

Oxidative dehydrogenation of isobutane over a titanium pyrophosphate catalyst

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Abstract: The catalytic properties of titanium pyrophosphate in the oxidative dehydrogenation of isobutane to isobutylene were investigated in the 400 – 550 °C temperature range. A significant change of the product distribution and of the apparent activation energy of the reaction was observed at about 490 °C. This phenomenon, already observed in the oxidative dehydrogenation of *n*-butane, has been interpreted by the existence of two reaction mechanisms depending upon the reaction temperature. Comparison with the *n*-butane reaction allowed different activation pathways for the activation of alkanes to be proposed. The catalytic properties of TiP₂O₇ in the oxidative dehydrogenation of isobutane was also compared to those obtained previously with several other pyrophosphates and TiP₂O₇ was found to be less active and selective for this reaction.

Keywords: isobutane, oxidative dehydrogenation, titanium pyrophosphate.

INTRODUCTION

The oxidative dehydrogenation of lower alkanes could become an alternative reaction for the production of olefins due to its potential advantages over dehydrogenation (exothermic reaction, lower temperature reaction,...). Recently, the oxidative dehydrogenation of isobutane to isobutylene has received considerable attention because of the increasing demand for *tert*-butyl methyl ether for which isobutylene is a precursor. This product is used as an additive for gasoline to enhance the octane number, reduce the oxidant products, and substitute lead. Up to now, many supported and unsupported, mixed and simple metal oxides have been shown to yield appreciable conversion and good selectivity in the oxidative dehydrogenation of isobutane to isobutylene.^{1–24} Catalysts based on chromium oxide have received considerable attention because of their good performance at relatively low reaction temperatures (less than 300 °C).^{1–7} Moriceau *et al.*⁵ reported 60 % isobutylene selectivity with 10 % isobutane conversion on a binary Cr–Ce–O catalyst at 270 °C. Good isobutylene selectivity was

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also obtained on a chromium oxide catalyst supported on lanthanum carbonate in the low temperature range 230–250 °C.³

Vanadium seems to be a key component of active and selective oxidation catalysts and, for this reason, vanadium-based catalysts have been intensively investigated for the oxidative dehydrogenation of isobutane.^{8–15} Hoang *et al.*⁸ showed that alumina-supported vanadia exhibits low (15 %) selectivity to isobutylene. An olefin selectivity of *ca.* 50 % was achieved at isobutane conversions of 10–15 % over vanadium-containing MCM-41 mesoporous catalysts.^{9–11} Over V-ZSM-48 catalyst, the olefin selectivity was 60 % at 28 % isobutane conversion.¹² An optimised alumina-supported V-Sb oxide catalyst exhibited high activity, selectivity and stability in the oxidative dehydrogenation of isobutane to isobutylene, giving rise to a yield of close to 26 %, which is one of the highest reported for this reaction.¹³

Good results for the oxidative dehydrogenation of isobutane were also obtained with heteropolyacids (molybdophosphoric acid, with or without vanadium, and tungstophosphoric acids with the Wells–Dawson structure),^{16,17} molybdenum-based catalysts^{18–20} and Zn–Ti mixed oxides systems.²¹

Finally, it should be mentioned that several pyrophosphate based catalysts have been claimed to be active and selective for the oxidative dehydrogenation of isobutane.^{22–24} The best of these catalysts was found to be CeP₂O₇ with 71 % selectivity for 21 % conversion at 500 °C.²⁴ Deep oxidation to CO and CO₂ was dominant for Mn, Cu and Sn pyrophosphates, while Ag, Zn and Mg pyrophosphates showed good selectivity, but very low conversions.²³

Recently Ti, Ce, Zr and Sn pyrophosphates were tested for the oxidative dehydrogenation of *n*-butane between 410 and 570 °C at atmospheric pressure.²⁵ The best yields of butenes and butadiene were obtained with TiP₂O₇, which appeared almost as efficient as the VMgO catalysts, which are known to be very efficient for this reaction.²⁶

In the present work, TiP₂O₇ was studied as the catalyst for the oxidative dehydrogenation of isobutane. A comparison between the catalytic performances of this catalyst and those of the other pyrophosphates reported in the literature for this reaction is presented and its comparative behavior in the oxidative dehydrogenation of isobutane and *n*-butane is discussed.

