

Zirconia supported phosphotungstic acid as an efficient catalyst for resorcinol *tert*-butylation and *n*-heptane hydroisomerization

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Abstract

The alkylation of resorcinol with *tert*-butanol was carried out using zirconia supported phosphotungstic acid (PTA) as catalyst in liquid phase conditions. Among the different PTA loaded catalysts, the 15% PTA/ZrO₂ calcined at 750 °C was found to be the most active and yielding 4-*tert*-butyl resorcinol and 4,6-*di-tert*-butyl resorcinol as the major products under the optimized reaction conditions.

In addition to the above, hydroisomerization of *n*-heptane was studied under vapor phase conditions using bifunctional catalysts comprising Pt, Pd and Pt–Pd clusters on 15% PTA/ZrO₂. The catalytic activity of the bimetallic Pt–Pd catalyst is higher than that of the monometallic Pt and Pd catalysts. The catalysts prepared from acetylacetonate complexes were more active than those prepared from amine complexes. Addition of Pd has no beneficial effect on the catalytic performance when the bimetallic catalyst is prepared from acetylacetonate complexes. © 2004 Elsevier B.V. All rights reserved.

Keywords: Zirconia; Phosphotungstic acid; Resorcinol; *tert*-Butylation; *n*-Heptane hydroisomerization

1. Introduction

Acid catalyzed reactions are among the most important in the chemical industry. Alkylation and isomerization are two classes of such reactions. These reactions are usually catalyzed by homogeneous Lewis acids (AlCl₃, BF₃) or strong mineral acids (HF, H₂SO₄), which are highly toxic, generate a substantial amount of waste and cause severe corrosion problems. Considerable efforts are being made to find suitable solid acid catalysts, which can use successfully to carry out the above type of transformations [1,2]. Heteropoly acids (HPAs) especially Keggin type HPAs are strong Brønsted acid catalysts [3,4]. Phosphotungstic acid (PTA) is the usual catalyst of choice out of various HPAs because of its high

acidic strength and relatively high thermal stability. A serious problem associated with the use of this type of materials as heterogeneous catalysts is their low surface area (5–8 m² g⁻¹). The use of HPA in supported form is preferable because of its high surface area compared to the bulk material. Recently, we have shown that zirconia supported PTA is an efficient solid acid catalyst for alkylation and acylation reactions [5].

Tert-Butylation of dihydroxy benzenes is important, since butylated dihydroxy benzenes are widely used as antioxidants and polymer stabilizers. In spite of its importance very few works are reported on *tert*-butylation of resorcinol using solid acid catalysts. Narayanan and Murthy [6] studied alkylation of resorcinol with *tert*-butanol using modified clay as catalysts.

Skeletal isomerization of alkanes has industrially important applications because branched alkanes are useful as clean high-octane fuels. These reactions are usually achieved over bifunctional catalysts containing fine dispersed noble metal

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clusters on a matrix, which contains Brönsted acid sites. During the reaction, the noble metal catalyzes hydrogen transfer reactions (hydrogenation–dehydrogenation), while isomerization and hydrocracking occur on the Brönsted acid sites [7,8]. For a catalyst where the metal function and the acid function are well balanced, isomerization and hydrocracking are consecutive reactions and the rate limiting step is the skeletal rearrangement of the alkenes obtained via dehydrogenation over the metal sites, which takes place on the Brönsted acid sites. However, the practical application of this process has been only confined to C₄/C₆ alkanes. The skeletal isomerization of *n*-heptane, for which the octane number RON is 0 and this, could be enhanced to 42–112. But, enhancement of RON of *n*-heptane is generally difficult because the isomerization is usually accompanied by undesirable cracking. Catalysts with sufficiently good balance of metal and acid functions under the suitable reaction conditions are generally needed to suppress cracking in order to achieve high isomerization selectivity for long chain alkanes. The exact value of isomerization maximum is expected to be depending on the balance between two catalytic functions, viz. density and the strength of Brönsted acid sites and the nature, amount and dispersion of the metal. There are a number of reports on the hydroisomerization of *n*-heptane over bifunctional catalysts such as Pt and/or Pd supported on zeolites [9–15], SAPOS [16–18], SO₄²⁻-ZrO₂ [19], WO₃-ZrO₂ [20,21], CS_{2.5}H_{0.5}PW₁₂O₄₀ [22,23] and on MoO₃ [24,25].

