ACADEMIC
PRESS

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Catalysis 216 (2003) 353–361

JOURNAL OF
CATALYSIS

www.elsevier.com/locate/jcat

Structure and properties of tungstated zirconia catalysts for alkane conversion ☆

Stefan Kuba,[a] Povilas Lukinskas,[a,1] Robert K. Grasselli,[a]
Bruce C. Gates,[b] and Helmut Knözinger [a,*]

[a] *Department Chemie, Physikalische Chemie, LMU München, Butenandtstrasse 5-13 (Haus E), 81377 Munich, Germany*
[b] *Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA*

Received 24 July 2002; revised 10 September 2002; accepted 11 September 2002

Abstract

Promoted tungstated zirconia (WZ) catalysts are active and selective for isomerization of light alkanes, offering good prospects for industrial application. This account is an abbreviated summary of what these catalysts are and how they work. WZ containing approximately a monolayer of tungstate covering the zirconia support was prepared by impregnation of zirconia, tested in a flow reactor, and characterized with a variety of spectroscopic methods. The catalytic activity is associated with interconnecting polyoxotungstate clusters on the surface of tetragonal zirconia. The polyoxotungstate species increase the acid strength of the catalyst relative to that of unmodified zirconia, but the acid strength is still less than that of zeolites and far below the superacidic range. Redox properties of WZ characterized by EPR spectroscopy suggest that alkane activation proceeds via homolytic C–H bond cleavage, leading to the formation of W^{5+} centers and organic radicals, which can be converted to alkenes, initiating catalysis. Unpromoted WZ has a low activity; reaction intermediates remain adsorbed on the surface, where they undergo polymerization and cracking, leading to fast deactivation and poor selectivity. The addition of platinum to the catalyst and H_2 to the feed drastically improves the catalytic activity, selectivity, and stability. The platinum enhances the desorption of reaction intermediates and minimizes the condensation reactions, so that monomolecular isomerization predominates. An additional promotion with iron compounds leads to further improvement in catalytic activity and selectivity.

Keywords: Zirconia; Tungstate; Co adsorption; EPR; Acidity; Redox properties; *n*-Pentane; Isomerization; Mechanism

1. Introduction

The need for gasoline without harmful lead and aromatics stimulated a search for new catalysts to produce environmentally friendly high-octane-number compounds by isomerization of widely available straight-chain alkanes. Alkane isomerization gives branched high-octane-number isopentane and isohexanes, which are good gasoline components, and isobutane, an important raw material for alkylation, a major source of gasoline-range branched alkanes. The capacity for $C_4/C_5/C_6$ isomerization was estimated to be more than 1 million barrels (160,000 m^3) per day in the early 1990s [1], and it continues to grow.

The most widely applied alkane isomerization catalysts are platinum-promoted solid acids, chlorinated alumina [2], and mordenite [3,4]. The former are highly active and operate at low temperatures (400–450 K), so formation of the desired branched alkanes is favored thermodynamically. These catalysts, however, require the constant addition of chlorine-containing compounds and are sensitive to moisture and sulfur impurities [5], and they are highly corrosive and subject to stringent environmental regulations [4]. The zeolite catalysts do not suffer from these disadvantages, but they are significantly less active, operating at higher temperatures (500–550 K) and characterized by low yields of branched alkanes as a consequence of the thermodynamic limitations.

More-active catalysts are needed that can operate at low temperatures while being environmentally friendly.

☆ Dedicated to Prof. Sir J.M. Thomas on the occasion of this 70th birthday.

[*] Corresponding author.
E-mail address: helmut.knoezinger@cup.uni-muenchen.de (H. Knözinger).

[1] Present address: Institute of Chemistry, Goštauto 9, LT-2600 Vilnius, Lithuania.

