Catalysis Letters 52 (1998) 69–72

Skeletal reactions of hydrocarbons on Pt/WO_x–(MoO_x–)ZrO_2 superacid catalysts

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Received 27 October 1997; accepted 27 March 1998

1% Pt/WO_3–(MoO_3–)ZrO_2 superacid catalysts (d_{app} of Pt ∼16–20 Å) gave activity in hydrocarbon isomerization reactions which was much enhanced relative to more customary forms of supported platinum. This is ascribed to dual-functional action. Isomerization selectivity was particularly high for Pt/WO_x–ZrO_2. The dideuterium/cyclopentane exchange "chemical probe" reaction on identical catalysts (reduction temperature 548 K (10 h)) revealed the action of electron-deficient platinum sites. While there is no clear evidence from hydrocarbon hydrogenolysis activities for such sites, comparison with published literature suggests that the exposure of electron-deficient sites may now be sensitive to the choice of precursor compound used in catalyst preparation.

Keywords: platinum, tungsta, molybdena, hydrocarbons, isomerization

Pt/WO_x–ZrO_2 solid superacid catalysts have been attracting attention for reforming applications on account of their stability and absence of containment and environmental problems. High isomerization selectivity is found with alkane feedstock [1]. Results are presented here for skeletal reaction of n-pentane, neohexane and methylcyclopentane on Pt/WO_x–ZrO_2 and on Pt/MoO_x–ZrO_2. Some differences in selectivities between the two catalysts and, also, related literature reports are noted. Use of the exchange reaction between cyclopentane and dideuterium as a chemical probe yields suggestive information on the nature of platinum sites on these catalysts.

Catalysts were prepared by calcination of zirconium hydroxide which had been impregnated with aqueous ammonium metatungstate (or molybdate) by an incipient wetness method to yield 13% w/w W or 6.6% w/w Mo loading, these proportions being found by experiment to lead to maximum activity. Platinum (1% w/w) was dispersed on the resultant material as previously described [2], following drying and calcination to a temperature found to optimise final catalytic conversion rates (383 K/3 h, increased to 1098 K at 5 K/min; 1098 K/6 h). The prepared materials were verified to be superacidic, both in the pre-platinised state and following reduction of the final catalyst, by their colour response to Hammett indicators (ρ values more negative than -9.5). Apparent platinum crystallite diameters in the range 16–20 Å, inferred from hydrogen chemisorption [3], were achieved by incorporating an oxidative redispersion step prior to the final 523 K hydrogen reduction as described earlier [2]. The catalyst charge was about 0.2 g. Reactant hydrocarbons were at 8–17 Torr partial pressure, the balance to 760 Torr being hydrogen. Hydrocarbons were outgassed before catalytic runs by repeated freeze–pump–thaw cycles *in vacuo*. Hydrogen was purified by diffusion through a palladium–silver membrane.

Isomerization selectivities of >95% were found with n-pentane and neohexane reactants on Pt/WO_x–ZrO_2; hydrogenolysis selectivity was comparable to isomerization selectivity on Pt/MoO_x–ZrO_2 (tables 1 and 2). The low "onset" temperatures (n-pentane, 380 K; neohexane, 400 K), while of interest, were still 70–90 K higher than found with a Pt/SO_x–ZrO_2 which also had highly dispersed platinum [2]. The methylcyclopentane reaction on Pt/WO_x–ZrO_2 showed very high selectivity for cyclohexane production, whereas ring opening and cyclohexane formation were of comparable rates on Pt/MoO_x–ZrO_2 (table 3).

Comparisons with published TONs of total skeletal hydrocarbon reaction for highly dispersed platinum on more conventional supports may be made:

Table 1
Reaction of n-pentane/hydrogen.

