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Dehydroisomerisation of *n*-butane over (Pt,Cu)/H-TON catalysts

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Abstract

Direct formation of isobutene from *n*-butane was investigated over zeolite TON and γ-Al_2O_3 supported platinum and platinum–copper catalysts. Addition of Cu decreases Pt dispersion, irrespective of preparation methods and nature of catalyst supports. The presence of potassium was found to reduce acidity and Pt dispersion. The experiments were performed in a fixed-bed microreactor system operating at 673 K and atmospheric pressure. Changing the support from γ-Al_2O_3 to TON, shows that *n*-butane conversion is almost independent of acidity. However, significant changes in products selectivities are observed. The selectivities to isobutene, C_1–C_3 fractions, and aromatics increases drastically from 3.5 to 32.6%, 20.3 to 27.2%, and 3.0 to 20.6%, respectively, for the TON-supported catalyst whereas dehydrogenation is largely predominant when γ-Al_2O_3 is used as support. Addition of Cu, as expected, has an adverse effect on *n*-butane conversion as less active sites are available due to the reduction in Pt dispersion. Though Cu addition has marginal effect on isobutene selectivity, it certainly suppresses hydrogenolysis which evidences a reduction in size of the Pt ensembles at the surface of the Pt particles.

Keywords: Alkane activation; *n*-Butane upgrading; Dehydroisomerisation; Platinum–copper catalysts; TON; Zeolites

1. Introduction

Different processes for isobutene production, especially the skeletal isomerisation of 1-butene [1–3], have received a lot of attention during recent years since isobutene is used as a feed to produce MTBE. The production of MTBE is at present limited by the supply of isobutene. Although there may be some concerns about the use of MTBE, it should not affect the demand for isobutene as the latter can be used to produce efficiently C8-branched hydrocarbons with high RON [4].

Since *n*-butane is readily available and is a cheaper feed than butene, the future demand for isobutene is likely to be satisfied by dehydrogenation [5]. Direct conversion of *n*-butane to isobutene is therefore an interesting alternative to the currently practised twin reactor system technology where an isomerisation step is followed by a dehydrogenation step or vice versa.

Dehydrogenation of alkanes to alkenes can be performed under oxidative or non-oxidative conditions. The main advantage of oxidative dehydrogenation is that it is thermodynamically more attractive [6,7]. However, the non-oxidative route offers a higher selectivity to higher hydrocarbon products since there is no combustion of hydrocarbons to carbon dioxide or partial oxidation to aldehydes or acids. It is the route explored in the current work.

Bifunctional noble metal(s)-modified acidic supports have been used to dehydroisomerise *n*-butane [8,9], where the metal(s) provides the dehydrogenation activity while Brønsted acid sites are responsible for isomerisation. A number of solid acids have been used for *n*-butane dehydroisomerisation and

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also *n*-butene isomerisation, which includes ferrierite, SAPO, alumina, and TON [10]. Zeolites offer the advantage of providing Brønsted acidity and shape selectivity, minimising the formation of heavier hydrocarbons. Chromium or platinum catalysts have generally been employed for dehydrogenation. However, because chromium has a negative impact on the environment, platinum type catalysts are preferred.

Bimetallic and multimetallic catalysts have been widely investigated in recent years [11–13]. Characterisation of highly dispersed, supported bimetallic catalysts is a subject of continuous research [13,14]. Important bimetallic catalysts are Pt–Re and Pt–Sn catalysts widely used for naphtha reforming. From a fundamental point of view, the Pt–Cu, Pt–Au, and Pt–Ag combinations are also interesting. The addition of Cu, Au, or Ag modifiers to a platinum catalyst can modify the electronic properties of Pt and/or lead to geometrical effects such as active site blocking or Pt ensemble size changes altering the relative importance of the isomerisation and hydrogenolysis reactions of hydrocarbons [15].

The purpose of our work was to study the influence of the addition of copper to platinum deposited on various acidic supports, in the course of the hydrogenolysis and isomerisation of *n*-butane with the objective to achieve the direct dehydroisomerisation of *n*-butane to isobutene. The effect of the preparation variables on the properties and performance of the finished catalysts was also addressed.

2. Experimental

2.1. Catalyst preparation

H-TON was obtained by calcining (NH_4,K)-TON (BP Amoco Oil, $Si/Al = 50$) at 773 K for 4 h. To restore the acidity to 100%, the parent TON was ion-exchanged three times (1 h each) with an ammonia aqeous buffer solution (1.7 M NH_4Cl and 1.0 M NH_3, pH = 9) at room temperature. The exchanged zeolite was washed several times with distilled water, dried overnight in an air oven at 383 K, and calcined in a furnace under a flow of air (50 ml min^{-1}) at 823 K (ramp 5 K min^{-1}) for 4 h. γ-Alumina was used as a reference support and was calcined prior to Pt and Cu impregnation.