0021-9517/03/$ – see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0021-9517(02)00125-2

Extensive research has been done in the search for such catalysts. Early industrial work by Holm and Bailey [6] led to the recognition of sulfated zirconia (SZ) as a promising candidate, and this was followed by investigations by Hino and Arata [7] and Yamaguchi and Tanabe [8], who found that SZ catalyzes isomerization of light alkanes at 300–420 K. Further work led to discoveries that the activity, selectivity, and stability of SZ are improved by the addition of noble metals and transition metal oxides, such as those of iron and manganese [9,10]. SZ catalysts, presumably with such modifiers, have found commercial application [11], but they appear to suffer from loss of sulfate groups during calcination, regeneration, or reduction, from deactivation by rapid coke formation, and from poisoning of the noble metal function by sulfur species formed from sulfate groups in reducing atmospheres [12].

Consequently, investigators, beginning with Hino and Arata in 1988 [13], sought alternatives to SZ, turning to tungstated zirconia (WZ). Rapid progress in the understanding and improvement of this class of catalyst has ensued, and we review it here. This account is too short to be exhaustive and is intended to highlight the path of recent advances and place the subject in the perspective of today's catalysis research. We emphasize results from our group, citing only some of the work of others; details are given in the cited literature.

Although WZ catalysts are markedly less active than SZ, they have superior stability under both reducing and oxidizing conditions and appear to be more suitable for industrial applications. The catalytic activity of WZ, like that of SZ, is greatly improved by promotion with platinum (activities comparable to those of Pt/SZ have been observed [14–16]) and with transition metal oxides. Pt/WZ catalysts are also significantly more selective than Pt/SZ for formation of branched alkane isomers, as shown by results characterizing the conversion of n-heptane [17] and n-octane [15]. Pt-promoted WZ catalysts appear already to have found commercial application [18].

2. Preparation of tungstated zirconia catalysts

The catalysts reported here were prepared by impregnation of $ZrO_x(OH)_{4-2x}$ with aqueous suspensions of ammonium metatungstate followed by drying and calcination at 923 K [19]. Other reported preparations are similar to these.

We emphasize that these samples, containing approximately a monolayer of the tungsten species (17 or 19 wt% W as WO_3 on ZrO_2), were found to be the most active catalysts among several obtained by variation of the preparation parameters. The catalysts are referred to as 17WZ or 19WZ, respectively.

Promotion by metals has a major effect on the performance of these catalysts, and thus we emphasize work with the promoted materials. For example, we prepared WZ catalysts promoted with both platinum and iron [20], and similar catalysts were reported in a patent by Chang et al. [21a]. In our preparations, $Fe(NO_3)_3$ or $FeSO_4$ was introduced in the impregnation step, giving catalysts denoted FeWZ(N) and FeWZ(S), each with a W content corresponding to 17.7 wt% WO_3 and an Fe content corresponding to 1 wt% Fe_2O_3. Subsequently, these FeWZ catalysts were impregnated with a platinum component to give samples with 1 wt% Pt, denoted PtFeWZ(S) and PtFeWZ(N) [22].

3. Structural characterization

The developing understanding of what these catalysts are and how they work has been built up in large measure from a foundation of structural data obtained by the concerted application of surface-sensitive spectroscopies. We stress the importance of applying a complementary set of methods for the characterization of the high-area catalytic materials themselves, in particular samples working as catalysts.

3.1. Structure of the ZrO_2 support

XRD patterns of 19WZ show the formation of the tetragonal ZrO_2 phase on calcination in air at 923 K in the presence of surface WO_x compounds [19]. This observation is in accord with earlier reports which indicate that the metastable tetragonal ZrO_2 formed on high-temperature treatment is stabilized by the addition of numerous metal oxides [23]. The WO_x species inhibit the sintering of ZrO_2 crystallites, as indicated by the much larger surface area of WO_x-promoted ZrO_2 than of similarly treated ZrO_2 itself [19]. 19WZ has a surface area of about 100 m^2/g [19].

