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Oxidation of isobutane on a heteropolycompound hydrogen reservoir

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Abstract

The selective oxidation of isobutane to methacrylic acid (MAA) has been studied on $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ which is a heteropolycompound (HPC). The oxidation mechanism isobutane → isobutene → MAL → MAA has already been proposed previously with a rate determining step corresponding to the first step of the reaction, i.e., to dehydrogenation of isobutane leading to isobutene. Here we show that the HPC which is active in the oxidation of isobutane possesses, in the reduced state, anionic vacancies able to store reactive hydrogen species H^* presenting the ability to diffuse through the solid. Such a result is of great importance since dehydrogenation requires the abstraction of hydrogen from the molecule which could be performed by a lacunar phase. Therefore, a mechanism of the dehydrogenation step is proposed, involving a heterolytic abstraction of a H^- species from the alkane.

Keywords: Isobutane oxidation; Heteropolycompounds

1. Introduction

Selective oxidation of alkanes is of great interest and growing importance from both the industrial and the fundamental point of view. Recently, some active heteropolycompounds (HPC) were reported as good catalysts for the direct oxidation of isobutane into methacrylic acid which is used for the synthesis of methylmethacrylate, an important monomer for resin production [1]. This study was initiated to participate to the open debate concerning some fundamental aspects of the selective oxidation mechanism.

2. Experimental

The heteropolyacid ($H_4PMo_{11}VO_{40}$) was prepared first by a method presented in Ref. [2] slightly modified. The catalyst $(NH_4)_{2.4}Cs_{1.6}P_{1.7}Mo_{11}V_{1.1}O_{40}$ was obtained by adding the stoichiometric quantity of Cs_2CO_3 salt (1.5 moles per mole of heteropolyacid) followed by the addition of the stoichiometric quantity of NH_4Cl salt (2.5 moles per mole of heteropolyacid) to an aqueous solution of $H_4PMo_{11}VO_{40}$. The resulting suspension was evaporated to dryness at 120°C, for ten hours. The loading measured by microanalysis corresponds after catalytic test to $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$.

The oxidation of isobutane was performed in

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a flow fixed bed stainless steel tubular reactor, under atmospheric pressure by co-feeding the nitrogen diluted reaction gases (26 vol% isobutane, 12 vol% O_2, 12 vol% H_2O, and N_2 balance). The total flow rate was 3 $l.h^{-1}$ (down flow), and the catalyst volume was of 3 cm^3 (about 4 g). The products obtained were isobutene (IS), methacrylic acid (MAA), methacrolein (MAL), acetic acid (AA), CO and CO_2 (CO_X). The products were sampled on-line using an automatic sampling valve (Valco) and analyzed by on line gas chromatography (Shimadzu GC 9-A).

The procedure for titrating the hydrogen H^* content that the solid is able to store has been described previously and applied to various catalytic systems [3–5]. The pretreatment and catalytic experiments were carried out in-situ at atmospheric pressure in an all-glass, grease-free flow apparatus. The solid (350 mg) was treated first under a purified hydrogen flow at various temperatures (250°C < T_T < 350°C), then, after elimination of molecular hydrogen, at 150°C, hydrogenation reaction was performed under isoprene + helium mixture (2 $l.h^{-1}$) which involves the participation of reactive hydrogen species H^* of the solid.

The thermogravimetric experiments were carried out under purified hydrogen in a Sartorius balance.

3. Results and discussion

The catalytic oxidation of isobutane has been performed at 349°C over $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$, and the results obtained after 15 hours (steady-state) are presented in Table 1. The sum of the yields MAA + MAL is 4.8%. Some patents have already reported some better results [6,7] and it has been published recently that compared to our results the yield for the production of MAA and MAL can be optimized by changing the Cs concentration and adding a transition ion like Ni, for instance, the most effective catalyst in the series studied was $Cs_{2.5}Ni_{0.08}H_{1.34}PMo_{11}VO_{40}$ [1]. After catalytic test the solid exhibits a dark blue color in agreement with a reduced state [6,7]. As a matter of fact, it has been already proposed that the HPC, under isobutane + O_2, works in a reduced state corresponding to 1 or 2 electrons increase per HPC. However, the degree of reduction depends on the composition of the catalyst and is not limited to the above range.