Two different methods of preparation were used, i.e. Method 1 and Method 2, described in Table 1. When using Method 1, a Pt/H-TON precursor, containing 1 wt.% of Pt (Pt/H-TON) was prepared by incipient wetness impregnation with an aqueous solution containing the desired amount of precursor (H_2PtCl_6, or $Pt(NH_3)_4Cl_2$, Aldrich, analytical grade). The resulting solid was dried in an oven at 393 K for 2 h. The second metal-source, $Cu(NO_3)$ was introduced after catalyst calcination and only thereafter was the catalyst calcined and reduced. In Method 2, some changes were made, i.e. $Pt(NH_3)_4Cl_2$ precursor was used, and its activations was performed at a slower heating rate, etc.

Two calcination procedures were used to oxidise the Pt precursors used. In Method 1, the calcination was performed in an air (N2.0 grade; BOC) flow of 16.7 ml min^{-1}, the temperature was ramped at 2 K min^{-1} from 298 to 673 K and held for 1 h at the latter temperature. While in Method 2, the temperature was increased at 0.2 K min^{-1} from 298 to 573 K.

A second calcination was performed after the introduction of Cu, similar to description of calcination in Methods 1 and 2, respectively, detailed above. The calcined powder was pressed into tablets, crushed, and sieved to 250–425 μm particles (40–60 mesh). All samples were then calcined

Table 1
Methods used to prepare (Pt,Cu) catalysts supported on H-TON and γ-Al_2O_3

Stages of preparation	Method 1	Method 2
(1) Pt precursor	H_2PtCl_6 (incipient wetness)	$Pt(NH_3)_4Cl_2$ (incipient wetness)
(2) Calcination (air)	673 K (2 K min^{-1})	573 K (0.2 K min^{-1})
(3) Reduction (H_2)	None	773 K (1 K min^{-1})
(4) Cu precursor	$Cu(NO_3)_2$	$Cu(NO_3)_2$
(5) Calcination (air)	673 K (2 K min^{-1})	573 K (0.2 K min^{-1})
(6) Reduction (H_2)	773 K (5 K min^{-1})	773 K (1 K min^{-1})

in hydrogen flow of 16.7 ml min^{-1}, the temperature was ramped at 5 K min^{-1} from 298 to 873 K and held for 1 h at the latter temperature. These samples are denoted Pt/Al_2O_3, $(Pt,Cu)/\gamma$-Al_2O_3, Pt/H-TON, (Pt,Cu)/H-TON, Pt/(H,K)-TON, and (Pt,Cu)/(H,K)-TON.

2.2. Catalyst characterisations

Prior to any characterisation, all samples were calcined under air and pre-reduced under H_2 using the following procedure: the samples were first heated up to 573 K under flowing air (50 ml min^{-1}) at a heating rate of 0.2 K min^{-1} and maintained at this temperature for 2 h. The samples were then flushed under N_2 (50 ml min^{-1}) for 30 min and the temperature was increased to 773 K under H_2 (50 ml min^{-1}) at a heating rate of 1 K min^{-1}, where it was held for 2 h. The samples were finally cooled down to room temperature under a flow of N_2.

Specific surface area and pore volume measurements were obtained from volumetric nitrogen adsorption using a Micromeritics ASAP-2000 instrument.

^{27}Al MAS NMR was used to detect the presence of non-framework aluminium species. ^{27}Al MAS NMR Bloch decay spectra were acquired on a Bruker Avance DSX-400 multinuclear NMR spectrometer operating at 104.27 MHz using 0.35 μs ($<10^\circ$) pulse lengths and 0.3 s recycle delays, with a spinning rate of ca. 4 kHz.

Brønsted acidity was measured using a Setaram TGA-DSC 111 thermal analyser connected to a Metrohm 716 DMS Titrino automatic titrator. The sample was first dehydrated at 823 K for 30 min with a 15 K min^{-1} ramp under flowing N_2. The temperature was then decreased to 398 K and 3%vol NH_3 in N_2 was passed through the sample. The sample was then purged at 398 K with a flow of wet N_2 [16]. The wet stream was prepared by flowing N_2 through a saturator filled with distilled water at room temperature for 4 h. The temperature was then increased to 873 K (10 K min^{-1}) under a N_2 flow. During this last ramping stage, the effluent was connected to the automatic titrator and passed through a buffer solution (1 ml of saturated boric acid solution +15 ml of a 1 M NH_4Cl solution). The pH of the solution was kept constant at $pH = 5.5$ by automatically titrating the adsorbed ammonia with ca. 3×10^{-3} M sulfamic acid solution. The volume of titrant needed to neutralise the NH_3 desorbed was used to calculate the effective number of Brønsted sites in the catalysts.

The Pt dispersion was measured volumetrically by H_2 chemisorption at 298 K using a Micromeritics TPD/TPR 2900 analyser and assuming a H:Pt ratio of 1. Prior to hydrogen chemisorption, the samples were reduced under the flow of a H_2/Ar mixture (5% H_2) at 773 K for 2 h, then flushed for 1 h under a flow of pure Ar. The technique used was called frontal method [17], where the amount of irreversible chemisorbed hydrogen is measured by the difference between a peak area corresponding to physisorbed hydrogen and a peak corresponding to the physisorbed and chemisorbed hydrogen.