3.2. Structure of surface tungsten species

Raman spectra of 19WZ in the dehydrated state (Fig. 1) include a sharp band at 1020 cm^{-1}, assigned to W=O

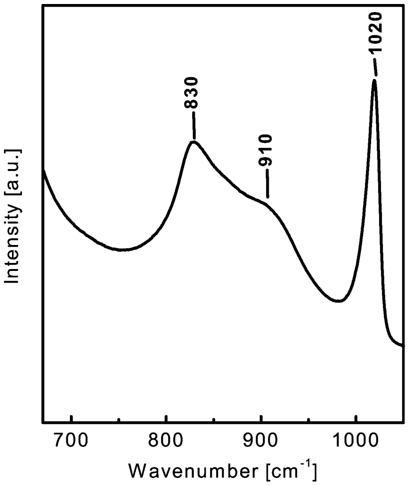


Fig. 1. Raman spectrum of dehydrated 19WZ catalyst.

stretching vibrations, with a broad band at 830 cm^{-1} characteristic of W–O–W stretching modes [24]. The band at 910 cm^{-1} was tentatively assigned to W–O–Zr stretching vibrations characterizing the bond anchoring WO_x species to the support [24]. The bands at 830 and 1020 cm^{-1} are typical of polyoxotungstates [24] and suggest the formation of interconnected tungsten species. UV–visible diffuse reflectance spectra indicate that even at the lowest loadings (3.6 wt% WO_3), there are tungsten–tungsten near-neighbor interactions, and the number increases with tungsten loading. We infer that the surface structures resemble three-dimensional polyoxoanion clusters [19,24]. This suggestion is consistent with postulated models [25,26] and X-ray absorption data [27].

Although polytungstate clusters are formed even at the lowest tungsten loadings, the catalytic activity of such samples is low. Higher tungsten loadings lead to the formation of larger, highly interconnected polytungstate clusters and increase the density of catalytically active sites on the surface [17–19]. The catalyst with the tungsten loading slightly exceeding the theoretical monolayer coverage was found to be the most active. At higher loadings, the catalytic performance of WZ decreases sharply, as an inactive WO_3 phase is formed.

UV–visible absorption spectra characterizing 19WZ indicate an absorption energy, E_{edge}, of 3.42 eV (indicating ligand-to-metal charge transfer) [19]. This value, in agreement with others reported for WZ [25], matches that representing ammonium metatungstate (AMT) (Table 1), which has a structure built up of polyoxoanions. The optical spectra thus support the proposal of tungstate clusters on the catalyst surface.

The formation of polytungstate layer is not unique to zirconia. Such layers are also formed on other oxides, including alumina and titania [28,29], but not on silica, on which inactive WO_3 particles are formed [28], and not on some strongly basic oxides (such as MgO), on which monomeric tetrahedral tungstate species are formed [28].

The W^{6+} ions in these clusters are inferred to be coordinatively saturated, as indicated by the fact that W^{6+}–CO complexes were not detected by IR spectroscopy when CO was added to the sample. This result is contrasted to observations of WO_x/TiO_2, for which W^{6+}–CO surface complexes were observed and five-coordinated W^{6+} surface centers were proposed [30]. Tetrahedral monomeric $WO_4{}^{2-}$ species and microcrystalline WO_3 are not present in 19WZ in detectable amounts, as indicated by the absence of the characteristic vibrational modes at 935 and 807 cm^{-1}, respectively, and by the fact that the absorption edge position measured for the catalyst (3.42 eV) deviates significantly from the values characterizing $WO_4{}^{2-}$ (4.89 eV) and WO_3 (2.85 eV) (Table 1).

Table 1
Absorption edge position, E_{edge}, and number of nearest tungsten atoms, N_{W}, in tungstated zirconia and comparison with several tungsten-containing compounds

Sample	E_{edge}/eV	N_{W}
WO_3	2.85	6.0
AMT[a]	3.45	4.0
19WZ	3.42	4.1

[a] Ammonium metatungstate, $(NH_3)_6H_2W_{12}O_{40}$.

We therefore propose that three-dimensional polyoxotungstate clusters are present on the surface of zirconia. Moreover, we suggest that the structure and the size of these clusters, as well as their specific interactions with the zirconia support, largely determine the acidic, redox, and catalytic properties of 19WZ. Similar views have also been expressed by others [31,32]. These same polyoxotungstate clusters are also present on the promoted catalysts containing 1 wt% Pt (or 1 wt% Pt and 1 wt% Fe_2O_3), discussed below.

