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Isobutane Dehydrogenation on Various Platinum Supported Mixed Metallophosphate Oxynitride Catalysts MM′PON (M = Al, M′ = Ga,Cr)

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Abstract

The very first results of isobutane dehydrogenation over metal-supported mixed metallophosphate oxynitrides $AlM^{III}PON$ (M^{III} = Ga, Cr) are presented. Catalytic tests show that the substitution of oxygen by nitrogen in the anionic network involves the appearance of new and more active sites. The substitution of a part of aluminium by gallium in oxynitride compounds increases significantly the activity while chromium does not modify to a great extent the conversion of isobutane. © 1997 Elsevier Science Limited.

1 Introduction

Catalytic studies concerning phosphates and, in particular, aluminophosphates $AlPO_4$ have been carried out for several years.[1] Aluminophosphates are considered as acidic catalysts in many chemical reactions.

Recently we reported that the substitution of oxygen by nitrogen in aluminophosphate $AlPO_4$ at high temperatures leads to the synthesis of high surface area catalysts,[2–7] so-called 'AlPON'. During this process of nitridation by ammonia, we substituted, in the anionic network, oxygen by nitrogen which presents a lower electronegativity, so we could consider that this exchange leads to a more pronounced basic character which agrees with literature.[6,7] By this synthesis method it is possible to adjust the O/N ratio while keeping a high surface area (up to 300 $m^2 g^{-1}$). We have shown that AlPON are good catalysts in Knoevenagel-type condensations[2,3,7] and metal supports for metals for isobutane dehydrogenation[8] or synthesis of methyl isobutyl ketone.[9]

It is also possible to substitute a part of the aluminium by another metal to give a new family of compounds, the so-called $AlM^{III}PON$ (M^{III} = Ga, Cr, Fe,...).[10] In this type of compounds, we can tune the O/N ratio and also the Al/M^{III} ratio which could increase the catalytic potential. All these oxynitrides constitute a series of novel catalyst families as compared to nitrides already reported, as promising supports or catalysts[11–14] or silicon oxynitride.[15,16] It is worthwhile mentioning that very few papers report the use of nitrides as catalysts and supports. This could be due to the generally difficult method of activation of the precursor, the low stability of the phase and the relatively low surface area of the bulk material previously obtained.

In the present study, we have compared the activities of different platinum-supported oxynitride metallophosphates for isobutane dehydrogenation. Dehydrogenation of isobutane to isobutene is an endothermic reaction, so high temperatures are required to obtain high conversions. However, during this transformation, isomerisation, hydrogenolysis reactions and coke deposit take place at high temperatures. Reference can be made to isobutane dehydrogenation studies where other catalysts have been used, such as zinc aluminate,[17] sulfided nickel supported on alumina[18] or metals supported on silica[19] or on zeolites.[20]

Platinum-supported are good dehydrogenation catalysts and it was shown in an earlier study[8] that platinum supported on oxynitride aluminophosphate presents high conversion while keeping isobutene selectivity at a high level during isobutane dehydrogenation. We will study in this paper the influence of nitrogen and the effect of substitution of a part of aluminium by gallium or chromium on the activity of Pt supported on $AlM^{III}PON$ catalysts in isobutane dehydrogenation.

2 Experimental

2.1 Catalysts preparation and impregnation of platinum

The oxides samples were prepared by soft chemistry routes. $AlPO_4$ was synthesized using the citrate method whereas the mixed metallophosphates $(Al,Ga)PO_4$ and $(Al,Cr)PO_4$ were obtained by the sol-gel method.[21] Both $(Al,Ga)PO_4$ and $(Al,Cr)PO_4$ gels were obtained after addition of propylene oxide to a mixture of phosphoric acid, aluminium and gallium or chromium salts. In the synthesis of $Al_{0{\cdot}9}Ga_{0{\cdot}1}PO_4$ gel from chloride salts, the addition of propylene oxide was stopped at pH close to 3 and the solution was kept at room temperature until a transparent gel was formed. In the preparation of $Al_{0{\cdot}85}Cr_{0{\cdot}15}PO_4$ gel, nitrate salts were used. The addition of concentrated ammonia increased the pH from 3 to 6–7. Before calcination at 650°C, both gels were washed with isopropanol and dried a 110°C. In the case of oxynitride catalysts, the preparation involves a solid-gas reaction at 750–800°C between the oxide precursor and ammonia.[22]

The 1·5wt% Pt/oxynitride metallophosphates were prepared by impregnation of platinum on the different supports. The Pt/impregnated samples were obtained by incipient wetness impregnation with a methanolic solution of $H_2PtCl_6.6H_2O$ (Merck). Methanolic solutions were used instead of aqueous solutions in order to avoid hydrolysis of the surface. In preliminary experiments of impregnation of nitride compounds, it has been evidenced that AlPON and GaAlPON compound are water-sensitive. After aqueous impregnation, a drastic decrease of the surface area is observed, which is connected to the formation of superficial hydroxydes of oxide species. The excess of methanol was evaporated under an argon flow and the sample was then dried overnight at 110°C. The sample was decomposed under N_2 flow with a temperature ramp of 2·5°C min^{-1} up to 500°C and held at that temperature for 2 h, after which the sample was reduced in pure hydrogen at the same temperature during 2 h.