In some cases, Transmission Electron Microscopy was used to estimate the Pt particle sizes.

2.3. Catalytic testing

Testing was performed at atmospheric pressure using a fixed bed continuous plug-flow microreactor system consisting of an 11-mm ID. Three-hundred-sixteen stainless steel reactor tube containing ca. 0.7 g of catalyst, plugged at both ends with quartz wool. The reaction temperature (673 K) was monitored using a K-type thermocouple positioned in the catalyst bed and gas flows were monitored and regulated with Brooks 5850S mass flow controllers. The outlet of the reactor was kept above 473 K to avoid condensation of heavy hydrocarbons. In order to avoid a pressure drop, the catalyst powders were pressed, crushed and the 425–600 μm sieve fraction was retained. The catalysts were activated as follows: the temperature was increased to 573 K (0.3 K min^{-1} ramping) under air (50 ml min^{-1}) and held for 2 h. The samples were then flushed under N_2 for 30 min and reduced at 773 K (1 K min^{-1} ramping) under H_2 (50 ml min^{-1}) for 2 h. The reduced catalysts were then cooled to the desired reaction temperature (673 K) under N_2. The feed mixture was 20% *n*-butane/80% N_2 at a total flow of 45 ml min^{-1} which correspond to a weight hourly space velocity (WHSV) of 2 h^{-1} for *n*-butane. On-line analysis of the effluent was performed with a Varian Star 3800 gas chromatograph using the Varian Star 4.5 data handling software. The products were separated using a capillary HP-PLOT/Al_2O_3 (50 m × 0.53 mm ×

15 μm) column and quantified using an FID detector.

3. Results

3.1. Catalyst characterisations

3.1.1. ^{27}Al MAS NMR

^{27}Al MAS NMR was used to characterise all catalysts before reaction. The ^{27}Al MAS NMR spectra showed no evidence for the presence of extra-framework aluminium in all cases. In this work, two different supports were used, i.e. γ-Alumina and TON. TON is a 10-membered-ring zeolite with unidimensional pores of cross-section 4.4×5.5 Å. Its Si/Al ratio is 50 which allows a maximum of 3.2 wt.% in Pt and 1 wt.% in Cu to be exchanged. For all catalysts prepared, the level of Pt incorporated was kept at 1 wt.% while the level of Cu was varied from 0 to 2 wt.%. γ-Alumina was used as reference support.

The acidity of the zeolite was measured by NH_3-TPD. Fig. 1 shows NH_3-TPD plots for both partially and fully proton-exchanged TON zeolites. Exchanging part of H^+ by K^+ (70% exchange) neutralises the strong acid sites while maintaining the medium strength acid sites.

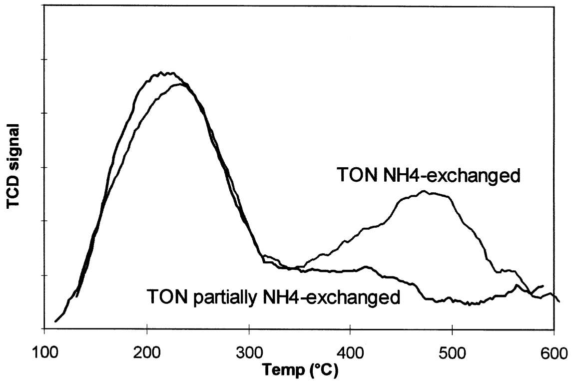

Fig. 1. Acid strength measurement by TPD-ammonia on two different forms of TON.

The dehydrogenation metal function which we selected is platinum. However, Pt is also known to catalyse hydrogenolysis which is a structure sensitive reaction [18]. Copper was added as a modifier with the hope that it could suppress this unwanted reaction due to geometric changes such as active sites blocking or reduction of the size of the Pt ensembles responsible for hydrogenolysis. Fig. 2 shows the dependence of Pt dispersion on Cu content for both catalyst series. The highest dispersion of Pt is obtained with γ-Al_2O_3 as support and Method 1. The higher than 100% Pt dispersion observed when no Cu is present is probably due to spillover of hydrogen [19]. The addition of Cu

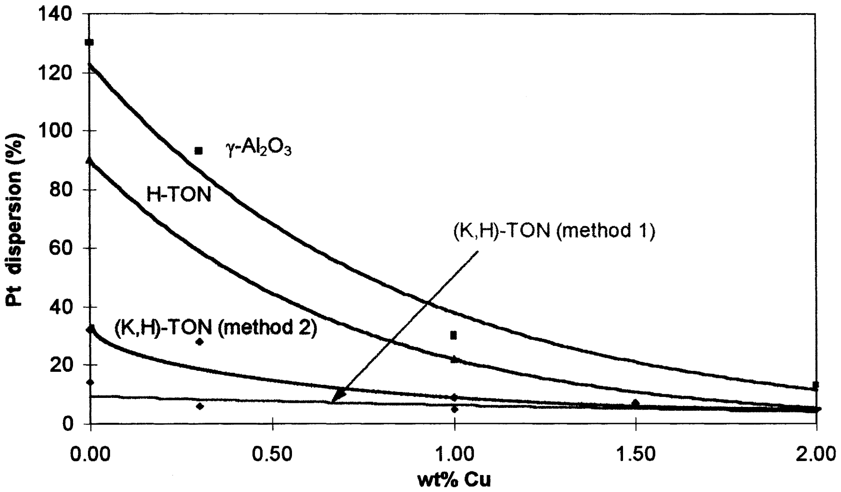

Fig. 2. Percentage Pt dispersion of various Pt and Cu supported on γ-Al_2O_3, H-TON, (K,H)-TON measured by hydrogen chemisorption.

