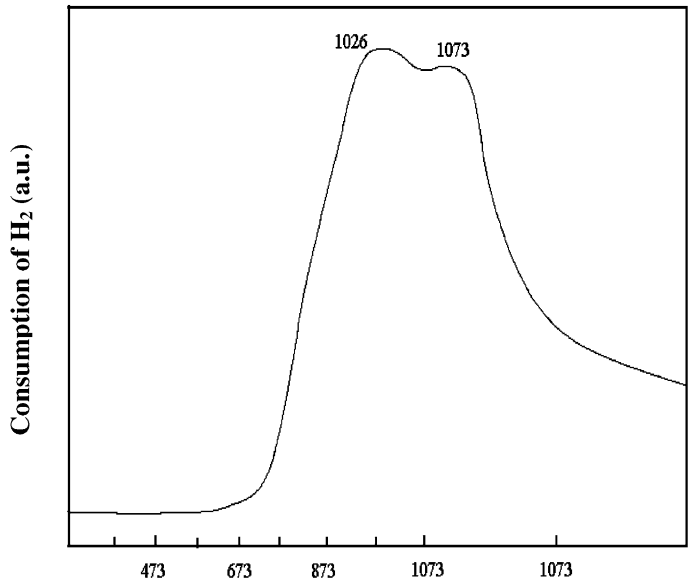

Fig. 1. H_2-TPR profile of pure VPO catalyst.

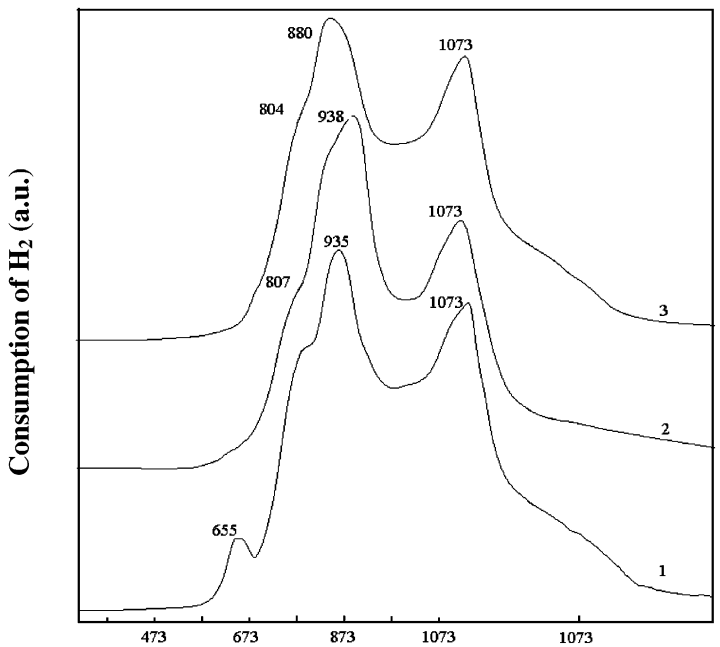

Fig. 2. H_2-TPR profiles of VPO/Ce–Fe catalysts: (1) Ce:Fe = 4:1; (2) Ce:Fe = 1:1; (3) Ce:Fe = 1:3.

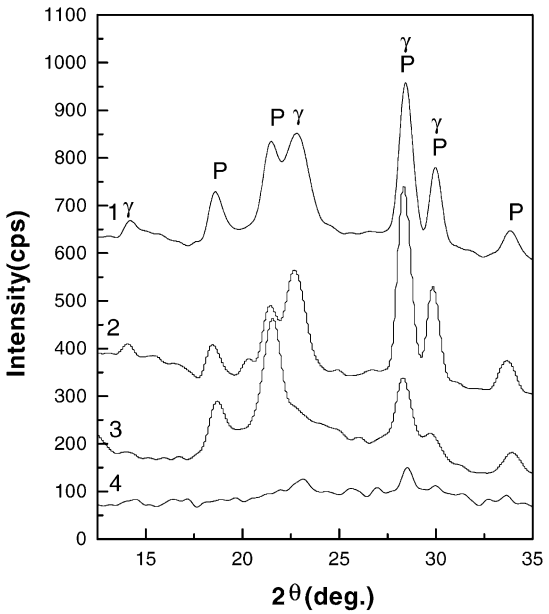

Fig. 3. XRD pattern of pure VPO and VPO/Ce–Fe series: (1) Ce:Fe = 4:1; (2) Ce:Fe = 1:3; (3) Ce:Fe = 1:1; (4) pure VPO.