The present study deals with preparation of zirconia supported PTA catalyst and its characterization by ³¹P MAS NMR spectroscopy and acidity measurements by temperature programmed desorption (TPD) of NH₃. These catalysts were used in the alkylation of resorcinol with *tert*-butanol. The catalyst with the highest activity was also used for the hydroisomerization on *n*-heptane after loading with Pt and/or Pd. The effect of the metal precursor on the hydroisomerization activity was also examined.

2. Experimental

2.1. Chemicals

Zirconyl chloride (ZrOCl₂·8H₂O), ammonia (25%), resorcinol and *tert*-butanol were procured from S.D. Fine Chemicals Ltd., Mumbai. Phosphotungstic acid (H₃PW₁₂O₄₀·21H₂O), Pt-acetylacetonate [Pt(acac)₂], Pd-acetylacetonate [Pd(acac)₂] and *n*-heptane were purchased from Aldrich. Methanol was obtained from E. Merck India Ltd., Mumbai. All the chemicals were used without further purification.

2.2. Catalyst preparation

The catalysts were prepared by impregnation method using zirconium hydroxide as the support. The support was prepared by the hydrolysis of an aqueous solution of zirconyl

chloride with ammonia solution and the precipitate obtained was washed free of chloride and dried at 120 °C for 24 h. A series of catalysts with different PTA loading (5–20 wt.%) were prepared by suspending dried zirconia powder in a methanol solution of PTA. This mixture was stirred for 8–10 h and the excess of methanol evaporated to dryness. The resulting samples were dried at 120 °C and calcined in air at 750 °C for 4 h.

Metal supported catalysts were prepared by impregnation of Pt(NH₃)₄Cl₂ and Pd(NH₃)₄Cl₂ to obtain a catalyst with 1 wt.% Pt and 0.54 wt.% Pd, respectively. The metal precursor was dissolved in 50 ml of distilled water and the solution was added drop wise to 1.5 g of 15% PTA/ZrO₂ calcined at 750 °C slurred in 50 ml of distilled water. After stirring the solution for 2 h at 40 °C, the water was removed in a rotary evaporator at 60 °C under vacuum. The samples were then dried at 120 °C for 12 h. The resulting materials were pressed, crushed and sieved to obtain catalyst particles with a diameter of 0.25–0.355 mm. In order to study the effect of metal precursor on the catalytic activity in isomerization reaction, metal supported catalysts were also prepared by Pt-acetylacetonate and Pd-acetylacetonate using benzene as solvent.

2.3. Characterization

³¹P MAS NMR spectra (Bruker DSX-300) were recorded at 121.5 MHz with high power decoupling using a Bruker 4 mm probehead. The spinning rate was 10 kHz and the delay between two pulses was varied between 1 and 30 s to ensure that a complete relaxation of the ³¹P nuclei occurred. The chemical shifts are given relative to external 85% H₃PO₄.

Acidity of the catalysts were measured using temperature programmed desorption of ammonia. NH₃ TPD was carried after 0.1 g of the catalyst sample was dehydrated at 500 °C in dry air for 1 h and purged with helium for 0.5 h. The temperature was decreased to 125 °C under a flow of helium and then 0.5 ml NH₃ pulses were passed through the samples until no more uptake of ammonia was observed. NH₃ was desorbed in He flow by increasing the temperature to 540 °C at 10 °C min⁻¹ measuring NH₃ desorption using a TCD detector.

2.4. Catalytic experiments

2.4.1. Resorcinol *tert*-butylation

The liquid phase *tert*-butylation of resorcinol was carried out in a 50 ml Parr autoclave. A typical reaction mixture consists of 6.6 g of resorcinol, 13.4 g of *tert*-butanol together with 0.66 g of catalyst. After a definite time interval, the reaction is stopped and the reaction mixture is diluted with 5 ml of methanol and 1 g of the product is taken and it is again diluted with 5 ml of methanol. It is then filtered and the filtrate is analyzed using a Shimadzu 14B gas chromatograph using SE-52 packed column, coupled with FID. The product identification was carried out using GC-MS. Conversion was defined as the percentage of resorcinol converted into products.