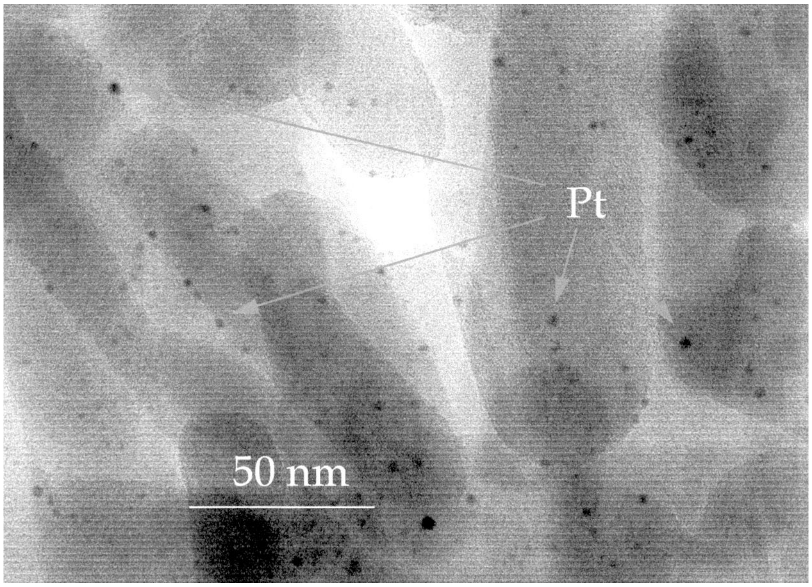

Fig. 3. Transmission electron micograph of Pt/(H,K)-TON prepared with Method 2.

clearly decreases the Pt dispersion. When 1–2 wt.% of Cu is added to the Pt/γ-Al_2O_3 catalyst, the degree of Pt dispersion diminishes to approximately one-fourth of its original value.

In the case of Pt supported on H^+-TON, a good Pt dispersion was attained though slightly less than with the γ-alumina support. Similarly to the case of Pt/γ-Al_2O_3, addition of Cu decreases drastically Pt dispersion. Surprisingly, the Pt dispersion of Pt/(H^+,K^+)-TON is very poor, only 14%. The addition of Cu further worsen the Pt dispersion as for 2 wt.% Cu added the Pt dispersion is less than 5%. This is probably due to the presence of K^+ ions inside the zeolite channels which hinder or even prevent the diffusion of the Pt species inside the zeolite channels. However, when a cationic Pt precursor $(Pt(NH_3)_4)^{2+}$ is used, coupled with a slow heating rate especially during calcination step, the Pt dispersion improves by a factor of 2.3.

Transmission electron microscopy shown in Fig. 3 (Pt/H,K-TON) confirms that the Pt particle diameters is ca. 2.5 nm, in reasonable agreement with the value calculated from its H_2 chemisorption value giving a value of 3.4 nm. It indicates that the small Pt particles must be located to a large extend at the surface of the zeolite crystals.

3.2. Catalytic results

The performance of the Pt and Pt–Cu catalysts supported on γ-alumina and TON, for *n*-butane dehydroisomerisation was evaluated at 673 K and atmospheric pressure. Figs. 4 and 5 show the variations of the *n*-butane conversion expressed on a carbon basis and Cu content for catalyst supported on γ-Al_2O_3 (Fig. 4) and H-TON (Fig. 5) as a function of time-on-stream.

Conversion using the Pt/γ-Al_2O_3 supported catalyst prepared by Method 1, gave an initial conversion of 20.4%, decaying progressively to ca. 10% at 1000 min (Fig. 4). The (Pt,Cu)/γ-Al_2O_3 catalysts show a slightly lower initial conversion. The latter decreases from 19.3% with 0.3% Cu to 16.5% with 1–2 wt.% Cu added. However, the (Pt,Cu)/γ-Al_2O_3 catalysts appear to be stable with time-on-stream (TOS). Changing the support to TON (100% acidic), has only a small effect on the initial conversion but results in a faster deactivation; after 1000 min, the extent of *n*-butane converted is less than 5%. Addition of Cu decreases the initial conversion and does not improve the stability of the catalyst. Both Pt1 and PtCu 1/H-TON behave similarly after ca. 100 min.

