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The characterization and the catalytic activity of modified Wells–Dawson-type polyoxometalates in the oxidehydrogenation of isobutane to isobutene

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

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Abstract

Thermal stabilities of Wells–Dawson polyoxometalates of overall skeleton composition $P_2W_{18}O_{62}{}^{6-}$ were examined and their catalytic properties in isobutane oxidehydrogenation were tested as a function of temperature, isobutane and oxygen content and presence of steam. It is shown that the lacunary $K_{10}P_2W_{17}O_{61}$ and the iron-substituted $K_7P_2W_{17}FeO_{61}$ are stable under oxidizing conditions up to 500 °C. At higher temperature structural modifications occur with breaking of the polyanion framework and formation of K/W/O and K/P/O-containing phases. These rearrangements are thermally induced (they occur under both air and inert atmosphere) and do not involve the formation of the Keggin-type phases, as previously observed with $K_6P_2W_{18}O_{62}$. The Wells–Dawson compounds were active and selective in isobutane oxidehydrogenation to isobutene. However, a high activity was evident only under conditions which favoured the polyoxometalate reduction, and the possible generation of radical species which propagated into the gas phase, thus yielding a reactivity typical of heterogeneously-initiated, homogeneous reactions. These conditions were found at temperature higher than 450 °C, high isobutane concentration and high oxygen concentration in feed. A specific role of water in the reaction has been found; specifically, in the presence of steam the contribution of homogeneous reactions was enhanced.

Keywords: Oxidative dehydrogenation; Polyoxometallates; Wells–Dawson; Keggin; Isobutane

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1. Introduction

A great interest exists for the study of heterogeneous catalytic systems able to perform with efficiency the oxidative transformation of light alkanes into the corresponding olefins, because of the possible advantages that oxidative dehydrogenation offers as compared to traditional, endothermal processes for the production of olefins [1–3]. Catalysts active in paraffins oxidehydrogenation can be divided into two classes: (i) reducible metal oxides, in which a heterogeneous redox-type mechanism prevails, provided reaction temperatures lower than 500 °C are used, and (ii) non-reducible metal oxides, which are active at higher temperatures, and in which often the mechanism begins on the catalyst surface and is then transferred into the gas phase.

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In the past, we have investigated the activity of Wells–Dawson polyoxometalate of composition $K_6P_2W_{18}O_{62}$ in the oxidative dehydrogenation of isobutane to isobutene [4–7]. The comparison of our results with literature data [8–11] evidenced the good performance of this material, both in terms of selectivity and yield of isobutene. Modification of this Wells–Dawson-type polyoxoanion can be achieved through the incorporation of transition metal ions in the oxide skeleton. An important example is the transformation of $P_2W_{18}O_{62}{}^{6-}$ polyanion to the $P_2W_{17}MO_{61}{}^{n-}$ where M is a transition metal. This can be done through the preparation of the lacunary polyanion $P_2W_{17}O_{61}{}^{10-}$ and its reaction with transition metal salts [7]. For example, the structure of $K_7P_2W_{17}FeO_{61}$ is derived from the classic Wells–Dawson $P_2W_{18}O_{62}{}^{6-}$ by replacing an apical $W^{VI} = O^{4+}$ with a $Fe^{3+}\cdot OH_2$ unit. We have prepared and tested a series of potassium salts of $P_2W_{17}MO_{61}{}^{n-}$ with M = Fe, Cu, Mn and Co. All of them show interesting properties in the catalytic oxidehydrogenation of isobutane, with the iron-substituted polyanion being the most promising [7].

In this study, we review and reanalyse the most important aspects of the work done by using Wells–Dawson polyoxoanions in heterogeneous catalysis and, specifically, we report in more detail about the structural features and stability of the $P_2W_{17}FeO_{61}{}^{7-}$ and the parent lacunary compound $P_2W_{17}O_{61}{}^{10-}$ in order to obtain a more complete characterization of its solid state and catalytic behaviour. The evolution of the lacunary and iron-substituted compounds under air and inert atmosphere have been followed by IR and X-ray diffraction and the catalytic behaviour in the oxidative dehydrogenation of isobutane was used as a probe reaction.