2.4.2. Hydroisomerization of *n*-heptane

n-Heptane hydroisomerization was carried in a fixed-bed flow type apparatus with on-line gas chromatographic analysis of the reaction products. The experiments were conducted at a hydrogen pressure of 1 MPa and the pressure of *n*-heptane was adjusted to 10 kPa to obtain an H₂/*n*-heptane molar ratio of 100. Changing the temperature of the reaction modified the conversion of *n*-heptane. The mass of the catalysts and the hydrogen gas flow were adjusted to achieve a residence time $W_{\text{cat}}/F_{n\text{-heptane}} = 400 \text{ g h mol}^{-1}$. Prior to the catalytic experiments, the catalysts were dehydrated at 250 °C for 2 h in argon flow, activated in oxygen at 300 °C for 4 h and flushed with argon at 400 °C for 4 h. Finally, the metal clusters were obtained by hydrogen reduction at 310 °C for 4 h.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. ³¹P MAS NMR

The ³¹P MAS NMR spectra of the catalysts with 5–20% PTA loading are shown in Fig. 1. It can be seen that the state

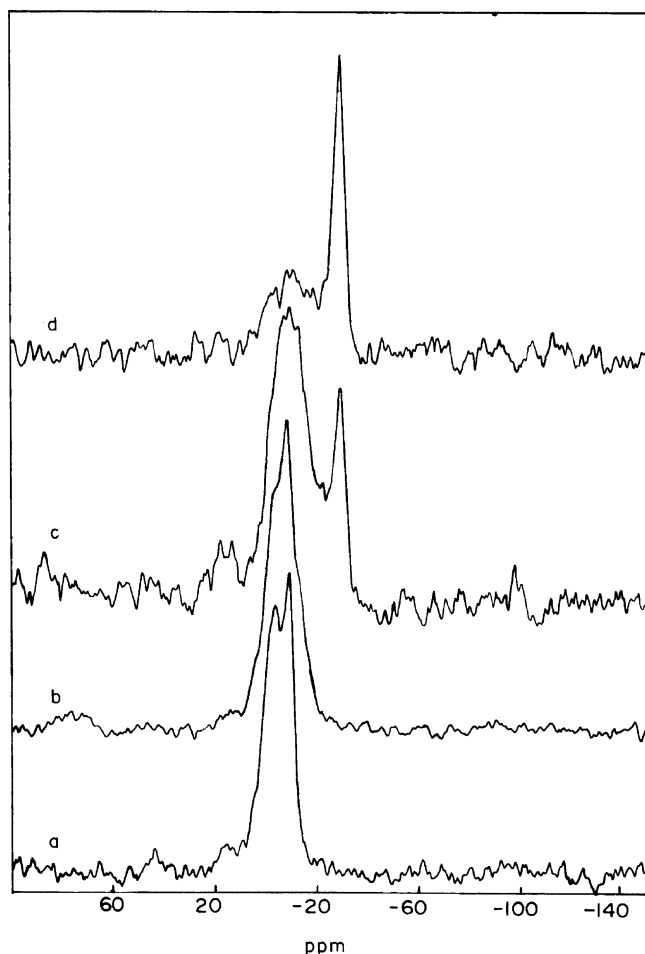


Fig. 1. ³¹P MAS NMR spectra of (a) 5%, (b) 10%, (c) 15% and (d) 20% catalysts.

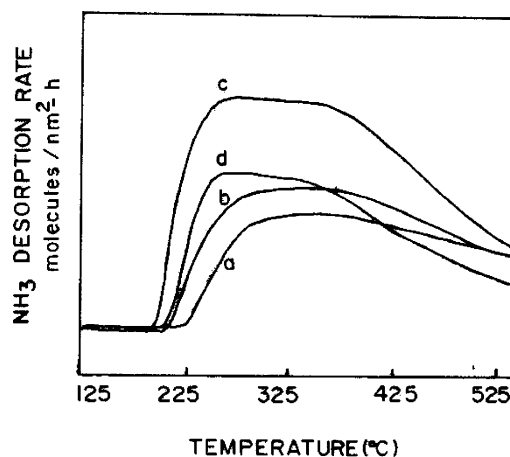


Fig. 2. TPD pattern of (a) 5%, (b) 10%, (c) 15% and (d) 20% catalysts.

of phosphorous in the catalyst depends on PTA loading. For low loadings, a broad signal above -20 ppm is observed. In agreement with literature data, this peak is attributed to phosphorous in the Keggin unit [5,26]. For high loadings, a second signal appears below -20 ppm, which can be attributed to phosphorous oxide resulting from the decomposition of the polyoxometalate [27]. This phosphorous oxide represents 20 and 45% of the total phosphorous for 15 and 20% PTA loading, respectively.