pattern of VPO/Ce–Fe (1:1) catalyst mainly consisted of $(VO)_2P_2O_7$ (2θ: 18.4, 21.4, 28.3, 29.9, 33.7°) with lesser amount of γ-$VOPO_4$ (2θ: 14.0, 22.7, 28.3°). However, the XRD pattern of pure VPO revealed that its crystallization is incomplete and it only contains a small amount of $(VO)_2P_2O_7$ and γ-$VOPO_4$.

From the XRD patterns it can be found that, no matter whether Ce–Fe complex oxides are added or not, the precursor of VPO catalyst is made up by $VOHPO_4{\cdot}0.5H_2O$. So it is reasonable to suppose that Ce–Fe complex oxides may play a role in promoting the formation of $(VO)_2P_2O_7$ and γ-$VOPO_4$ during the calcination step. The activation of catalyst in our study is carried out in air, which simplifies the preparation, and possesses the advantages of forming high valence species under oxidative environment.

Fig. 4 shows the contrast between the fresh VPO/Ce–Fe (4:1) and reacted VPO/Ce–Fe (4:1) with six pulses of *n*-butane (in method 1). The feature of the fresh VPO/Ce–Fe (4:1) is a mixed phase of $(VO)P_2O_7$ and γ-$VOPO_4$. However, the XRD pattern becomes more complicated for the reacted catalyst. The main change is that γ-$VOPO_4$ phase (2θ: 18.5, 21.5, 28.4°) was reduced to α-$VOHPO_4{\cdot}2H_2O$ (2θ: 12.4, 29.2°) identified according to [14], while $(VO)P_2O_7$ phases still exists after reaction(Fig. 4 curve 3).

XRD pattern (Fig. 4 curve 2) of VPO/Ce–Fe (4:1) after TPR up to 873 K is, on the whole, similar to that after reaction with butane, viz. γ-$VOPO_4$ phase (2θ: 14.0, 22.7, 28.3°) was reduced to α-$VOHPO_4{\cdot}2H_2O$ (2θ: 12.4, 29.2°). However, there is an obvious difference, $(VO)P_2O_7$ phase after TPR is stronger than after butane reaction, while α-$VOHPO_4{\cdot}2H_2O$ phase is just the opposite. The XRD pattern of VPO/Ce–Fe (4:1) after TPR up to 1073 K (Fig. 4 curve 1) changes

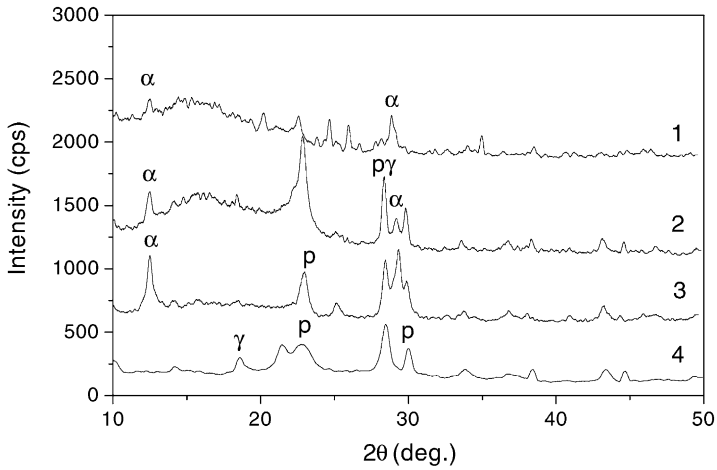

Fig. 4. XRD patterns after different pretreatment of VPO/Ce–Fe (4:1): (1) after H_2-TPR up to 1073 K; (2) after H_2-TPR up to 873 K; (3) after TPSR with 5% *n*-butane in He up to 873 K; (4) fresh VPO/Ce–Fe (4:1).