EXPERIMENTAL

Catalyst preparation and characterization

The method used to prepare the pyrophosphate catalyst was based on the reaction of phosphoric acid (85 %) with the corresponding metal oxide.²⁵ The homogeneous slurry formed was dried and calcined at 120 and 700 °C, respectively.

Crystal structure of the obtained compound was determined by X-ray diffraction analysis on a Bruker D5005 diffractometer with Cu K α radiation. The solid corresponded to a well crystallized pure phase of TiP₂O₇. Its BET surface area was equal to 6 m² g⁻¹.

Catalytic test

The catalyst was tested in a fixed-bed, U-type quartz laboratory reactor, operated at atmospheric pressure. The experimental reaction temperature range was 410–550 °C and the feed contained isobu-

tane, oxygen and helium. The isobutane/oxygen ratio was equal to 2 (the stoichiometric ratio) and the contact time, expressed as the ratio of the catalyst weight to the total feed flow rate, was $W/F = 0.8 \times 10^{-2}$ g min cm⁻³ (the partial pressures of isobutane and oxygen were 0.166 bar and 0.083 bar, respectively, helium balance). The flow rates of the three gases were fixed by mass flow controllers (Brooks Instrument). 0.5 g of the catalyst was placed in the reactor, which had an internal diameter of 8 mm in the reaction zone and an internal diameter of 2 mm after the reaction zone. This reduction in diameter ensured very rapid removal of the gases in order to minimize possible gas phase reactions. The temperature of the catalyst bed was monitored by a thermocouple positioned in the catalyst bed. In a typical reaction run, the reactor was heated to the desired temperature in a flow of the reactants. The system was allowed to stabilize for about 1 h at the reaction temperature before the first product analysis was made. Two gas chromatographs were used for on-line analysis of both the reaction feeds and products. Isobutylene, CO, CO₂, and cracking products (methane, propene) were the products formed under the employed reaction conditions. Traces of oxygenates were detected, but not considered in the calculations. The alkane conversion was calculated from the concentrations of products and unreacted alkanes. The carbon balance was systematically evaluated and was generally better than 95 %.

RESULTS AND DISCUSSION

The catalytic properties of TiP₂O₇ in the oxidative dehydrogenation of isobutane, in the temperature range of 410 – 550 °C and the conditions described in the experimental section, are shown in Table I.

TABLE I. Catalytic properties of TiP₂O₇ in the oxidative dehydrogenation of isobutane. Reaction conditions: isobutane/oxygen ratio = 2, $W/F = 0.8 \times 10^{-2}$ g min cm⁻³

Temperature/°C	Conversion/%	Product selectivity/%					Rate of isobutane transformation/ 10^7 mol s ⁻¹ m ⁻²
		<i>i</i> -C ₄ H ₈	C ₃ H ₆	CH ₄	CO ₂	CO	
410	3.1	52.5	–	–	–	47.4	0.73
450	6.0	47.6	–	–	–	52.3	1.42
490	13.2	23.1	11.2	–	37.2	28.4	3.12
530	18.1	22.8	13.8	–	34.4	28.9	4.28
550	21.0	21.9	15.4	1.7	31.3	29.6	4.97

The isobutane conversion increased with increasing reaction temperature. Parallely, the selectivity for isobutylene dropped rapidly (from 52.5 to 23.1 %) when the reaction temperature was increased from 410 to 490 °C, but decreased very slowly between 490 and 550 °C (from 23.1 to 21.9 %). The selectivity to CO passed through a maximum at around 450 °C and reached a plateau for reaction temperatures higher than 490 °C. It is interesting to note that CO₂ appeared in the reaction products at 490 °C but decreased with increasing temperature to the benefit of cracking products formation. From the Arrhenius plot presented in Figure 1, the apparent activation energy corresponding to the transformation of isobutane on the titanium pyrophosphate catalyst was calculated.