3.1.2. NH₃ TPD

Acidity of the catalysts were measured by TPD of NH₃. Fig. 2 gives the TPD patterns of the various catalysts while Fig. 3 represents the amount of sorbed ammonia per square nanometre as a function of the PTA loading. It is evident from these data that there is initially an increase of the acidity until 15% loading and then a decrease for higher loadings. If we take into account the above result, these result can be explained easily: at low loadings, the polyoxometalate retains its structure (and its acidity) while for higher loadings it decomposes, at least partially into its oxides. The highest acidity corresponds to a monolayer of polyoxometalate as it

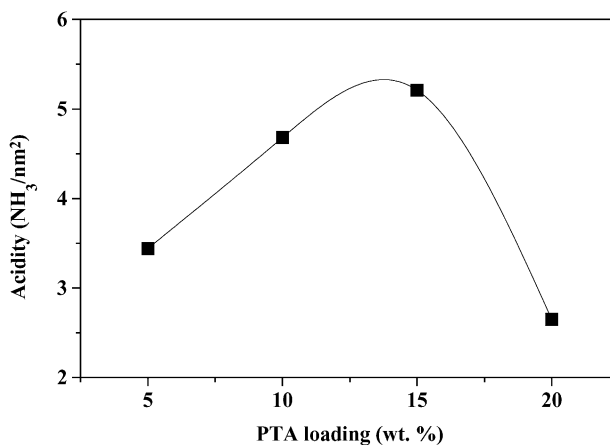


Fig. 3. Acidity of the catalysts as a function of the PTA loading.

is evident from ^{31}P MAS NMR. So, we can describe the evolution of the catalysts as follows: until a PTA loading of ca. 15%, the heteropolyanion is well dispersed on the zirconia surface and it retains its integrity. For higher loadings, the coverage is higher than the monolayer and the polyanion is not stabilized by zirconia and decomposes by heating at 750°C .

3.2. Catalytic activity

3.2.1. Resorcinol *tert*-butylation

The liquid phase alkylation of resorcinol with *tert*-butanol was carried out using zirconia supported PTA as catalysts. The analysis of the products showed that the reaction resulted in the formation of ring alkylated products, 4-*tert*-butyl resorcinol (4-tbr) and 4,6-di-*tert*-butyl resorcinol (4,6-dtbr) and O-alkylated products like resorcinol mono *tert*-butyl ether (rmtbe) and 4-*tert*-butyl resorcinol mono *tert*-butyl ether (4-tbrmtbe). In a first step, the reaction was studied as a function of PTA loading. The catalyst with optimum loading was then used to study the effect of temperature, catalyst concentration and reaction time.

Fig. 4 gives the variation of the conversion and of the selectivities (after 1 h reaction) as a function of the PTA loading. The conversion shows a maximum for a 15% PTA loading, which corresponds to the catalyst with the highest acidity, as determined by NH_3 TPD. The selectivities are also varying as a function of the PTA loading. First of all, it must be pointed out that, in contrast to what is observed on modified clays [6], O-alkylated products (rmtbe and 4-tbrmtbe) are formed in addition to C-alkylated products (4-tbr and 4,6-dtbr). In addition, the products result from one (rmtbe and 4-tbr) or two successive reactions (4-tbrmtbe and 4,6-dtbr) corresponding to a C- and O-alkylation or two C-alkylations (we did not observe the product corresponding to two O-