2. Experimental

2.1. Materials

The synthesis of $K_6P_2W_{18}O_{62}\cdot 14H_2O$, $K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ and $K_7P_2W_{17}FeO_{61}\cdot 8H_2O$ were carried out according to established procedures [12]. Briefly, $K_6P_2W_{18}O_{62}\cdot 14H_2O$ was obtained by refluxing for 20 h a solution of 100 g of Na_2WO_4 dissolved in 250 ml of boiling water and 350 ml H_3PO_4 (85%). The product was precipitated by addition of KCl at room temperature. Addition of $KHCO_3$ followed by acidification with HCl yielded the pure compound.

Preparation of the lacunary $K_{10}P_2W_{17}O_{61}\cdot 10H_2O$ was carried out by base degradation of $K_6P_2W_{18}O_{62}$. A water solution of $K_6P_2W_{18}O_{62}\cdot 14H_2O$ is mixed with a solution of $KHCO_3$ with vigorous stirring. The white powder precipitated of $K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ is recrystallized in boiling water followed by cooling at 5 °C.

For the preparation of iron-substituted polyanion the pure $K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ is dissolved in water and a solution of $Fe(NO_3)_3\cdot 9H_2O$ is added under vigorous stirring. The product $K_7P_2W_{17}FeO_{61}\cdot 8H_2O$ is formed according to reaction (1) and crystallized. Purity of all these products was checked by elemental analysis and solution ^{31}P NMR spectra.

$$\begin{aligned}&K_{10}P_2W_{17}O_{61}\cdot 15H_2O + Fe(NO_3)_3\cdot 9H_2O\\&\quad\to K_7P_2W_{17}FeO_{61}\cdot 8H_2O + 3KNO_3 + 16H_2O\end{aligned}\tag{1}$$

Thermal treatments were carried out by placing the materials in a quartz crucible inserted in a tubular oven under constant flow of air or inert gases (He).

2.2. Techniques

The infrared spectra were carried out using KBr pellets with a Digilab FTS-40 instrument. X-ray powder diffraction patterns were collected with an Inel instrument using Co radiation. Specific surface area were measured with a Carlo Erba 1990 Porosimeter using N_2 adsorption.

The catalytic activity for the gas-phase oxidative dehydrogenation of isobutane was examined using a stainless steel flow reactor operating at atmospheric pressure. Three grams of catalyst were loaded for the tests; reaction conditions were as follows: feedstock composition 26 mol.% isobutane, oxygen 13%, water (when present) 12%, remainder helium. The residence time was 3.6 s, and results were collected after approximately 50 h time-on-stream. No effect of catalyst deactivation was observed up to 300 h time-on-stream. Preliminary tests made at the same reaction conditions (temperature 470 °C), but in the absence of catalyst demonstrated that the contribution of homogeneous reactions was negligible (isobutane conversion less than 1%). All products were analyzed by gas chromatography. A column packed with 10% SP-1200 + 1% H_3PO_4 on Chromosorb WAW connected to a FID detector was used to separate isobutane, methacrolein, isobutyric acid, acetic acid and methacrylic acid. The oven temperature was programmed to rise from 40 to 100 °C at a rate of 16°/min. The isobutane–isobutene separation was carried out using a 5 m column packed with 23% SP-1700 on Chromosorb PAW connected to a FID detector. The analysis of carbon oxides and oxygen was carried out using two columns connected to a TCD detector in isothermal conditions at 40 °C: a 4 m column of Porapak QS was used for the analysis of CO_2 and a 2 m column of Carbosieve was used for CO and oxygen.