greatly in crystal structure, in which only a weak mixed phase of α-$VOHPO_4{\cdot}2H_2O$ and $(VO)P_2O_7$ as well as other minor phases at $2\theta = 20.2$, 24.6, 26.0, 35.0, 38.5° is present. It shows that the crystal structure of VPO/Ce–Fe (4:1) has been broken, In combination with the TPR results it can be ascertained that the reducible lattice oxygen, which gives the first TPR peak, is involved in the redox cycle of butane oxidation. Doping with Ce–Fe complex oxides, probably, increases the activity of lattice oxygen.

3.2. Evaluation of the available lattice oxygen in different VPO catalysts

In the primary experiment, the optimum amount of Ce–Fe complex oxides was found to be about 5 wt.% of catalyst. The effects of adding Ce–Fe complex oxides with different atomic ratios of Ce:Fe on the available lattice oxygen of VPO catalyst were evaluated by means of pulse reaction, and the results are listed in Table 1. It can be seen that the selectivity to MA increases while the conversion of C_4H_{10} decreases with the increase the ratio of Ce:Fe atom. It was also revealed that the addition of Ce is conducive to the formation of highly selective oxygen species, while Fe increases the reactivity of oxygen species. The synergic effect of Ce–Fe complex oxides is different from the single compound as mentioned in patents [10–12]. Among them, VPO/Ce–Fe (4:1) is the best catalyst, which possesses the highest selectivity (81–83%) to MA at relatively high conversion of *n*-butane. It is known that Ce forms quite stable carbonate species. If the CO_2 from *n*-butane oxidation reacts with Ce to form carbonate species, which will not decompose below 773 K, the improvement of selectivity may be due to the fact that a part of CO_2 remains trapped on the catalyst. In order to clarify this problem, after 25 consecutive pulses of 0.39 ml 20% *n*-C_4H_{10}/Ar over VPO/Ce–Fe (4:1), the CO_2-TPD experiment was carried out using 20 ml/min He flow as the carrier gas and an on-line quadrupole mass spectrometer to monitor the desorbed products. TPD result shows that no CO_2 desorption peak appears in the temperature range from 300 to 1023 K, while an O_2 desorption peak appears at temperature range of 920–1010 K. This implies that Ce in Ce–Fe complex oxides cannot react with CO_2 to form Ce carbonate species. The O_2 desorption peak is probably came from decomposition of V/P oxides.

Table 1
$X_{C_4H_{10}}$, S_{MA} and Y_{MA} over pure VPO and VPO/Ce–Fe catalysts in the absence of gas-phase oxygen (evaluated by method 1)

Catalyst	$X_{C_4H_{10}}$ (%)	S_{MA} (%)	Y_{MA} (%)
Pure VPO	43.7	62.6	27.4
VPO/Ce–Fe (1:3)	60.4	65.8	39.7
VPO/Ce–Fe (1:1)	56.0	72.7	40.7
VPO/Ce–Fe (4:1)	51.5	83.0	42.7

Comparing the XRD patterns with reactivity results, it was inferred that the high conversion and selectivity of VPO/Ce–Fe (4:1) may be partly due to the coexistance of γ-$VOPO_4$ and $(VO)_2P_2O_7$. Some other researchers also considered that all of γ-$VOPO_4$, δ-$VOPO_4$ and $(VO)_2P_2O_7$ possess activity and selectivity to produce MA [15].