T (K)	Conv. (%)	TON[a]	C_1[b]	C_2	C_3	nC_4	iC_5	cC_5	S_H	S_I	S_C
					Pt/tungsta–zirconia; $d_{app} = 18$ Å						
383	0.01	0.06	–	–	–	–	100	–	–	100	–
412	0.27	2.00	Tr	Tr	Tr	Tr	100	–	Tr	100	–
435	1.62	12.0	0.4	0.4	0.5	0.5	98	–	2	98	–
					Pt/molybdena–zirconia; $d_{app} = 18$ Å						
429	0.05	0.32	4	8	13	16	59	–	41	59	–
450	0.29	2.06	3.2	6.4	14.2	14.9	61	–	39	61	–
465	1.32	9.6	4.8	7.4	12.9	14.2	61	–	39	61	–

[a] Units are molec. $s^{-1}\,cm^{-2}$(Pt) × 10^{11}.
[b] Products have units of mass.
Tr, trace.

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Table 2
Reaction of neohexane/hydrogen.

T (K)	Conv. (%)	TON[a]	C_1	C_2	C_3	iC_4	neoC_5	nC_4	iC_5	nC_5	2MP + 23DMB	3MP	nC_6	S_H	S_I
Pt/tungsta–zirconia; $d_{app} = 16$ Å															
403	0.07	0.23	–	0.8	–	1.2	–	–	1.0	–	97	Tr	–	3	97
420	0.68	2.52	0.2	0.9	Tr	1.9	–	–	1.7	–	91	4.1	–	5	95
450	10.2	37.8	0.4	0.4	0.2	0.8	0.3	Tr	1.4	Tr	90	5.5	0.7	3.5	96.5
Pt/molybdena–zirconia; $d_{app} = 20$ Å															
440	0.01	0.07	12	–	–	41	–	–	–	–	47	Tr	–	53	47
461	0.12	0.50	14	Tr	Tr	37	–	–	–	–	46	3	–	51	49
485	0.91	4.07	7.3	10.3	15.4	21.5	0.7	–	0.2	Tr	41	3.9	–	55	45

[a] Units are molec. s^{-1} cm^{-2}(Pt) $\times 10^{11}$.

Table 3
Reaction of methylcyclopentane/hydrogen.

T (K)	Conv. (%)	TON[a]	$<C_6$	2MP	3MP	nC_6	cC_6	2MP/3MP	2MP/nC_6
Pt/tungsta–zirconia; $d_{app} = 18$ Å									
408	0.28	2.31	–	3.1	1.5	0.7	95	2.1	4.4
420	0.86	7.07	–	0.8	0.4	0.5	98	2.0	1.6
432	3.64	30.0	Tr	0.4	0.2	0.3	99	2.0	1.3
Pt/molybdena–zirconia; $d_{app} = 16$ Å									
418	0.05	0.40	–	30	13	–	57	2.3	–
445	0.21	1.54	Tr	26.7	9.5	14.4	49	2.8	1.9
460	0.76	5.83	2.1	24.4	7.2	10.0	56	3.4	2.4
471	2.19	16.7	6.5	19.0	6.6	9.2	59	2.9	2.1

[a] Units are molec. s^{-1} cm^{-2}(Pt) $\times 10^{11}$.

(a) n-pentane: Total TONs were of the order of 20 times greater on Pt/WO$_x$–ZrO$_2$ than previously found for 1% w/w Pt/Aerosil [4] of similar platinum dispersion and under comparable reaction conditions. In contrast, total TONs were closely similar for Pt/MoO$_x$–ZrO$_2$ and the same 1% Pt/Aerosil. The high TON on the tungsten-based catalyst was due to the preponderant isomerization process there.