3. Results and discussion

3.1. The thermal behaviour of Wells–Dawson-type polyoxometalate of composition $K_6P_2W_{18}O_{62}\cdot 10H_2O$

The thermal evolution of $K_6P_2W_{18}O_{62}\cdot 10H_2O$ under air was followed by recording the FT-IR spectra at increasing temperatures; in Fig. 1 are reported profiles relative to the fresh material and the material treated at 800 °C (profiles a, a′). The starting material shows bands typical of the P = O (ca. 1090 and 1020 cm^{-1}), W = O (ca. 780 cm^{-1}) and W–O–W (ca. 910 and 950 cm^{-1}) vibrations. The profiles are not modified in the region corresponding to P–O and W–O vibrations when the treatment is carried out at temperatures lower than 500 °C; thus, apart from the dehydration of the compound (which occurs already after treatment at 200 °C), no structural changes occur up to this temperature. At higher temperatures, the IR features change, with a shift in the position of the bands and with the appearance of two new signals in the range 1100–1200 cm^{-1}. This new spectrum, which closely resembles the spectrum of a Keggin-type polyanion $K_3PW_{12}O_{40}$ except for the two new bands, does not change when the sample is subjected to further treatment up to 800 °C. X-ray diffraction patterns following these treatments are reported in Fig. 2. In correspondence with the loss of water, partial amorphization of the structure is observed; this is not accompanied by changes in the primary structure, since the IR features remain unaffected. After thermal treatment at 500 °C, the pattern corresponding to that of Keggin-type polyanion $K_3PW_{12}O_{40}$ develops, according to FT-IR spectra. Therefore, rearrangement of the Wells–Dawson structure into the more stable Keggin framework has taken place; the latter is then stable up to 900 °C, in agreement with previous indications [5]. The additional bands which appear in the spectrum of the calcined compound at 1143 and 1203 cm^{-1}, suggest the presence of one or more additional phases. These bands fall in the region of P–O vibrations, and this indicates

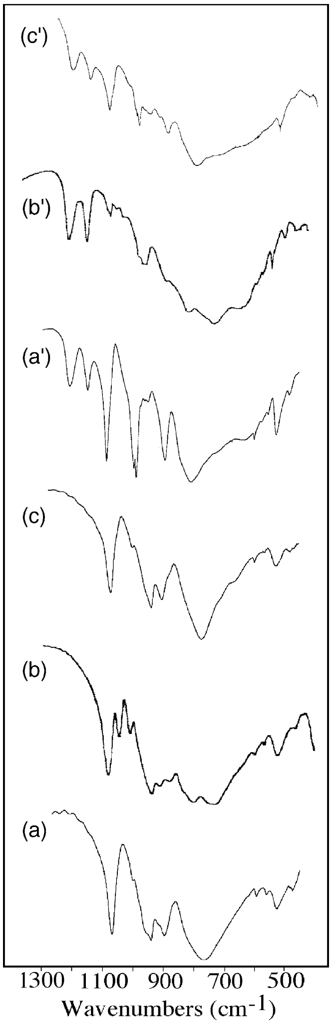

Fig. 1. FT-IR spectra of fresh $K_6P_2W_{18}O_{62}\cdot 14H_2O$ (a) $K_{10}P_2W_{17}O_{61}\cdot 15H_2O$; (b) $K_7P_2W_{17}FeO_{61}\cdot 8H_2O$; and (c) after air treatment at 800 °C for 3 h (a′, b′, c′).

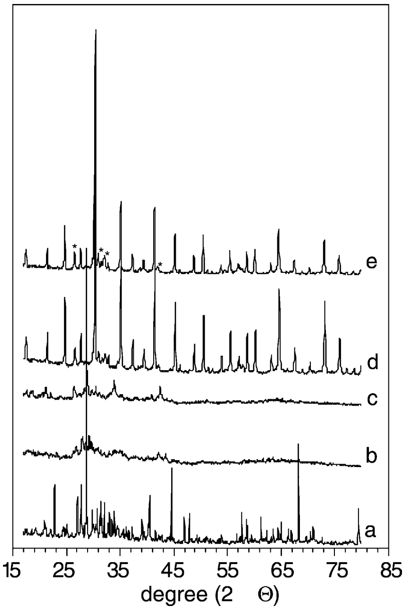

Fig. 2. X-ray powder diffraction patterns of $K_6P_2W_{18}O_{62}\cdot 14H_2O$ after treatment under air at the following temperatures: (a) fresh, 25 °C; (b) 200 °C, 3 h; (c) 400 °C, 3 h; (d) 600 °C, 3 h; (e) 800 °C, 3 h.