2.2 Physico-chemical characterisation

The specific surface areas of the samples were measured by single point BET method ($P/P_0 = 0{\cdot}3$). Nitrogen contents of samples were determined by the Grekov method.[23]

2.3 Catalytic evaluations

Catalytic evaluations of isobutane dehydrogenadon were carried out in a conventional continuous flow micro-reactor system operating at atmospheric pressure, and using isobutane in helium (Air Liquide 0·95% isobutane N25 in 99·05% He N50) and hydrogen in helium (Air Liquide 1% H_2 N50 in 99% He N50). The molar ratio between isobutane and hydrogen was maintained in each case at 1/6. The reaction products were anaiyzed using an on-line Packard (model 428) gas chromatograph equipped with a flame ionizarion detector, with helium as a carrier gas. A 60 m×0·32 mm (RSL 160 Alltech) column was used for the separarion of the various compounds. The space velocity is defined as the ratio between the weight flow of isobutane per hour and the weight of the catalyst. Total isobutane conversion is defined as the percentage of isobutane transformed into all products. The selectivity to isobutene is defined as the amount of isobutane converted into isobutene divided by the total isobutane conversion. Initial conversion is obtained by extrapolating the curve conversion versus time to time zero.

3 Results and Discussion

3.1 Characteristics of samples

All the solids are X-ray amorphous and present very high surface areas. The characteristics of the oxide and oxynitrides are reported in Table 1.

All the samples were impregnated by platinum (1·5% wt) in order to investigate their potentiality for isobutane dehydrogenation.

3.2 Catalytic tests

Figure 1 gives the evolution of the initial conversion versus temperature at a space velocity of 0·3 h^{-1} for the different tested samples. Globally, an increase of the conversion is shown with temperature up to 500–550°C. Table 2 gives initial conversions, isobutene selectivities and yields at 550°C.

Table 1. Sample characteristics

Samples	*Formulations*	*N at%*	S_{BET} m^2 g^{-1}
AlGaPO	$Al_{0{\cdot}9}Ga_{0{\cdot}1}PO_4$	0	310
AlGaPON	$Al_{0{\cdot}9}Ga_{0{\cdot}1}PO_{2{\cdot}89}N_{0{\cdot}74}$	13	280
AlCrPON	$Al_{0{\cdot}85}Cr_{0{\cdot}15}PO_{2{\cdot}29}N_{1{\cdot}14}$	21	215
AlPON	$AlPO_{3{\cdot}16}N_{0{\cdot}56}$	10	305

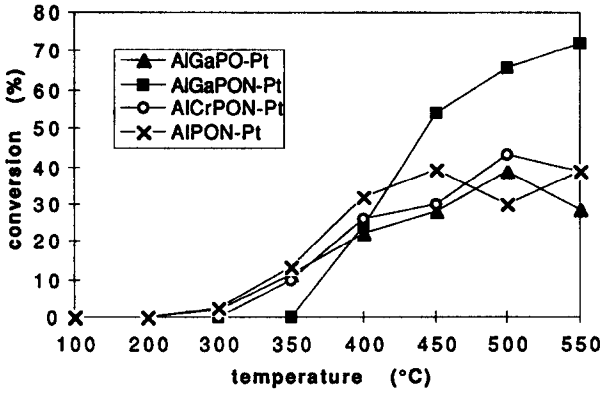

Fig. 1. Evolution of conversion versus temperature.

Table 2. Initial isobutane conversions, isobutene selectivities and yields at T = 550°C

Sample	*C isobutane %*	*S isobutene %*	*Yield %*
$AlGaPO_4$-Pt	28·7	100	28·7
AlGaPON-Pt	72·2	100	72·2
AlCrPONPt	38·9	92·8	36·1
AlPON-Pt	38·7	89·6	34·7

3.2.1. Influence of the anionic substitution

The influence of nitrogen on the reactivity is shown in Fig. 2, in which we compare AlGaPO-Pt and AlGaPON-Pt activities. For AlGaPON-Pt catalysts, an increase of the conversion with the temperature up to 550°C is observed, with a great increase at 450°C. In contrast, AlGaPO-Pt is more active at lower temperatures and presents its maximum of conversion at 500°C. These evolutions suggest, in the absence of diffusion limitations, that new and more active sites are generated by the introduction of nitrogen and that they need more activation to be efficient. We have already shown in another reaction, the Knoevenagel condensation,[7] that the oxynitrides are much more active than the oxide and that the amount of nitrogen influences the performance of the catalyst. The selectivity to isobutene is almost 100% for both catalysts; by-products of reactions are due to hydrogenolysis and isomerisation reactions.