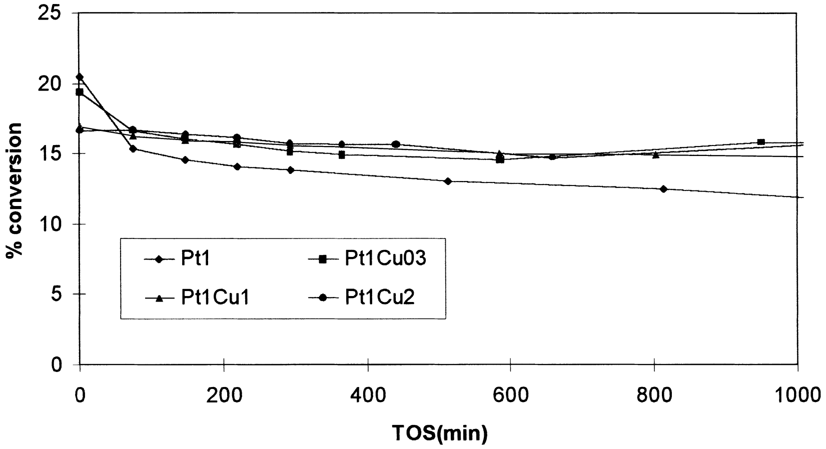

Fig. 4. Percentage conversion vs. TOS of various Pt–(Cu)/γ-Al_2O_3 prepared by Method 1.

In Figs. 6 and 7, the initial conversion of *n*-butane and its products selectivities are plotted as a function of Pt dispersion which is related to the amount of Cu added. The points on the extreme right-hand side of the graphs represent the catalytic performance in the absence of Cu. For Pt–(Cu)/γ-Al_2O_3 prepared by Method 1, the initial conversion was 20.4% with selectivities for linear $C_4^=$s, isobutene, and C_1–C_3 products of 69.3, 3.5, and 20.4%, respectively. These results are to be expected as dehydrogenation is the dominant reaction contributed by the platinum, the isomerisation of the olefins to isobutene being limited due to low acidity of γ-alumina. Hence also, the 20.4% selectivity to C_1–C_3 products obtained is mainly due to hydrogenolysis on Pt rather than acidic cracking.

The addition of copper, while decreasing the platinum dispersion and hence also *n*-butane conversion has a positive effect on the olefinic products selectivities. The selectivity to linear butenes increases to almost 91.2% while that for cracking products decreases to 3.4%. In addition, the major fraction of C_1–C_3 products was found to be saturated, which supports the view that hydrogenolysis is responsible for the C_1–C_3 selectivities reduction. The addition of copper inhibits this reaction which consequently competes less with the dehydrogenation reaction. The initial selectivity to

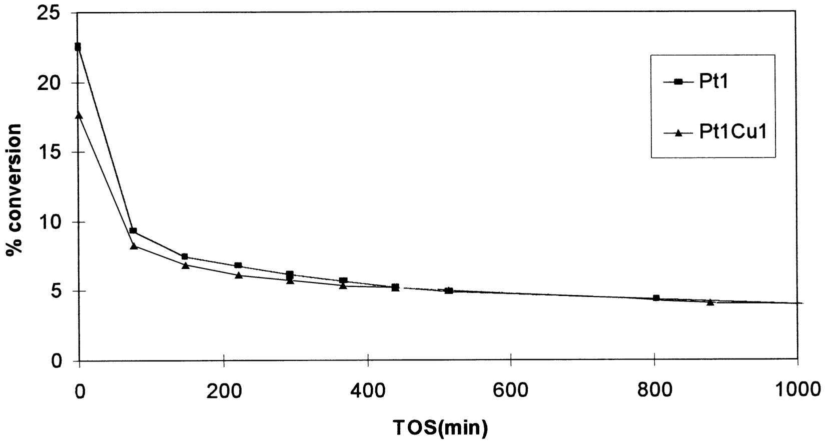

Fig. 5. Percentage conversion vs. TOS of various Pt–(Cu)/H-TON prepared by Method 1.

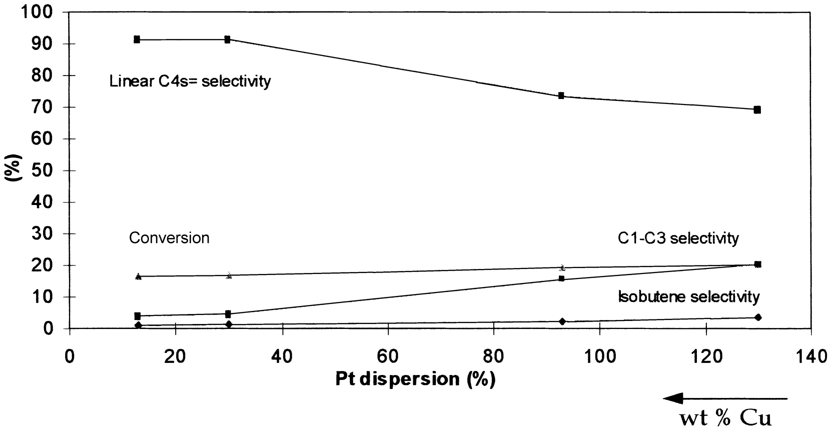

Fig. 6. Initial conversion and product selectivities vs. % Pt dispersion of various Pt–(Cu)/γ-Al_2O_3 prepared by Method 1.

isobutene on alumina supported catalysts was 3.4% in the absence of copper, and dropped to 1% when 2 wt.% Cu was added.