the development of a new phosphorus-containing compound. The presence of another phase is also confirmed by the X-ray diffraction pattern which shows a few additional weak reflections (marked by an asterisk in Fig. 2), which do not belong to the Keggin phase, and which are positioned at $d = 3.82$, 3.27, 3.16, 2.44 and 1.95 Å. These were previously tentatively assigned to a K/W/O-containing phase, the hexatungstate $K_2W_6O_{19}$ (JCPDS-ICDD 31-1115) [5]. Thus, the rearrangement of the Wells–Dawson structure could occur through the following simplified reaction scheme

$$K_6P_2W_{18}O_{62} \rightarrow (1.5 - a)K_3PW_{12}O_{40} + 2aK_2W_6O_{19} + K_{1.5-a}P_{1.5+a}O_{2+2a} \quad (2)$$

in which $K_{1.5-a}P_{0.5+a}O_{2+2a}$ may be considered as a mixture of P_2O_5, K_2O and KPO_3 in relative amounts which are a function of the a value. Since the XRD spectrum indicates that $K_2W_6O_{19}$ is formed in a minor amount, the value of a is likely very low, and in this case the stoichiometry of decomposition takes account of the co-formation of $(0.5 + a)$ mol of KPO_3 and $(0.5 - a)$ mol of K_2O. The stoichiometry of decomposition of $K_6P_2W_{18}O_{62}$ to $K_3PW_{12}O_{40}$ indeed might involve the formation of a K/P/O phase, according to the following stoichiometry:

$$2K_6P_2W_{18}O_{62} = 3K_3PW_{12}O_{40} + K_3PO_4 \quad (3)$$

The additional formation of $K_2W_6O_{19}$, as inferred from XRD pattern, might arise from a further rearrangement of the $K_3PW_{12}O_{40}/K_3PO_4$ mixture. In order to confirm the above reported hypothesis, a mechanical mixture was prepared which contained 2% by weight of K_3PO_4 and 98% of $K_3PW_{12}O_{40}$ (as required by the above reported stoichiometry), which was then heated up to 800 °C. This treatment yielded a material whose IR and XRD spectral features are identical to those of the calcined $K_6P_2W_{18}O_{62}$. This means that the additional formation of $K_2W_6O_{19}$ is due to the presence of K_3PO_4 which induces partial transformation of $K_3PW_{12}O_{40}$ into $K_2W_6O_{19}$.

3.2. *The thermal behaviour of the lacunary and transition metal-modified Wells–Dawson-type polyoxometalate*

The main characteristics of IR spectra of $K_6P_2W_{18}O_{62}$ are still observed on the lacunary $K_{10}P_2W_{17}O_{61}$ and the iron-substituted $K_7P_2W_{16}FeO_{61}$. The main adsorption bands in the region 500–1500 cm^{-1} are located at ca. 780, 910, 950 and 1090 cm^{-1} with a shoulder at ca. 1030 cm^{-1}. The bands in the spectrum of $K_{10}P_2W_{17}O_{61}$ are less resolved but the main peaks are still observed in the position indicated. No major modification of the IR profile are observed under air treatment up to 400 °C. This indicates that elimination and/or substitution of a W element with Fe does not modify the stability of the polyanion framework at these low temperatures. Treatment at much higher temperature, however, causes a broadening of bands in the region 600–1000 cm^{-1} in both materials, with the appearance of two new bands in the region 1150–1250 cm^{-1} which are indicative of important phase changes (b′, c′, Fig. 1). This has been confirmed by X-ray diffraction profiles recorded at increasing temperatures and reported in Fig. 3 for the lacunary compound (a similar evolution of XRD profiles is observed on the iron-based compound). On increasing temperature amorphization of the structure