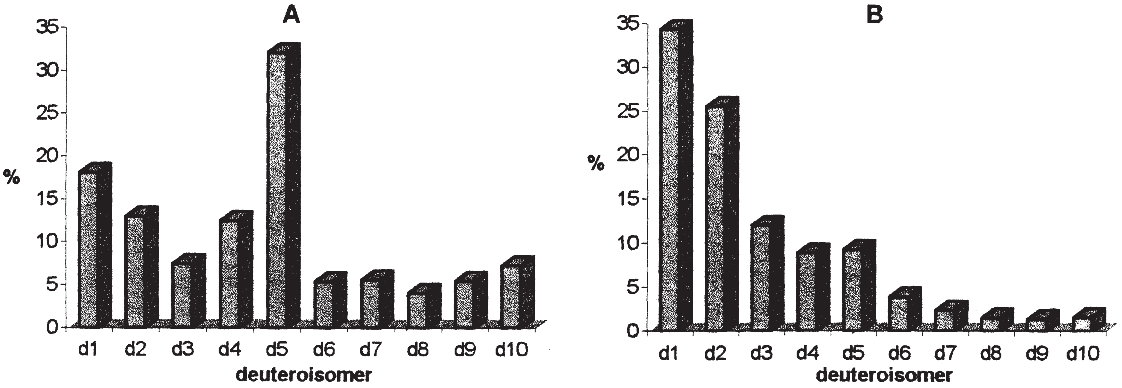
Inspection of the hydrogenolysis product distribution with the Pt/MoO$_x$–ZrO$_2$ catalyst shows that chain scission was substantially random. This is a general finding with monofunctional platinum catalysts including the Pt/Aerosil cited.

(b) Neohexane: TONs for Pt/WO$_x$–ZrO$_2$ were roughly ten times greater than those for 1% Pt/Aerosil [4]. As found for n-pentane, TONs were comparable for Pt/MoO$_x$–ZrO$_2$ and for 1% Pt/Aerosil.

(c) Methylcyclopentane: TONs for Pt/WO$_x$–ZrO$_2$ were roughly 10^2 times those for a Pt/magnesia catalyst having $d_{app} \sim 20$ Å [4]; TONs for Pt/MoO$_x$–ZrO$_2$ were, very approximately, ten times those for the same Pt/magnesia catalyst. The rate of the prominent ring scission process on Pt/MoO$_x$–ZrO$_2$ can be equated as to order of magnitude with the TON for this process on platinum metal itself, taking for the latter the Pt/magnesia standard (on which ring hydrogenolysis was the predominant process). It is also possible to reconcile the extremely small ring hydrogenolysis processes on Pt/WO$_x$–ZrO$_2$ with a reaction occurring solely on the platinum metal surface taking the same Pt/magnesia standard as the basis of comparison for the latter.

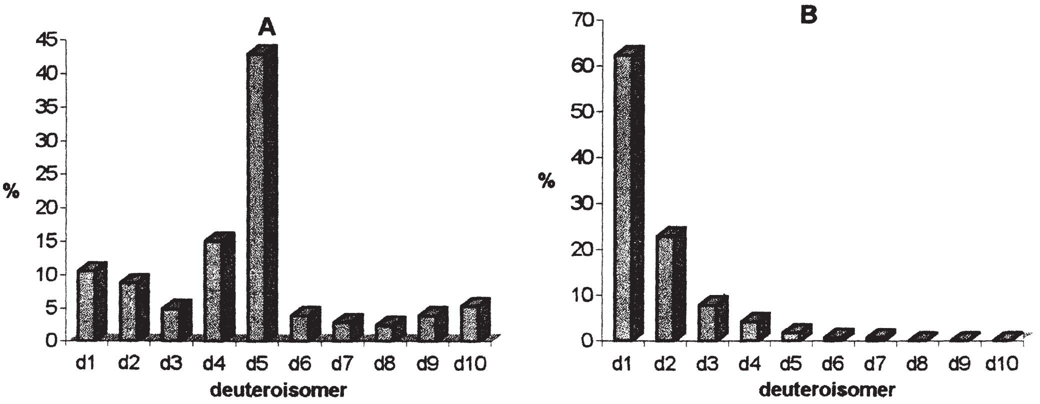
High hydrogenolysis selectivity is characteristic of highly dispersed platinum on conventional supports [5]. For Pt/MoO$_x$–ZrO$_2$, the random scission of the n-pentane chain is (as noted) characteristic of metallic platinum. Hydrogenolysis TONs were similar with n-pentane and with neohexane to those on conventionally supported platinum. It may be inferred that substantially all of the hydrogenolysis on Pt/MoO$_x$–ZrO$_2$ with these alkanes took place on the platinum surface. For Pt/WO$_x$–ZrO$_2$, hydrogenolysis – while very small relative to the high isomerization rate – has a rate of the same order of magnitude as expected for that process on the platinum surface. The lesser isomerization activity of Pt/MoO$_2$–ZrO$_2$ is tentatively explained from the inferred lower acidity of the Brønsted sites on the MoO$_x$ surface than on WO$_x$. The comparisons so far made appear to be in broad agreement with those of Iglesia and his co-workers [1], particularly in confirming the outstandingly high isomerization selectivity of Pt/WO$_x$–ZrO$_2$.