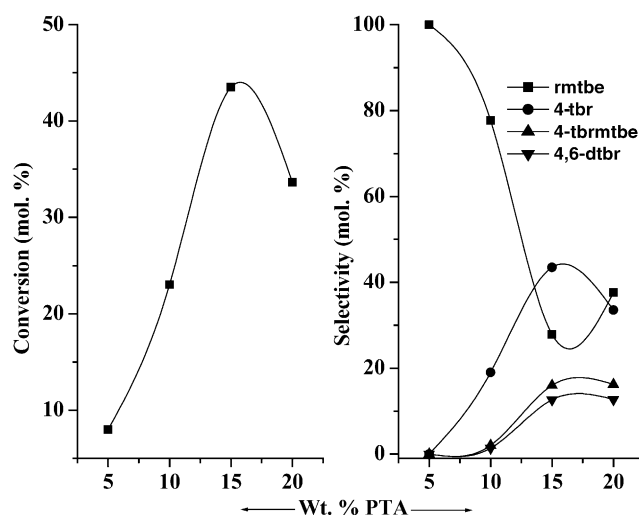
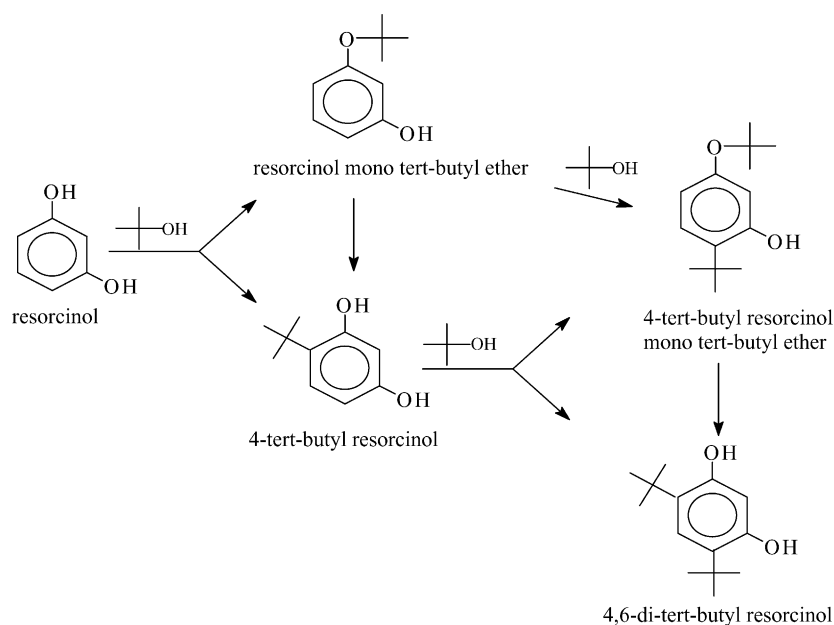


Fig. 4. Effect of PTA loading on resorcinol conversion and product selectivity. Conditions: resorcinol = 6.6 g; *tert*-butanol = 13.4 g; catalyst weight = 0.66 g; temperature = 70°C ; time = 1 h; resorcinol/*tert*-butanol (mol ratio) = 1:3.

alkylations). Fig. 4 shows that until the PTA monolayer, the rate of the C-alkylation increases more rapidly than that of the O-alkylation. For higher loadings, it is seen that the rate of C-alkylation decreases while that of O-alkylation remains constant.

Scheme 1 represents the formation of different products during liquid phase *tert*-butylation of resorcinol. The different pathways corresponding to the transformation of O-alkylated products into C-alkylated products have been shown in Scheme 1. Indeed, it has been shown that such rearrangements occurred on heating or by contact with an acid catalyst [28]. It is clear from the reaction scheme that rmtbe is



Scheme 1.

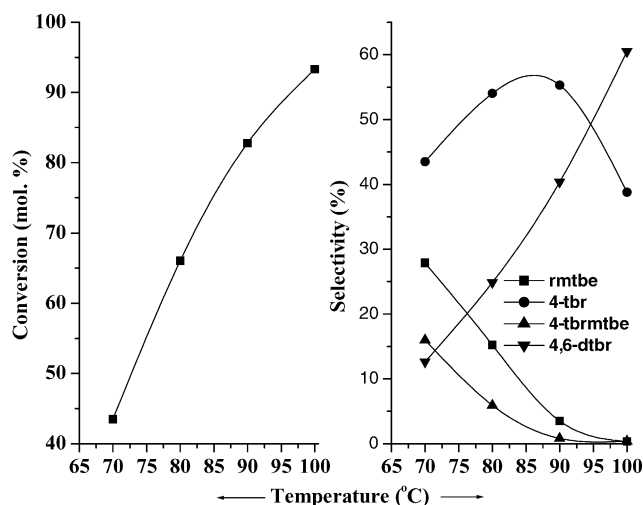


Fig. 5. Effect of temperature on resorcinol conversion and product selectivity. Conditions: resorcinol = 6.6 g; *tert*-butanol = 13.4 g; catalyst weight = 0.66 g; time = 1 h; resorcinol/*tert*-butanol (mol ratio) = 1:3.

a primary product while 4-*tbr* is a primary and/or a secondary product, depending on the kinetics of the butylation reaction.