Table 1
Isobutane conversion and selectivities obtained on $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ at 349°C

Conv. (%)	IS (%)	MAA (%)	MAL (%)	AA (%)	CO_X (%)	CB (%)	PB (%)
10.6	2.6	37.6	7.9	24.8	14.5	99.4	94.9

CB = carbon balance, PB = products balance

In order to obtain some mechanistic informations, the oxidation of each reaction product obtained from isobutane (isobutene, methacrolein, methacrylic acid, acetic acid) has been studied separately, and each time, the more oxidized products have been obtained i.e. isobutene giving MAL, MAA, and AA, and methacrolein giving MAA and AA, etc., and, the product immediately more oxidized (for example, MAL issued from the oxidation of isobutene) is always the major product obtained [8]. Therefore, the oxidation mechanism isobutane → isobutene → MAL → MAA is proposed. Moreover, the partial pressures of the products obtained have been reported as a function of isobutane conversion and whatever the isobutane conversion, the partial pressures of isobutene and MAL are always constant. This result has been verified on a wide number of different HPC [8]. So, it appears that the isobutene and MAL disappearance rates are rapid compared to their rate of appearance i.e. compared to the transformation rate of isobutane. These results confirm the consecutive mechanism for the activation of isobutane until the formation of MAA and show that the rate determining step is the first step of the reaction corresponding to dehydrogenation [8]. It has

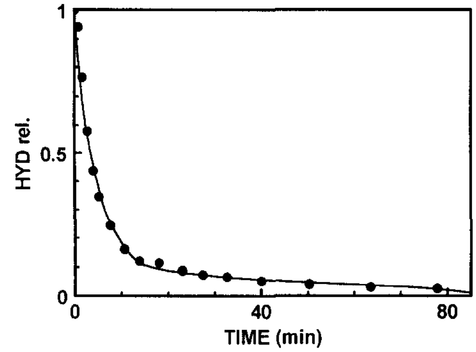

Fig. 1. Relative hydrogenation activity at 150°C under helium + isoprene flow versus time on $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ treated in H_2 at 350°C.

been already often proposed that the breaking of the C–H bond corresponds to the rate determining step for the conversion of alkanes such as propane or butane [9].

Therefore, since dehydrogenation requires the abstraction of hydrogen from isobutane, the hydrogen H^* content that the HPC is able to store in the reduced state has been determined. At 150°C, under a helium + isoprene flow, alkadiene hydrogenation occurs on the HPC pretreated "in-situ" under H_2 (Fig. 1). One must remark that the hydrogenation activity obtained on the untreated catalyst is null. As a function of time on stream, the isoprene conversion decreases and by integrating the curve obtained, the extractable H^* content that $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ is able to store has been determined. The value obtained for a treatment temperature (T_T) of 350°C is 1.3×10^{-3} $mol.g^{-1}$ which corresponds to 2.7 moles per mole of HPC, in good agreement with some values presented in the literature. As a matter of fact, Baba et al. have reported that $Ag_3PW_{12}O_{40}/SiO_2$ is able to sorb 2.32 moles of hydrogen per mole of HPC [10].

Evidence is provided for the existence of particular reactive hydrogen species of the solid (denoted H^* since the exact charge of these species was not the aim of the study). Even, if the hydrogen uptake by the HPC has already been reported in the literature, it has been attributed to the formation of different H^+ species

Table 2
H^* content measured on $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ as a function of the pretreatment temperature under H_2

	T_T = 250°C	T_T = 320°C	T_T = 350°C
H^* (10^3 $mol.g^{-1}$)	0.04	1.2	1.3

[10,11]. Nevertheless, in the present study, the H^* species are able to hydrogenate alkadienes at 150°C without the presence of H_2 when the solid has been previously treated under H_2; otherwise no H^* species is found. Hence these H^* species are different from those of hydroxyl groups still present on the solid. Moreover, it appears that the H^* concentration depends on the treatment temperature under H_2 (Table 2), almost no H^* is found for T_T lower than 250°C, and the H^* content increases with the treatment temperature up to 350°C. Besides, for each T_T, the relative hydrogenation rate consuming H^* can be reported as a function of the H^* content of the solid and no proportionality is obtained (Fig. 2). Therefore, the kinetics of H^* consumption by the alkadiene is a complex phenomenon, in particular a diffusional process of H^* from the "bulk" to the "surface" of the solid must be considered [3].

For temperatures higher than 250°C, anionic vacancies are created in the catalyst produced by the elimination of constitution water (OH groups), as controlled by thermogravimetry (Fig. 3) and in agreement with the literature [11,12].