Fig. 7 shows that by using a more acidic support, H-TON, with the same platinum content, has a positive effect on the initial conversion which is now 22.5% in the absence of Cu. The products selectivities to linear butenes, C_1–C_3 fractions, and isobutene are 22.2, 32.0, and 18.3%, respectively. The other products observed are aromatics. Using a support with higher acidity promotes skeletal isomerisation of butene but also acid catalysed cracking. As dehydrogenation and hydrogenolysis/cracking are competing in the initial stage of the reaction, facilitating cracking reduces the selectivity to butenes. The C_1–C_3 fractions are now composed of saturated and unsaturated hydrocarbons, formed by metal and acid catalysed reactions, respectively. The addition of copper, though causing the dispersion of platinum to decrease and the conversion of *n*-butane to decrease slightly, improves the selectivities to linear butenes and isobutenes as less C_1–C_3 products are formed. Upon close inspection, it was further observed that within the C_1–C_3 fractions, there is a drastic reduction in the amount of saturated light hydrocarbons, which provides further evidence that hydrogenolysis is suppressed. This can be explained if

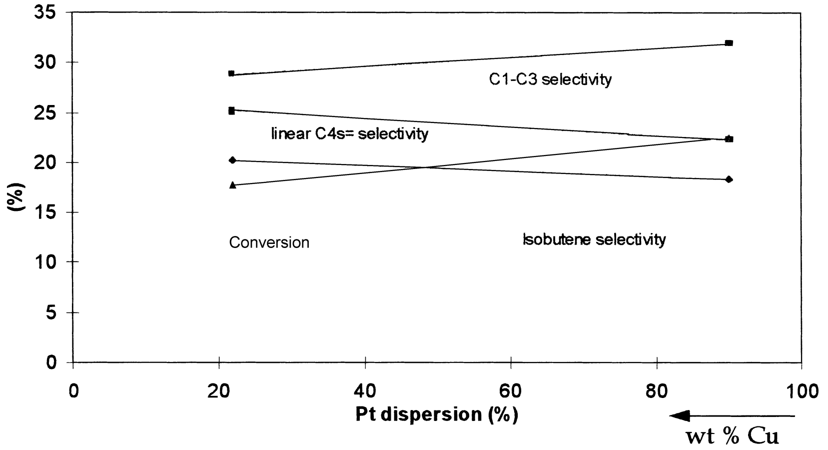

Fig. 7. Initial conversion and product selectivities vs. % Pt dispersion of various Pt–(Cu)/H-TON prepared by Method 1.

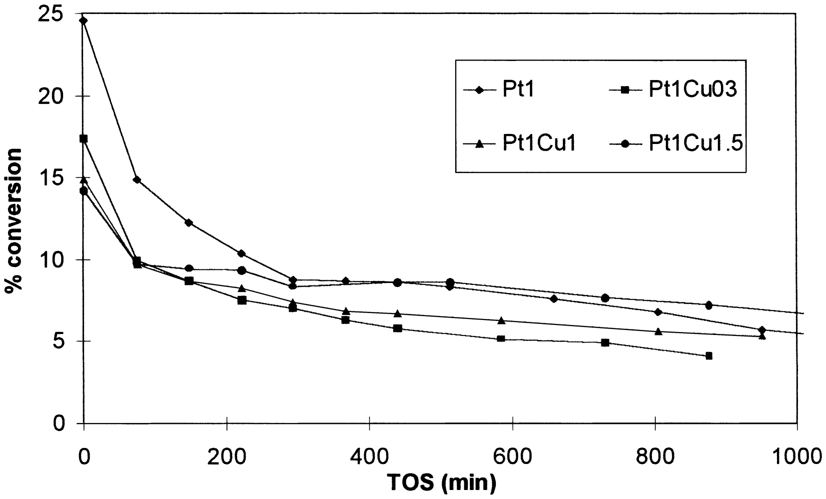

Fig. 8. Percentage conversion vs. TOS of various Pt–(Cu)/(H,K)-TON prepared by Method 2.

Cu addition has decreased the size of the Pt ensembles required to support such a demanding reaction.

There is a dilemma in increasing the acidity of the support from γ-alumina to TON. Though, the catalyst becomes more active for skeletal isomerisation of linear butenes yielding isobutene, the acid sites also cause acid catalysed cracking to be more significant, increasing from 20.4 to 32.0% when changing from γ-alumina to TON. Acidity can be moderated by ion-exchange. Fig. 8 depicts the catalytic performance when Method 2 is used. Pt/(K^+,H^+)-TON has only 30% number of acid sites. Surprisingly, the extent of initial conversion improves slightly when using Method 2, with less number of acid sites. This may be attributed to an increase in platinum dispersion by a factor of 2. The addition of copper, as expected, reduces the initial conversion of *n*-butane. After prolonged time on stream, the higher platinum dispersion and the lower number of acid sites did not significantly improve the catalytic stability.