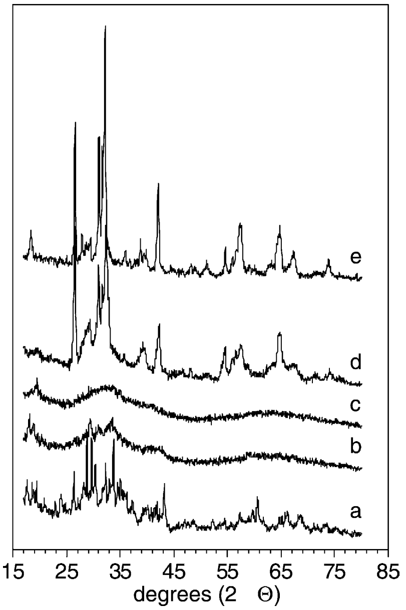

Fig. 3. X-ray powder diffraction patterns of $K_{10}P_2W_{17}O_{61}{\cdot}15H_2O$ after treatment under air at the following temperatures: (a) fresh, 25 °C; (b) 200 °C, 3 h; (c) 400 °C, 3 h; (d) 600 °C, 3 h; (e) 800 °C, 3 h.

is observed in coincidence with the loss of water (200–400 °C). The fact that IR profiles are not modified in this region suggests that primary structure remains intact. In the temperature range between 400 and 600 °C, important phase changes occur with formation of a new diffraction profile. The evolution of X-ray diffraction pattern is different from that observed with $K_6P_2W_{18}O_{62}$ (compare Figs. 2 and 3); the presence of the Keggin phase is not observed, at least in major amounts. The peaks positioned at $d = 6.33$, 3.82, 3.27, 3.17, 2.44 and 1.83 Å can be assigned to a K/W/O-containing phase of the type $K_{0.33}W_{0.944}O_3$ (JCPD file 81-0005) [13]. Moreover, the presence in the IR spectrum of two new bands in the region of P–O vibrations (1145, 1205 cm^{-1}) indicates the formation of a P-containing phase. The rearrangement could take place according to the following reaction schemes:

$$K_{10}P_2W_{17}O_{61} \rightarrow 18K_{0.33}W_{0.944}O_3 + K_4P_2O_7(+\,\text{trace}\ K_3PW_{12}O_{40}) \quad (4)$$

$$K_7P_2W_{17}FeO_{61} \rightarrow 18K_{0.33}W_{0.944}O_3 + KFeP_2O_7(+\,\text{trace}\ K_3PW_{12}O_{40}) \quad (5)$$

A quite similar behaviour has been observed with other metal-substituted polyanion (M = Cu, Co, Mn). More generally, with metal-substituted polyanion, rearrangement takes place through the formation of a major amount of a K/W/O phase plus residual metal/phosphorus-containing phase M/P/O/K and traces Keggin-type polyanion. Therefore, the lack of one tungsten atom induces a stronger fragmentation of the polyanion structure compared with results obtained with the $K_6P_2W_{18}O_{62}$.

3.3. The reactivity of $K_7P_2W_{17}FeO_{61}$ in the oxidation of isobutane to isobutene

In Fig. 4, the conversion of isobutane and of oxygen (top) and the selectivity to the products (bottom) as functions of the reaction temperature are reported for the compound of composition $K_7P_2W_{17}FeO_{61}$. Tests have been carried out with oxygen as the limiting reactant under isobutane-rich conditions, both in the absence and in the presence of steam.

The activity of the Fe-containing polyoxometalate was substantially the same as that of $K_6P_2W_{18}O_{62}$ [7]; also, the distribution of products obtained was similar for the two catalysts. The prevailing product of partial oxidation was isobutene, with minor amounts of oxygenated compounds (mainly acetic acid, methacrolein and methacrylic acid).

Steam did not affect considerably the conversion and the distribution of products up to the temperature of 440 °C. In both cases, the selectivity to isobutene was around 60–65%. Marked differences were observed above 440 °C. Specifically, in the presence of steam a sudden increase of conversion was observed at 460 °C, accompanied by a decrease of selectivity to isobutene in favour of the formation of carbon oxides, while the same did not occur in the absence of steam. Therefore, steam plays an important role at high reaction temperatures. This can be explained either by a modification of active sites, or by a participation of water in the high-temperature mechanism, under conditions at which mixed heterogeneous-homogeneous reactions become relevant. It is worth noting that the effect was quite reversible; tests repeated at