There is interest currently in the role of electron-deficient metal atoms in oxide-supported catalysts of platinum and palladium: determination of initial product distributions for the exchange reaction between cyclopentane and dideuterium has been informative on this aspect for Pd [6]. For Pt/WO$_x$–ZrO$_2$ and, also, Pt/MoO$_x$–ZrO$_2$ catalysts, the type of deutero-isomer distribution observed depends on the severity of the reductive treatment which is applied following a 703 K/15 h treatment in oxygen. Reduction of the platinum catalysts in the cyclopentane/dideuterium reaction mixture itself, representing the mildest possible condition (pretreatment (A)), yielded the well known U-shaped deutero-isomer distribution [7] in the subsequent exchange reaction. If, however, the reduction stage was in D_2 at 548 K (10 h) (pretreatment (B)), there resulted a falling distribution of isomers from d_1 to d_5, previously noted with Pd (albeit at lower temperatures reflecting easier reducibility, mobility and possibly different oxide/metal wetting characteristics [8] with Pd). The falling distributions, following pretreatment (B), were also accompanied by an increase in rates, ten-fold in the case of the of MoO$_x$–ZrO$_2$-supported Pt.



k_0 = 4,060% min^{-1} g^{-1}(Pt) k_0 = 3,180% min^{-1} g^{-1}(Pt)

Figure 1. Initial product distributions in exchange between cyclopentane and dideuterium on the Pt/WO$_x$–ZrO$_2$ catalyst. Pretreatment (A) involved reduction *in situ* with the reaction mixture, whereas pretreatment (B) involved reduction at 548 K. Both exchange experiments were performed at 273 K.



k_0 = 386% min^{-1} g^{-1}(Pt) k_0 = 3,076% min^{-1} g^{-1}(Pt)

Figure 2. Initial product distributions in the exchange between cyclopentane and dideuterium on the Pt/MoO$_x$–ZrO$_2$ catalyst. Pretreatments (A) and (B) and exchange reaction temperature were as given in figure 1 caption.

The isomer distributions, following pretreatment (B) which corresponds closely to that received by Pt/WO$_x$–ZrO$_2$ and Pt/MoO$_x$–ZrO$_2$ catalysts which yielded the skeletal reaction results of tables 1–3, are shown for the two catalysts in figures 1 and 2. The development of the "falling" isomer distribution is more marked for the Pt/MoO$_x$–ZrO$_2$ catalyst. This type of distribution has been shown to derive from small coordinatively unsaturated electron-deficient Pd(Pt) particles [6]. The electron deficiency is likely to manifest as M$^{\delta+}$ or surface M only (M = metal), but EXAFS and TPR show that cationic M is not present in extensive quantities [6]. Most pertinently for the present catalysts, an acid support (WO$_3$) has been found to promote electron-deficient palladium following *either* pretreatments (A) *or* (B), and EXAFS results for Pd/WO$_x$–TiO$_2$ reveal that increase in WO$_3$ loading led to the development of higher coordination unsaturation of the palladium [6]. The picture which emerges for these Pt(Pd) catalysts is then that: (i) the larger metal particles with standard U-shaped exchange patterns are formed readily by reduction; (ii) the more highly dispersed particles are only reduced and come into play via higher-temperature reduction by dihydrogen or dideuterium, and are more active, but give a falling exchange pattern. Other work using low-loaded Pt/H-mordenite containing effectively monoatomic platinum, which was demonstrated to be formally Pt^0 by TPR, also yielded falling isomer distribution from d$_1$ to d$_5$ [9]. We suggest that such very highly dispersed or monoatomic platinum may be inherently electron-deficient.