Fig. 9 shows the initial conversion and products selectivities observed for Pt–(Cu)/(K^+,H^+)-TON catalysts. Optimising acidity has a positive effect on catalytic performance: activity and products selecti-

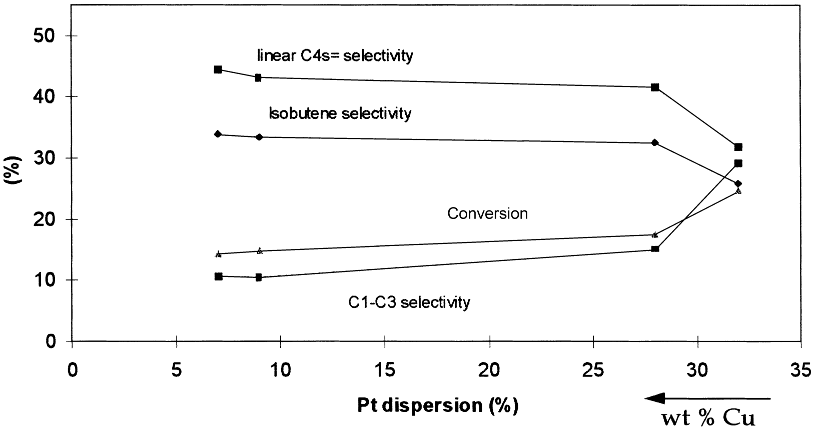

Fig. 9. Initial conversion and product selectivities vs. % Pt dispersion of various Pt–(Cu)/(H,K)-TON prepared by Method 2.

vities. While conversion increases marginally, there is a slight reduction in the C_1–C_3 fractions selectivity accompanied by a more drastic increase in the linear $C_4^{=}$s and isobutene selectivities by 12 and 8%, respectively. This suggests that the modified TON contains a smaller number of acid sites, of which few are strong. As a consequence, the cracking selectivity of K^+-modified H-TON decreased when compared to the fully acidic TON. The high selectivity to isobutene implies that strong acid sites are not needed for the isomerisation of butene to isobutene. Evaluating further the catalyst where the acidity has been moderated (number, strength), the effect of copper addition is comparable to that observed for the 100% protonated catalyst and prepared by Method 1. With the addition of copper, the trend is similar but its extent differs. There is a drastic decrease in selectivities to C_1–C_3 fractions by a factor of three, and an increase in $C_4^{=}$s and isobutene selectivities by ca. 1.7 in both cases.

4. Discussion

We have shown that the dispersion of platinum, in the absence of Cu, depends on both the nature of the Pt source and that of the support. At similar Pt content (1 wt.%), dispersions decrease in the order H_2PtCl_6–Pt/γ-Al_2O_3 (130%), H_2PtCl_6–H-TON (90%), $[Pt(NH_3)_4]Cl_2$–(H,K)-TON (28%), H_2PtCl_6–(H,K)-TON (15%) (Fig. 2). These observations can be rationalised by remembering that the Pt precursor species are anionic or cationic when using H_2PtCl_6 or $[Pt(NH_3)_4]Cl_2$ as Pt sources, respectively, and that the isoelectric points of a high silica zeolite such as H-TON and Al_2O_3 are about 2 and 8, respectively. When H_2PtCl_6 is used as the Pt source, the impregnation pH is about 3–4, in which conditions the zeolite surface is negatively charged whereas that of alumina is positive. It is therefore expected that Method 1 should result in a higher dispersion of Pt on alumina. Interestingly, Method 1 yields a very poor dispersion of Pt when (H,K)-TON is used as support. There may be several reasons for this. One is that the presence of potassium ions in the zeolite channels hinders or even prevent the diffusion of the Pt species in the intracrystalline zeolite volume. The other is that H-TON is an acid of which the dissociation is restricted at pH $=$ 3–4 whereas (H,K)-TON is partially a salt which can dissociate, thus causing the zeolite framework to be even more negative. It should also be considered that the medium size pores of the TON structure restrict the access of $PtCl_6^{2-}$ species to the intracrystalline volume of the zeolite and that $PtCl_{6-x}^{(2-x)-}$ species, smaller and less negatively charged that the original $PtCl_6^{2-}$ anion, will only migrate in the zeolite channels as the precursor anion is progressively stripped of his chlorine ligands during calcination. It is therefore not surprising that Method 2 which uses $[Pt(NH_3)_4]Cl_2$ as Pt source and provides a cationic Pt species during impregnation and calcination increases the dispersion of Pt on (H,K)-TON by a factor of 2.3. $[Pt(NH_3)_{4-x}]^{2+}$ species remain cationic as they are progressively stripped from their NH_3 ligands, they can compete with potassium ions in ion-exchange position, and their adsorption is favoured as the zeolite surface is negative at pH $=$ 3–4. A Pt dispersion exceeding 100%, as measured by hydrogen chemisorption is observed for the system H_2PtCl_6–Pt/γ-Al_2O_3. This should not be surprising as it is well known that Pt promotes the spillover of hydrogen on alumina and that part of this hydrogen may be relatively strongly bound [19].