First of all, increasing in temperature of the reaction increases the substrate conversion and affects the product distribution selectivities towards C-alkylated products in the butylation reaction (Fig. 5). At 100 °C, only C-alkylated products are formed like that of clays [6] and this can be due to the rate of transformation of O- to C-alkylated products increases more rapidly than that of the alkylation reaction.

A second parameter is the catalyst to substrate ratio. Fig. 6 gives both the conversion and the product selectivities as a function of the amount of catalyst in the butylation reaction. It is known that PTA/ZrO₂ also acts as catalyst for isomerization and hence increase in the catalysts amount increases both substrate conversions and isomerization of O- to C-alkylated

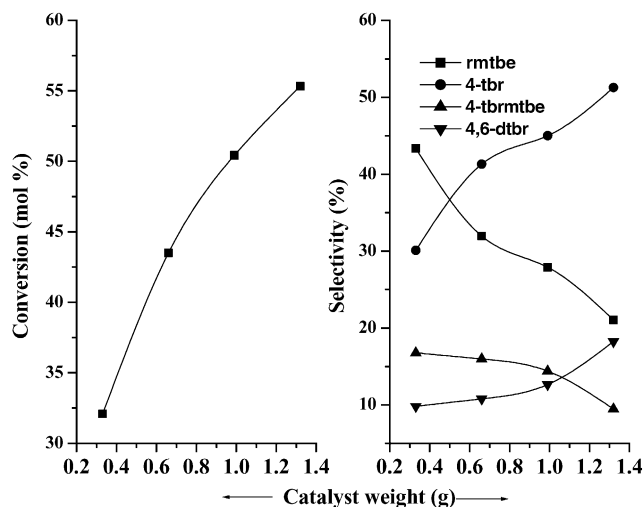


Fig. 6. Effect of catalyst weight on resorcinol conversion and product selectivity. Conditions: resorcinol = 6.6 g; *tert*-butanol = 13.4 g; temperature = 70 °C; time = 1 h; resorcinol/*tert*-butanol (mol ratio) = 1:3.

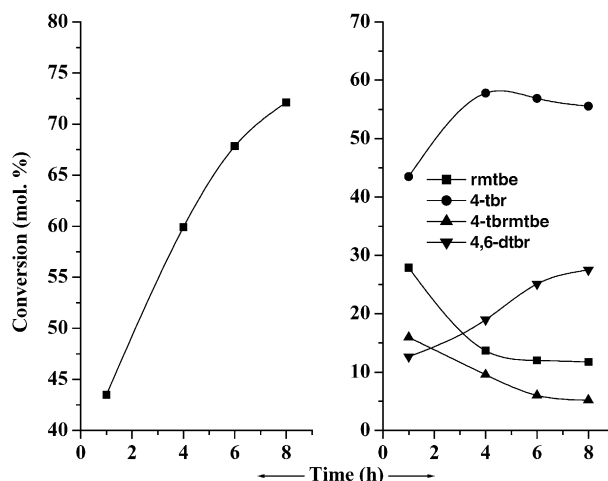


Fig. 7. Effect of time on resorcinol conversion and product selectivity. Conditions: resorcinol = 6.6 g; *tert*-butanol = 13.4 g; catalyst weight = 0.66 g; temperature = 70 °C; resorcinol/*tert*-butanol (mol ratio) = 1:3.

products. Hence, for 5 wt.% of catalyst, the selectivity to O-alkylated products is 60%, which decreased with the increase in catalysts amount in the butylation reaction.

Finally, the effect of the reaction time is shown on Fig. 7. When the reaction time increases, the isomerization of O- to C-alkylation products also increases to give higher selectivities for C-alkylated products in the butylation reaction. The results of butylation of resorcinol can be summarized as at the conditions of lower reaction temperature, reaction time and catalyst to substrate ratio results in higher selectivities for O-alkylated products. C-alkylated products become major at high temperature (100% at 100 °C). Corma et al. [29] also found a similar observation in the alkylation of phenol by *tert*-butanol over the solid acid HNa-Y zeolites.