The preceding comments prompt the question: given the superacid nature of the support, are there indications in the results of tables 1–3, or in the published literature on skeletal hydrocarbon reactions on formally similar catalysts to these, for the action of electron-deficient platinum sites? There is, in fact, no significant indication in the present results of enhancement of hydrogenolysis TONs on either the Pt/WO$_x$–ZrO$_2$ or the Pt/MoO$_x$–ZrO$_2$. However, while the methylcyclopentane reaction on the former catalyst gives a ring hydrogenolysis product ratio 2MP/3MP close to the statistical value of 2.0, the 2MP/3MP ratio on the latter catalyst shows values greater than statistical (2.3–3.4), and this could indicate a contribution from electron-deficient sites [2].

Larsen and his co-workers have reported results for Pt/WO$_x$–ZrO$_2$ prepared for the most part by chloroplatinic acid impregnation of WO_3–ZrO_2 and having platinum crystallites of >100 Å diameter [10]. Very high isomerization selectivity was found for n-butane reactant, similar to the present finding. However, a high Pt dispersion catalyst ($\sim$30 Å diam.) prepared by Pt(acac)$_2$/ether impregnation gave high hydrogenolysis selectivity. This interesting result differs also from the findings of Iglesia et al. [1] who impregnated their oxide support with tetraammine platinum hydroxide precursor. This experimental finding of Larsen et al. is suggestive that electron-deficient platinum site atoms resulted from the choice of platinum precursor. A number of factors differ between these precursor compounds, e.g., presence of chlorine, reducibility [11] and a further especially suggestive one. Pt(acac)$_2$ is not an appreciably ionic compound which would bond to specific locations on the oxide surface there to produce metal clusters on reduction (see Acres et al. [12]). Tetrammine platinum hydroxide (Iglesia) bonds to cation-exchange surface sites on acidic oxides causing metal to nucleate on these. Chloroplatinic acid (Larsen et al. [10], present work) bonds to anion-exchange sites or couples to hydroxyl groups by Pt–Cl bond scission giving, in turn, localised nucleation [12]. The result of Larsen et al. suggests that location of the active platinum site atoms can be a sensitive determinant of the required degree of electron deficiency to effect enhanced alkane hydrogenolysis. Their highly dispersed Pt/WO$_x$–ZrO$_2$ catalyst appears to have shown platinum electron deficiency more decisively than the majority of catalysts based on Pt/WO$_x$–ZrO$_2$, thereby leading to greater than usual hydrogenolysis selectivity. Vaarkamp et al. have correlated enhanced hydrogenolysis activity in supported platinum systems with electron deficiency at the metal sites so characterised by XANES [13]. The dideuterium-exchange reaction with cyclopentane represents an alternative ("chemical probe") characterisation defining surface sites in the catalytic act [14].

Iglesia and co-workers have recently shown a seven-fold depression of hydrogen chemisorption on 0.3% Pt/WO$_x$–ZrO$_2$ following an increase in reduction temperature from 473 to 623 K [15]. They suggested that this might arise from decoration of platinum crystallites with reduced WO$_x$, similar to the metal oxide decoration of supported platinum metal in SMSI systems [16]. While such an effect cannot be excluded in the present catalysts, it is likely to be small. The final reduction temperature was at the lower end of the range stated and Pt particle diameters estimated from hydrogen chemisorption were of a similar magnitude to those found with platinum on conventional supports formed using the same catalyst preparation procedure.[1]

In summary, the superacid supports in the present catalysts enable dual-functional catalysis at temperatures well below that for skeletal rearrangement on the metal *per se*. Hydrogenolysis processes, however, take place on the metal function, have enhanced rates reflecting high platinum dispersion and have characteristic product distributions as for customary supported platinum catalysts. It is suggested that the participation of electron-deficient platinum sites in hydrocarbon skeletal reactions may be sensitive to the platinum precursor compound used in catalyst preparation.

Acknowledgement

We thank Professor E. Iglesia for an advance copy of the paper cited here as ref. [15].

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[1] These considerations also provide justification for the use in the present study of hydrogen chemisorption to measure platinum dispersion.