Two temperature ranges can be considered, with an obvious change of activation energy from 80 kJ mol⁻¹ below 490 °C to 38 kJ mol⁻¹ above 490 °C. A similar change

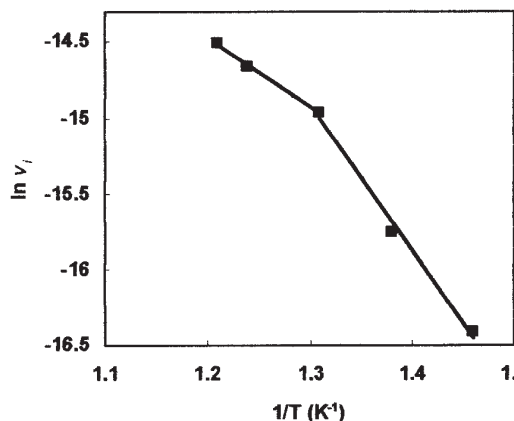
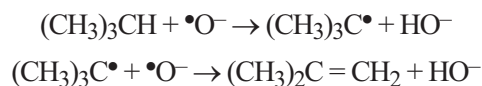


Fig. 1. Arrhenius plot for isobutane conversion on a TiP_2O_7 catalyst.

of apparent activation energy was observed during the oxidative dehydrogenation of *n*-butane, on the same catalyst, but at 450 °C.²⁵ In this case, the activation energies were 129 kJ mol⁻¹ and 38 kJ mol⁻¹ at low and high temperatures, respectively.

At low temperatures, it has been shown that the mechanism of the first C–H bond breaking of *n*-butane on TiP_2O_7 was homolytic with hydrogen abstraction by a surface O^- species, the presence of which is related to the p-type semiconductivity of the solid, and the formation of a radical species.^{27,28} This radical would similarly undergo a second hydrogen abstraction to form butenes.

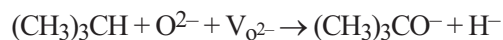
It may be proposed that the same type of mechanism takes place in the case of isobutane:



The fact that the activation energy in the case of isobutane was lower than in the case of *n*-butane may be explained by taking into account the fact that the rate-limiting step is the same in both cases, *i.e.*, the first hydrogen abstraction giving a radical, and that from this point of view isobutane is more reactive than *n*-butane.²⁹

At high temperatures, the values of the apparent activation energies appeared identical for the two reactions. Consequently, it may be proposed that the rate-limiting step at high temperatures is the same in both cases and that the mechanism of alkane activation should be the same.

The C–H bond dissociation should occur at the central carbon atom (secondary and tertiary atoms of *n*-butane and isobutane, respectively). It has been shown that, at high temperatures, the titanium in TiP_2O_7 is partially reduced and that a linear correlation exists between the activity in *n*-butane transformation and the extent of titanium reduction.²⁵ Simultaneously, the catalyst became an n-type semiconductor under *n*-butane.²⁷ It may, thus, be proposed that the activation of *n*-butane and isobutane would proceed with the formation of an alkoxide intermediate, as already mentioned^{29,30} with the trapping of a H^- on an oxygen vacancy:



The activation energy observed in both reactions did not exceed 38 kJ mol^{-1} . Such a low value can only be explained by a rate-limiting step corresponding to the reoxidation of the catalytic site by diffusion of lattice oxygen or directly by gas phase oxygen. The first process has to be considered since electric conductivity measurements under the presence of reactants show that the reaction on TiP_2O_7 at high temperatures implies not only the formation of surface anion vacancies, but also the diffusion of O^{2-} from the sub-layers to the surface.²⁷ The fact that the apparent activation energy was the same in spite of the alkane molecule changing is a strong argument supporting the supposition that the limiting step of the reaction is related to the reoxidation of the catalyst, independently of the reactant.