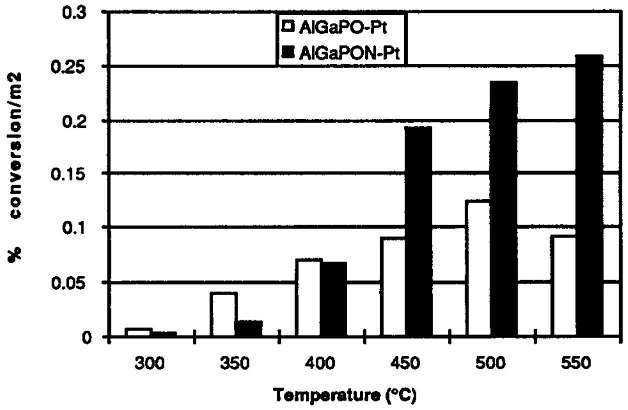

Fig. 2. Conversion versus temperature.

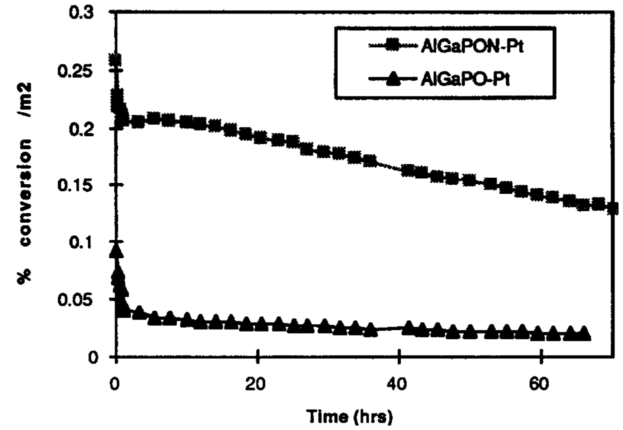

Fig. 3. Conversion of isobutane versus time.

The evolution of conversion per unit of surface versus time at 550°C for the two catalysts is illustrated in Fig. 3. In both cases, deactivation mainly occurs in the first hours of the reaction, but, for the oxynitride catalysts, the conversion remains at a high level, around 40%, even after 70 h on stream.

3.2.2. Influence of the cationic substitution

The substitution of a part of aluminium by chromium or gallium is known to improve the dehydrogenation potential of Pt-zeolite catalysts.[18] We can consider the same trend for Pt supported on oxynitride catalysts. Due to the difference of specific areas of our compounds, we report in Fig. 4 the evolution of conversion per unit of surface versus time for AlPON-Pt, AlCrPON-Pt and AlGaPON-Pt catalysts.

The substitution of aluminium by chromium does not affect greatly the activity of aluminium because of its similar behaviour, but the substitution of aluminium by gallium significantly increases the conversion. It has been suggested that Ga improves the recombination of hydrogen in molecular form during the reaction.[24] This hypothesis has not yet been verified. However, it is worthwhile

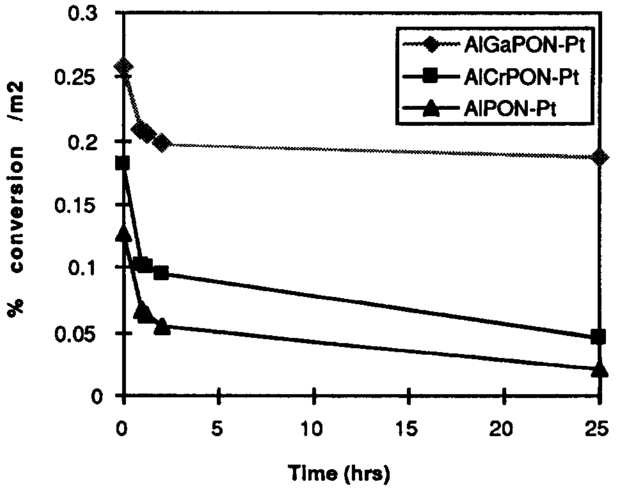

Fig. 4. Comparison in function of cationic substitution.

mentioning that several other hypotheses can be proposed since the nitrogen content and the overall Pt dispersion on the different oxynitrides are not exactly the same. In particular, the global acid base properties of the solids, the support interaction and the inhibiting effect of hydrogen adsorption on the reactivity of isobutene may also have an important influence. These different hypotheses will be further investigated.

4 Conclusion

Pt supported on metallophosphate oxynitride has a high ability to transform isobutane in isobutene. In this study, we have shown the influence on reactivity of cationic and anionic substitution in a new family of metallophosphate oxynitrides, the so-called AlM^{III}PON (M^{III} = Ga, Cr). The introduction of nitrogen in the anionic network involves the creation of new strong sites for this type of reaction. The cationic substitution of aluminium by gallium induces a large increase of conversion due to the potentiality of gallium to recombine hydrogen in the molecular form. As a matter of fact, the Pt-AlGaPON catalyst clearly gives the best results for isobutane conversion as well as for selectivity.

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