In order to evaluate the available lattice oxygen, an on-line quadrupole mass spectrometer was used to monitor the pulse products. Fig. 5 shows the profile of 25 consecutive pulses of 0.39 ml 20% *n*-C_4H_{10}/Ar over VPO/Ce–Fe (4:1). It can be seen that the decrease of *n*-butane consumption rate in the first four pulses is much greater than that in the subsequent 13 (5th to 17th) pulses, and keeps almost constant in the last seven ones. The decreases of CO and CO_2 with pulse have the same tendency. Fig. 6 shows the variation of conversion and selectivity versus pulse number. For pure VPO catalyst the same tendency

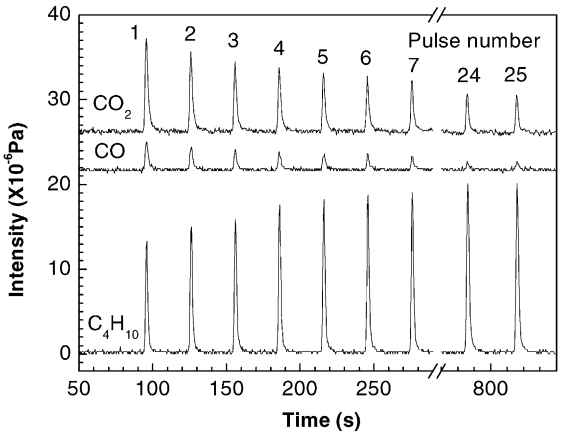

Fig. 5. The profile of 25 continuous C_4H_{10}/He pulses over VPO/Ce–Fe (4:1), pulse interval of 20 s.

Table 2
Amounts of different lattice oxygen species in VPO/Ce–Fe (4:1) and pure VPO catalyst (evaluated by method 2)

Catalyst	Total amount ($\times 10^{-5}$ mol/g cat.)		Surface oxygen (*a*)		Subsurface oxygen (*b*)		Diffused bulk oxygen (*c*)	
	O_s[a]	O_n[b]	O_s[a]	O_n[b]	O_s[a]	O_n[b]	O_s[a]	O_n[b]
VPO/Ce–Fe (4:1)	45.5	8.5	10.7	3.2	21.1	4.0	12.7	2.3
Pure VPO	24.5	16.7	4.8	3.3	12.3	8.2	7.7	5.2

[a] O_s stands for oxygen species selective to produce MA.
[b] O_n stands for oxygen species non-selective to MA.

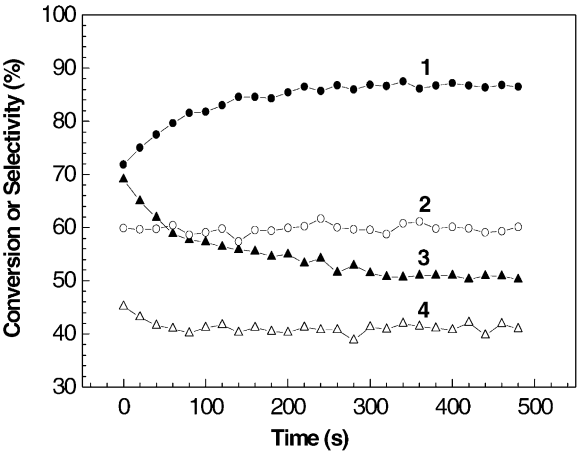

Fig. 6. The function of conversion and selectivity vs. pulse number: (1) S_{MA} over VPO/Ce–Fe (4:1); (2) S_{MA} over pure VPO. (3) $X_{C_4H_{10}}$ over VPO/Ce–Fe (4:1); (4) $X_{C_4H_{10}}$ over pure VPO.

has also been observed except the lower conversion and selectivity than that of VPO/Ce–Fe (4:1). The amounts of different oxygen species (mol/g cat.) are listed in Table 2. Compared with pure VPO catalyst, the available oxygen species with high selectivity in the Ce–Fe promoted VPO catalysts are greatly increased. It is shown that the activity of lattice oxygen is increased by doping Ce–Fe complex oxides. However, the role of Ce–Fe complex oxides in VPO catalyst is still not clear. Further study is needed to clarify these problems.

4. Conclusion

In the oxidation of butane to MA in the absence of gas-phase oxygen, the Ce–Fe oxide promoted VPO catalysts possess higher conversion and selectivity than that of the unpromoted VPO catalyst. Among them VPO/Ce–Fe (4:1) catalyst exhibits the best performance. It is supposed that the introduction of Ce–Fe complex oxides improves the redox performance of VPO catalyst and increases the activity of lattice oxygen. However, the catalytic role of Ce–Fe complex oxides is still not clear.

Acknowledgements

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