To compare the TiP_2O_7 catalyst with other pyrophosphates tested in the literature in the oxidative dehydrogenation of isobutane, the same reaction conditions as in Ref. 24 were used : a reaction temperature of $550 \text{ }^\circ\text{C}$, a contact time W/F of $1.3 \times 10^{-2} \text{ g min}^{-1} \text{ cm}^{-3}$ and an isobutane to oxygen ratio equal to 4 (the partial pressures of isobutane and oxygen were 0.266 bar and 0.066 bar, respectively). Under such conditions, it was observed that the catalyst suffers deactivation with time on stream (Fig. 2).

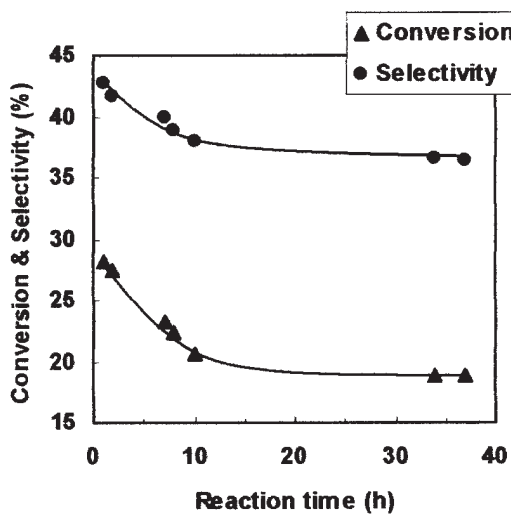


Fig. 2. Effect of the reaction time on isobutane conversion and isobutylene selectivity, during the oxidative dehydrogenation of isobutane on TiP_2O_7 at $550 \text{ }^\circ\text{C}$ for an isobutane/oxygen ratio equal to 4.

During the first 15 h of reaction, both the conversion and the selectivity to isobutylene decreased, but the conversion more rapidly than the selectivity. The catalytic test run for an additional 22 h of reaction did not show any more deactivation. The initial decrease was probably due to a poisoning of the catalyst by coke. The product distribution obtained after 37 h of reaction is shown in Table II.

A comparison of the isobutane conversion and isobutylene selectivity obtained with a series of pyrophosphates (data taken from Ref. 24) and titanium pyrophosphate is shown in Figure 3. The catalytic performances of the TiP_2O_7 catalyst were the lowest, both in terms of conversion and selectivity. Moreover, for the titanium pyrophos-

phate catalyst, the sum of the selectivities of CO, CO₂ and CH₄ was not equal to that of propene, as was in the case with the other pyrophosphates, but much higher. This suggests that total oxidation products (CO_x) were formed not only from C₁ species resulting from the cracking of isobutane, but also by the direct oxidation of isobutane or by further oxidation of isobutylene.

TABLE II. Catalytic reaction of isobutane over TiP₂O₇ at a reaction temperature of 550 °C and an isobutane/oxygen molar ratio of 4

Conversion/%	Product selectivity/%				
	isobutylene	propene	methane	CO ₂	CO
18.9	36.4	19.0	5.5	20.5	18.5