For heterogeneous catalysts, it is also important to study the recycling of the catalyst. For this purpose, the reaction was stopped when the conversion reached 60% and the catalyst removed by filtration. The filtrate immediately reused in the butylation of resorcinol and it is found that there was no increase in substrate conversion. In addition, the catalyst separated is reused after filtration with fresh reaction mixture and is found no loss in its catalytic activity. These data are in agreement with the absence of catalyst leaching and a purely heterogeneous nature of the reaction.

3.2.2. Hydroisomerization of *n*-heptane

The hydroisomerization of *n*-heptane, which is believed to require stronger acidic sites than the alkylation of resorcinol was also studied with the 15% PTA/ZrO₂ catalyst. It is well known that for this reaction a bifunctional catalyst is necessary which combines an acid and a metal function on the same support. We studied platinum and palladium as the metal components forming monometallic or bimetallic clusters supported on 15% PTA/ZrO₂ in hydroisomerization of *n*-heptane under vapor phase conditions. The effect of the nature of the metal precursor was also investigated

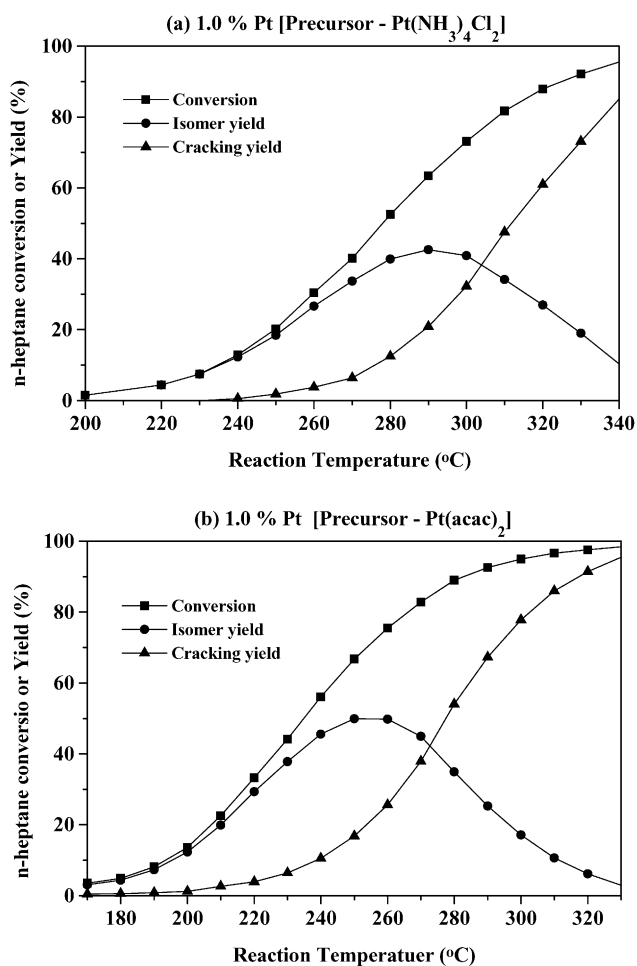


Fig. 8. *n*-Heptane conversion or yield (%) as a function of reaction temperature for different catalysts. Conditions: H₂ pressure = 1 MPa; *n*-heptane = 10 kPa; residence time = 400 g h mol⁻¹.

by preparing catalysts from the deposition of acetylacetonate complexes and dichloro–tetrammine complexes of Pt and Pd. The results obtained with 1% Pt on PTA/ZrO₂ prepared using dichloro–tetrammine complexes and acetylacetonate complexes are shown in Fig. 8a and b, which gives the *n*-heptane conversions and the yields of isomerization and cracking products as a function of the reaction temperature.

The conversion of *n*-heptane and the yield of the cracking products increase with temperature, while the isomer yield reaches a maximum and declines thereafter. The continuous increase in cracking yield with temperature is a result of

both increased hydrogenolysis activity of the metal and enhanced cracking over the acidic sites of the catalyst. At low temperatures, isomerization is the dominant reaction, while at elevated temperature cracking of the isomers dominates resulting in the observed decrease of the isomer yield. The maximum isomer yield and the temperature at which it is obtained together with the cracking yield are given in Table 1.