The addition of Cu decreases the dispersion of Pt evaluated from the amount of hydrogen strongly adsorbed (“irreversible hydrogen”) at the surface of the Pt particles. It should be emphasised that, in this case, such measurements only measure the amount of accessible and active Pt adsorption sites and that dispersion values cannot be translated into Pt particle size. Several factors can be responsible for the decrease of Pt dispersion, observed for all supports, when Cu is added. The presence of Cu ions could promote the growth of Pt particles; this is unlikely as Pt is impregnated first and the resulting material calcined after impregnation. Addition of Cu could modify the electronic properties of Pt and reduce its affinity for hydrogen; this is also unlikely as the same trend is observed for catalysts which either have a very high or a very low Pt dispersion in the absence of Cu. We propose therefore that Cu sitting at the surface of the Pt particles reduces the size of the Pt ensembles and, thus, the number of Pt atoms on which hydrogen adsorption can occur. This proposal agrees with the observation that the formation of C_1–C_3 products via hydrogenolysis is reduced upon Cu addition. Hydrogenolysis is known to be a structure-dependent, demanding, reaction [18].

The dehydroisomerisation of *n*-butane to *i*-butene involves the dehydrogenation of *n*-butane to *n*-butenes on the metal function and the subsequent isomerisation of *n*-butenes to *i*-butene. As a general remark, it should be mentioned that the equilibrium amount of *i*-butene in the butenes fraction should be about 45% at 673 K, which is indeed achieved for the Pt–(H,K)-TON catalysts prepared by either Method 1 or Method 2.

The effect of acidity is clearly shown from a comparison of the results obtained using the Pt/γ-Al_2O_3 and Pt/H-TON catalysts prepared by Method 1. *n*-Butenes are the dominant products in the former case (Fig. 6) whereas all butenes are at equilibrium in the latter one (Fig. 7). Partial exchange of H-TON to neutralise the strong acid sites also yields a catalyst producing the butenes in equilibrium concentrations (Fig. 9) confirming, as it is well-known, that only medium strength acid sites are needed for the *n*-butene to *i*-butene isomerisation but most importantly that in the present situation the reaction indeed proceeds in the order *n*-butane — *n*-butenes — *i*-butene. Dehydrogenation predominates when the metal function only is operative. Isomerisation is observed when acidity is present. Another important consequence of acidity is catalyst deactivation by deposition of carbonaceous residues. The (Pt,Cu)/γ-Al_2O_3 catalysts (Fig. 4) are certainly more stable in terms of conversion as compared to the (Pt,Cu)/(H or H,K) TON catalysts (Figs. 5 and 8). For the latter systems, the presence of acid sites promotes the formation of these carbonaceous residues responsible for deactivation as well as acidic cracking yielding unsaturated C_1–C_3 products.

The addition of Cu has remarkable effects. Although it does not affect much the conversion achieved by the (Pt,Cu)/γ-Al_2O_3 catalysts, it decreases noticeably the formation of C_1–C_3 products and increases therefore the yield in *n*-butenes (Fig. 6). It clearly demonstrates that the addition of Cu reduces hydrogenolysis by limiting the size of the Pt ensembles available at the surface of the Pt particles as also suggested by the hydrogen chemisorption results. Similar effects are observed for the (Pt,Cu)/(H or H,K) TON catalysts. In the latter case, however, conversion is somewhat decreased when Cu is added (Figs. 7 and 9), probably because Cu^{2+} cations contribute to the neutralisation of acid sites in addition to modifying the surface of the Pt particles. As mentioned before, it is unlikely that addition of Cu modifies the size of the Pt particles although Pt dispersion and thus the number of active Pt atoms may be affected.

The optimal catalyst, based on our work, is (Pt,Cu)/(H,K-TON). Isobutene selectivity does not vary much when more than 0.3 wt.% of Cu is added. The isobutene yield (conversion × selectivity) from the Pt/(H,K)-TON catalyst is 6.8% compared to a yield of 5.6% for the more selective catalyst modified with Cu (0.3 wt.%). It thus appears that the choice of an appropriate catalyst for this reaction may be guided mostly by practical and process considerations although it is also obvious that more work should be devoted to balance the dehydrogenation (Pt), acidic (zeolite), and modifier (Cu) functions.

5. Conclusions

The one-step dehydroisomerisation of *n*-butane to isobutene can be effectively achieved using Pt/H-TON zeolite catalysts whose strong acidity have been neutralised by partial ion-exchange with potassium.

A satisfactory dispersion of Pt on the zeolite is achieved when cationic precursors such as $[Pt(NH_3)_{4-x}]^{2+}$ are used. The zeolite acidity must be moderated, e.g., by potassium-exchange, to minimise undesired cracking reactions leading to C_1–C_3 products.

The medium pore size structure of zeolite TON prevents the formation of carbon residues responsible for long term catalyst deactivation. The addition of Cu reduces the contribution of hydrogenolysis by decreasing the size of the Pt ensembles accessible at the surface of the supported Pt particles.

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