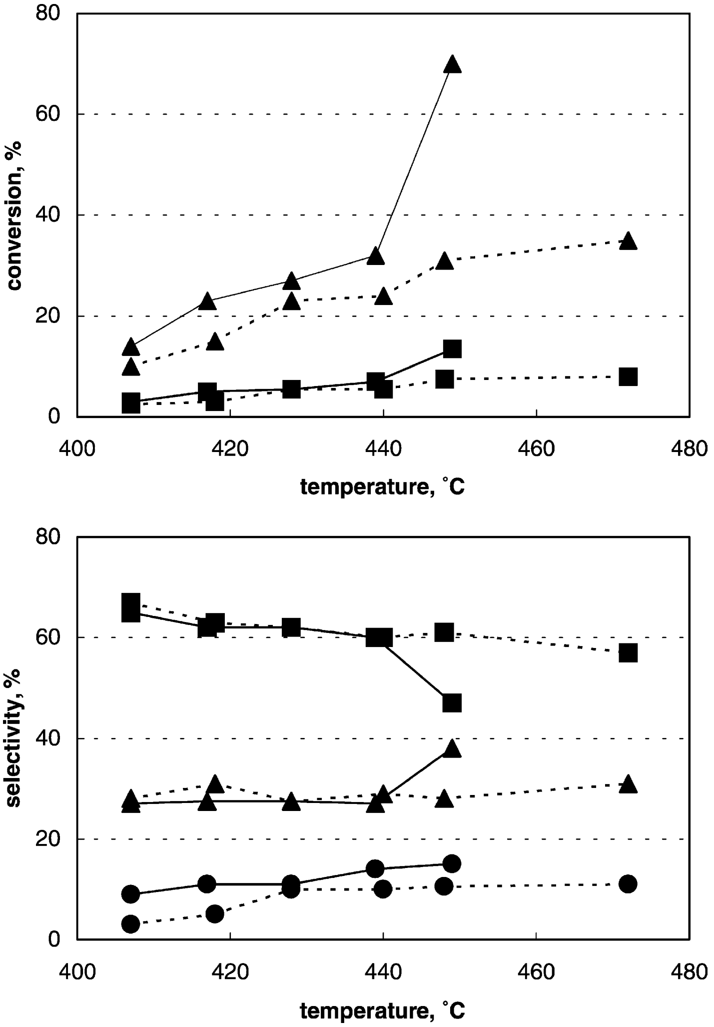

Fig. 4. Top: effect of temperature on isobutane conversion (■) and on oxygen conversion (▲) in the presence of steam (13 mol%; full lines), and in the absence (dotted lines) of steam. Bottom: effect of temperature on selectivity to isobutene (■), to carbon oxides (▲) and to other oxygenated by-products (●) in the presence of steam (13 mol%; full lines), and in the absence (dotted lines) of steam. Conditions: feed composition: 26% isobutane, 13% oxygen, remainder helium; residence time: 2.0 s.

temperatures lower than 450 °C, gave the same results as tests made before running the catalyst at above 450 °C. This indicates that the phenomenon observed was not due to an irreversible structural modification of the catalyst. XRD and IR characterization of the catalyst after reaction confirmed that no structural modifications had occurred during reaction.

The effect of the isobutane partial pressure on catalytic performance is reported in Fig. 5. Tests were carried out at the temperature of 472 °C and residence time 1 s, in the presence of steam; these conditions were chosen so to enhance the possible contribution of homogeneous reactions, and thus, to confirm the above formulated hypothesis. The effect was relevant on both isobutane conversion and product selectivity: an increase of the isobutane partial pressure caused a considerable increase of alkane and oxygen conversions, as well as an increase of selectivity to isobutene, with a corresponding decrease of the formation of carbon oxides. The result is an increase