At a given temperature, the *n*-heptane conversion over platinum and palladium containing catalysts is similar, however, the platinum-containing catalysts is more selective towards isomerization products than palladium-containing one. This effect is more pronounced when the catalysts have been prepared from Pt(NH₃)₄Cl₂ or Pd(NH₃)₄Cl₂. It is also found that catalyst prepared by using metal acetylacetonate precursors is more active resulting in higher *n*-heptane conversions and isomerization yields.

The bimetallic Pt–Pd catalyst prepared from chlorides is more active than the respective monometallic catalysts, while the catalysts prepared using acetylacetonates do not differ significantly in activity. For all catalysts prepared from the later precursor a higher isomer yield is observed at a lower (by ca. 40 °C) reaction temperature. Blomsma et al. [30] reported a similar increase in activity on *n*-heptane hydroisomerization with bimetallic Pt/Pd on H-beta and USY zeolite.

It is important to mention that the activity and selectivity of the catalyst under study significantly depend on the metal precursor used for their preparation. This can be explained by the nature of the interaction between the metal complex and the support. It is well known that the ZrO₂ gel has an isoelectric point (IEP) or zero point of charge (ZPC) between six and seven [31]. In the case of supported metal oxides, a change in ZPC is observed compared to the supports: Yori et al. [32] reported a decrease in ZPC, for zirconia supported tungsten oxide catalysts compared to ZrO₂. A similar decrease in ZPC has been reported by Gil-Liambias et al. [33] for V₂O₅ supported on TiO₂ and Al₂O₃ compared to TiO₂ and Al₂O₃. We can then reasonably assume that the ZPC of 15% PTA/ZrO₂ catalyst is lower than that of pure ZrO₂. For the adsorption of cationic metal precursor, e.g. tetrammine-platinum, the surface should be negatively charged but it is probable that the charge on the surface of the catalyst is not high (the surface charge depends on the pH of impregnating metal precursor solution and will be smaller for the PTA/ZrO₂ catalyst compared to pure ZrO₂). As a consequence, this will limit the amount of complex adsorbed on the support and bound to it by ionic interactions. The non-negligible amount

Table 1
Catalytic activity in hydroisomerization of *n*-heptane

Precursor	Pt and Pd(NH ₃) ₄ Cl ₂			Pt and Pd (acac) ₂		
	1.0Pt	0.54Pd	0.5Pt–0.27Pd	1.0Pt	0.54Pd	0.5Pt–0.27Pd
Metal loading (wt.%)	1.0Pt	0.54Pd	0.5Pt–0.27Pd	1.0Pt	0.54Pd	0.5Pt–0.27Pd
Temperature (°C)	290	280	270	250	260	260
<i>n</i> -Heptane conversion (%)	63.5	43.0	58.9	66.7	68.6	64.5
Isomer yield (%)	42.6	11.8	39.7	49.9	44.1	50.2
Cracking yield (%)	20.9	31.2	19.2	16.8	24.5	14.3

Conditions: H₂ pressure = 1 MPa, *n*-heptane = 10 kPa, residence time = 400 g h mol⁻¹.

of metal complex in the impregnation solution will precipitate on the support when drying and form relatively large particles which by treatment under hydrogen will lead to large metal particles which are less active (per metal atom) than small particles. Such surface charge effects are absent in the case of acetylacetonate complexes resulting in an increase of the metal dispersity and so of the conversion. As a consequence, these catalysts exhibit a better balance between acid and metal functions and hence higher yields of isomerization products (which occurs at a lower temperature) are obtained.

4. Conclusions

Alkylation of resorcinol with *tert*-butanol was carried over zirconia supported PTA calcined at 750 °C as catalysts under liquid phase conditions. The catalyst with 15% loading was found to have the highest activity under optimized reaction conditions, which gave 4-*tert*-butyl resorcinol and 4,6-*di-tert*-butyl resorcinol as the major products. The catalyst with 15% PTA on zirconia was used in *n*-heptane hydroisomerization after loading with Pt and/or Pd. The supported metal catalysts prepared from acetylacetonate complexes of Pt and Pd were more active than those prepared from amine complexes.

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