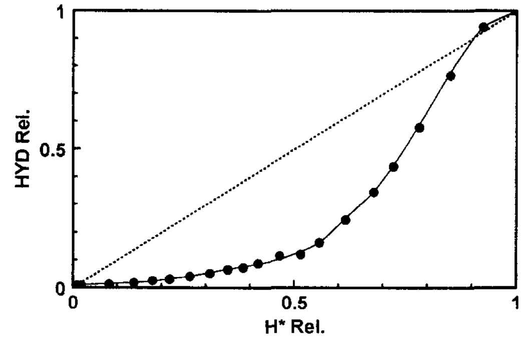

Fig. 2. Relative hydrogenation activity at 150°C under helium + isoprene flow versus the relative hydrogen H^* species concentration of $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ treated in H_2 at 350°C.

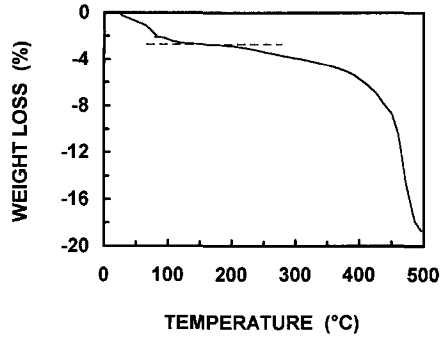

Fig. 3. Thermal treatment under H_2 of $Cs_{1.6}H_{2.4}P_{1.7}Mo_{11}V_{1.1}O_{40}$ followed by thermogravimetry.

As a function of treatment temperature under H_2, before the decomposition of the HPC, the number of anionic vacancies increases. Therefore there exists a correlation between the creation of anionic vacancies with the H^* species storage in the solid. The anionic vacancies are able to store reactive hydrogen species which quantity increases with the treatment temperature up to 350°C. An important analogy exists between these results and those obtained in our laboratory on copper-based oxides [3,5] and on Mo-based sulfides [4]. As a matter of fact, several studies dealing with the concept of Coordinative Unsaturated Sites (CUS) participating in the active site composition for alkadiene hydrogenation reaction, and with hydrogen reservoirs, have already been published. It has been shown that the first hydrogen species introduced in the alkadiene hydrogenation reaction comes from the solid and is of hydridic nature. Indeed, it has been proposed that under helium + alkadiene, the titrated H^* species are for a half H^- species and the second half H^+ species (coming from OH groups) [3].

The HPC possesses this character of being hydrogenation and oxidation catalyst in agreement with the well known redox properties of such compounds. According to the results obtained and by analogy to the heterolytic dissociation of H_2, we propose that the first step of activation of the paraffin, under isobutane + O_2, corresponds to the dehydrogenation reaction involving a heterolytic abstraction of a H^- species from the alkane which could be performed by a low coordination site involving an anionic vacancy. Of course, there is no direct relationship between the H^* storage and the catalytic performance. And, this is true whatever the reaction (oxidation or hydrogenation), mainly because (i) the H^* species storage involves ''bulk'' and ''surface'' phenomena whereas the activity is related to catalytic sites located at the ''surface'' of the solid, and (ii) activity and especially selectivity for a given reaction depend on specific kind of sites. Moreover, the activation of the CH bond may involve different possibilities and even if the hydride abstraction from alkanes has already been proposed in the literature[13], the abstraction of a H^+ species from the alkane has been much more often proposed. Anyway, in the case of a heterolytic rupture, the two species (H^-, H^+) can exist, but due to its high reactivity (as for example with O_2), the H^- species is not easy to detect. Therefore, in the present study, the isobutane dehydrogenation reaction leading to isobutene, is modeled by the abstraction of a H^- species performed by an anionic vacancy and a H^+ species performed by the O^{2-} species of the solid forming an OH^- group, according to the following scheme:

$$O^{2-}Mn + \square + \text{isobutane} \rightarrow OH^-M^{n+}H^- + \text{isobutene},$$

where □ is the anionic vacancy.

The isobutane activation site is therefore represented by the ''O^{2-} M^{n+} □'' ensemble at the surface of the solid. Even if yet, there is no proof that the O^{2-} species activate isobutane, it has been already shown by work function measurements performed in the laboratory that O^{2-} species located at the surface of oxide catalysts are able to activate propane [14] or methane [15]. Moreover, the OH group formed has been shown to be labile on oxide systems [5] and it is possible that it can react with the alkene to lead to selective oxidation products. Nevertheless, this aspect needs further investigations and will be developed in the next papers.

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