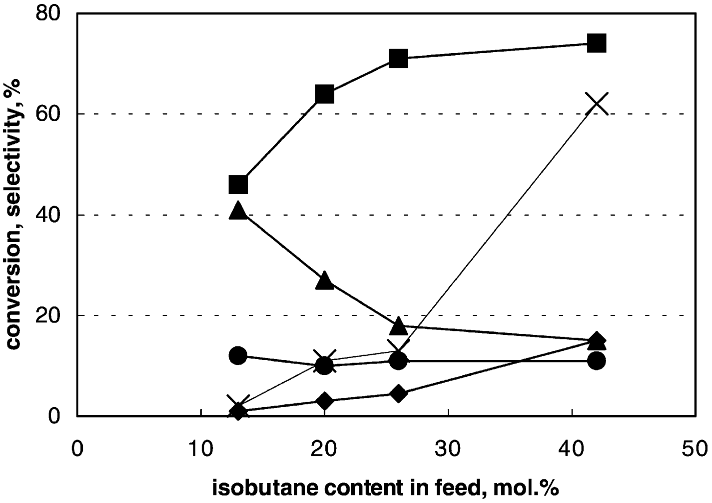

Fig. 5. Effect of the isobutane concentration in feed on isobutane conversion (◆), oxygen conversion (×) and on selectivity to isobutene (■), to carbon oxides (▲) and to other oxygenated by-products (●). Conditions: feed composition: 13% oxygen, 13% steam, remainder helium; temperature: 472 °C; residence time: 1.0 s.

of the yield to isobutene, which is equal to 1.6% when isobutane in feed is 20 mol.% (with a productivity of 0.6 mol isobutene/(h lt_{cat})), and become equal to 11.3% when isobutane is 42% in feed (with a productivity to isobutene equal to 4.3 mol isobutene/(h lt_{cat})). It is worth noting that under these conditions, but for isobutane concentrations in feed lower than 15%, the catalyst was practically inactive, the conversion of isobutane being lower than 2%. The same effect is observed when the oxygen partial pressure is changed (Fig. 6); in this case, however, higher oxygen concentrations led to lower selectivity to isobutene and to higher selectivity to carbon oxides. Also in this case, in the presence of low oxygen partial pressures, very low isobutane conversion was reached, despite the high temperature employed.

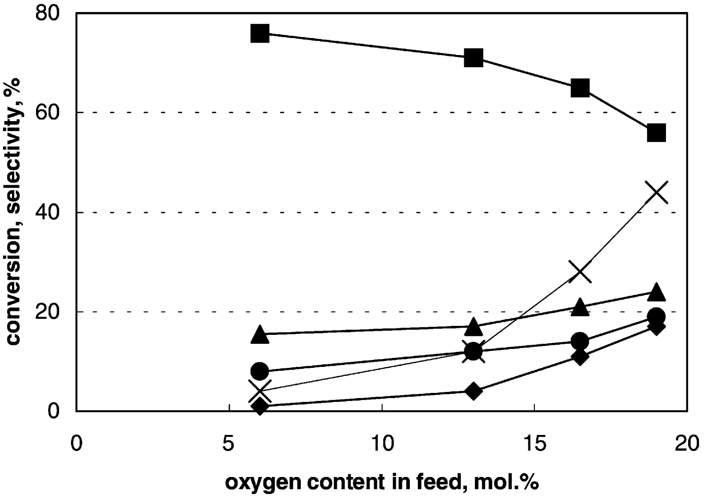

Fig. 6. Effect of the oxygen concentration in feed on isobutane conversion (◆), oxygen conversion (×) and on selectivity to isobutene (■), to carbon oxides (▲) and to other oxygenated by-products (●). Conditions: feed composition: 26% oxygen, 13% steam, remainder helium; temperature: 472 °C; residence time: 1.0 s.

These effects can be explained by making two different hypothesis.

1. A modification of the redox properties occurs as due to specific reaction conditions, which generates an autocatalytic effect. One possibility might be the development of a reduced surface occurring when high concentrations of hydrocarbons (isobutane and the product isobutene) develop, with generation of sites which are intrinsically more reactive than the corresponding sites in oxidized form. However, since the effect was observed even for increasing oxygen concentrations, it might be related to the reaction advancement (e.g. to the isobutene formed), rather than to isobutane.
2. A contribution of an homogeneous mechanism, favoured under conditions of high concentration of oxygen, of hydrocarbon, and of high temperature as well. High gas-phase partial pressures of reactants (isobutane or oxygen) are necessary to develop the surface concentration of radical fragments necessary to initiate the reaction and to continue it into the gas phase. The strong dependence of reaction rates on the alkane and oxygen partial pressures indeed is typical of radical gas-phase reactions (which involve bimolecular mechanisms to initiate, propagate, and terminate the chain) [14,15].