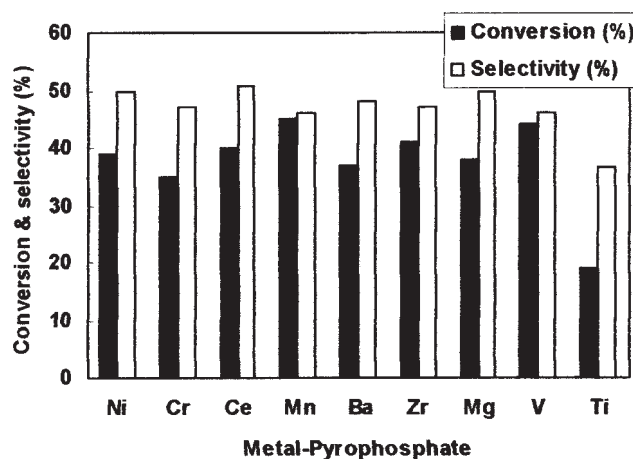


Fig. 3. Comparison between the catalytic performances of TiP₂O₇ and of other metal pyrophosphates (data taken from Ref. 24) in the oxidative dehydrogenation of isobutane at 550 °C.

The higher oxidizing ability of the TiP₂O₇ catalyst which had a positive effect on the catalytic properties for the oxidative dehydrogenation of *n*-butane at higher temperature worked negatively for the oxidative dehydrogenation of isobutane. This is presumably again related to the higher reactivity of isobutane. When the oxygen content in the feed gas was increased, up to an isobutane/oxygen mole ratio of 2 (the partial pressures of isobutane and oxygen were 0.266 bar and 0.133 bar, respectively), the catalytic activity and selectivity did not decrease anymore with time on stream (Table III). Probably, in this case, the oxygen content in the feed was high enough to oxidize the coke.

TABLE III. Catalytic reaction of isobutane over TiP₂O₇ at a reaction temperature of 550 °C and an isobutane/oxygen mole ratio of 2

Reaction time/h	Conversion/%	Product selectivity/%				
		isobutylene	propene	methane	CO ₂	CO
2	25.2	28.9	14.1	1.9	30.1	24.9
15	25.6	29.5	14.6	2.1	29.5	24.2

On the other hand, when the oxygen content in the feed gas was doubled, an increase of the isobutane conversion (from 18.9 % to 25.6 %) and a decrease of the isobutylene selectivity (from 36.4 % to 29.5 %) were observed (Tables II and III). At the same time, the CO_x selectivity increased from 39 % to 53.7 %. These results are explained by the increase of the available oxygen related to the decrease in the isobutane/oxygen ratio.

CONCLUSION

Increasing the reaction temperature results in higher isobutane conversions but lower isobutylene selectivity to the benefit of cracking products and CO_x formation. As in the case of the oxidative dehydrogenation of *n*-butane, a significant change of the apparent activation energy was observed during the oxidative dehydrogenation of isobutane, which was interpreted as a change in the reaction mechanism occurring at 490 °C.

Compared to other pyrophosphates tested in the literature, TiP₂O₇ was found to be less active and selective for the oxidative dehydrogenation of isobutane. Using an isobutane-rich feed gas, a deactivation of the catalyst with time was observed, probably due to coke formation on its surface. When the oxygen content in the feed was increased, this deactivation was not longer observed. At the same time, the conversion increased but the selectivities of isobutylene and propene decreased to the benefit of CO_x formation.

ИЗВОД

ОКСИДАТИВНА ДЕХИДРОГЕНИЗАЦИЈА ИЗОБУТАНА НА ТИТАН-ПИРОФОСФАТНОМ КАТАЛИЗАТОРУ

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Испитиване су каталитичке особине титан-пирофосфата на оксидативну дехидрогенизацију изобутана у опсегу температура 400–450 °C. Запажена је значајна прерасподела продуката и привидне енергије активације при око 490 °C. Ова појава, иначе уочена и при оксидативној дехидрогенизацији *n*-бутана објашњена је постојањем два механизма, појединачно доминантна при различитим температурама. Поређење са реакцијом *n*-бутана омогућило је да се предложи различити реакциони путеви за активацију алкана. Такође, упоређене су каталитичке особине TiP₂O₇ при оксидативној дехидрогенизацији изобутана са раније добијеним активностима неколико других пирофосфата, при чему је констатовано да је TiP₂O₇ мање активан и мање селективан од других.

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