It is interesting to observe that when some of the above reported conditions are not fulfilled, the catalyst is substantially inactive. Specifically, either at very low isobutane concentration, or at very low oxygen concentration in feed, the conversion of isobutane itself is in practice negligible, even though the reaction temperature is kept at above 450 °C. While the absence of reactivity in presence of low oxygen concentration might be explained by the inactivity of the catalyst in isobutane dehydrogenation, the negligible conversion in the presence of low isobutane concentration (and high oxygen concentration) in feed indicates that the catalyst is intrinsically inactive, and that only when some specific conditions are realized, an *in-situ* modification of active sites occurs which makes the catalyst active. In a previous work [4] evidence was found that the oxidation degree of W in polyoxometalate is a function of feed composition; a partially reduced polyoxometalate develops at high reactants concentration in feed. On the other hand, an high concentration of isobutane might be necessary to develop a sufficient concentration of radicals at the adsorbed state. Thus, neither of the two above reported hypothesis can be excluded on the basis of data presented here.

Another surprising result concerns the role of steam. In the presence of steam (and in the presence of high concentration of isobutane) the effects previously described are clearly more evident. Steam might play a direct role in the reaction, i.e. by transforming isobutane to carbon monoxide and hydrogen; the reaction between H_2 and O_2, catalyzed by the polyoxometalate, may lead to the formation of OH radicals, which accelerate the radical-chain reactions.

In a previous work [5], it was found that when the $K_6P_2W_{18}O_{62}$ compound is thermally treated at 400 °C in the presence of steam, it develops an intense blue colour which is typical of a reduced polyoxometalate. When the same compound is treated in dry atmosphere, the same phenomenon does not occur. Also, it was found that the reduction process leads to evolution of O_2 from the catalyst, but only when H_2O is present, indicating that water is essential to the spontaneous reduction process. This seems to favour a model in which water serves as a catalyst for the self reduction of $K_6P_2W_{18}O_{62}$ and might support the hypothesis that the effect observed with reactivity tests is indeed due to a catalyst reduction. Water is also a reaction product, but its concentration is very low (and the autocatalytic effect is negligible) as long as the isobutane conversion is low. It is also worthwhile reminding that the effect is typical of Dawson P/W polyoxometalates, since in the case of Keggin-type P/W polyoxometalates the spontaneous reduction did not occur, and accordingly no unusual catalytic effect was observed. The reaction rate was in fact first order with respect to isobutane concentration [4]. On the other hand, Keggin-type P/W polyoxometalates are active in isobutane oxidehydrogenation even under low hydrocarbon concentration in feed, and in the absence of steam as well.

4. Conclusions

The structural stability of Wells–Dawson-type polyoxometalates has been studied as a function of the temperature of thermal treatment. It was found that the structural evolution of the compounds is a function of their starting composition. While $K_6P_2W_{18}O_{62}\cdot 10H_2O$ is transformed into Keggin-type $K_3PW_{12}O_{40}$

plus K/P/O and K/W/O-containing compounds by calcination at 500 °C, the lacunary and transition metal-substituted Wells–Dawson polyoxometalates transform, under the same conditions, into different K/W/O and K/P/O-containing phases via amorphous intermediates.

The reactivity of $K_7P_2W_{17}FeO_{61}$ in isobutane oxidehydrogenation was studied. It was found that the catalyst is substantially inactive in the reaction, but becomes very active under conditions which (i) favour the reduction of the catalyst surface, and (ii) enhance the contribution of heterogeneously-initiated, homogeneous reactions. Steam plays an important role in the reaction, since it catalyzes the surface reduction of the compound. Yield to isobutene as high as 11% can be reached under these conditions.

Acknowledgements

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