4. Surface properties of the catalysts

4.1. Surface acidity

Initial interpretations of the catalytic properties of SZ and WZ focused on their acidity. The high activity of SZ for alkane conversion, combined with reports that its Hammett acidity function was comparable to values characterizing superacids, led researchers to postulate that SZ was a superacid [7,33,34]. However, it was realized within a few years that the acidic properties of SZ are not sufficient to explain its catalytic properties, and points made in the early literature included the following: (a) the activity of SZ for high-temperature alkane reactions was found to be similar to that of moderately strong acids such as zeolites, although the activities of these two classes of catalyst for alkane isomerization at low temperatures differ by several orders of magnitude;[2] (b) the limitations of measurements of Hammett acidity functions of the catalysts became apparent [35]; and (c) other methods of measurement of acid strength, including low-temperature IR spectroscopy of adsorbed CO [36], gave no indication of any extraordinarily strong proton donors in the catalyst.

Catalytic titration experiments [37a] have shown that the number of catalytically active sites is small (0.002–0.004 meq H^+/g of catalyst). The suggestion that a small, undetectable minority of extremely strong acidic sites might be present on these catalysts and play a role as reaction initiators [4,38] is inconsistent with the observations of essentially zero conversion at short times-on-stream[3] (see

---

[2] It has been shown that the acidic strength of SZ decreases when it is brought to a high temperature under reducing conditions; H_2S was observed to form during alkane reactions at 523 K [40].

[3] The possibility that some very strong acidic sites exist on a fresh catalyst and are deactivated very rapidly under reaction conditions, and, thus, not detected at the shortest times-on-stream, cannot be ruled out. Any such sites would not contribute to the overall catalytic activity and would not be mechanistically important, although they could be precursors of catalytically active sites.

Table 2
Frequency shifts, $\Delta\nu_{OH}$, of O–H stretching frequencies induced by low-temperature CO adsorption on zirconia, tungstated zirconia, and zeolite HZSM-5

Sample	$\Delta\nu$(OH) (cm^{-1})
ZrO_2	60
19WZ	160
HZSM-5	320

below) [24,39]. There is increasingly, persuasive evidence that other mechanisms of initiation prevail. The recent work focuses on bifunctional mechanisms and redox chemistry in the initiation of catalysis; details are provided below for WZ.

Characterization of oxidized WZ by low-temperature CO adsorption indicates the presence of both Lewis and Brønsted acid centers [24]. Lewis acidity is attributed to coordinatively unsaturated Zr^{4+} sites, present both on pure ZrO_2 and on WZ. The acid strengths of these centers are enhanced by the presence of polytungstate species [24]. OH groups of the catalyst are characterized by bands or shoulders at 3670 and about 3620–3630 cm^{-1} [19]. Low-temperature CO adsorption leads to hydrogen bonding between OH groups and the weak base CO, which results in a red shift of the O–H stretching frequencies. The frequency shift, $\Delta\nu_{OH}$, is a measure of the hydrogen bond energy and it has been suggested that it correlates, with the Brønsted acid strength [36].

A comparison of the $\Delta\nu_{OH}$ values of several materials is shown in Table 2. The frequency shift characterizing 19WZ is 160 cm^{-1}, which is significantly greater than the shift of 60 cm^{-1} recorded for pure ZrO_2 [24]. The presence of polytungstate species on the surface thus enhances the Brønsted acidity, and the results suggest that larger WO_x domains create stronger acid sites [17–19]. The $\Delta\nu_{OH}$ value of 160 cm^{-1} representing 19WZ is significantly less than the values reported for the zeolites HZSM-5 [41] and H-mordenite [41a]. Qualitatively similar relationships between the acid strength of WZ catalysts and zeolites were also found in NMR investigations of adsorbed pyridine [42] and in calorimetric investigations [43]. We emphasize that these acidity measurements were carried out on as-prepared catalysts rather than under reaction conditions. Although it is suggested that some very strong acid sites might be formed on the working catalyst on the interaction with a feed [37b],[4] our measurements of the catalyst in the presence of H_2 indicate the opposite (see below).

Thus, in summary, there is no evidence that WZ catalysts have superacidic properties or sites with the acidic character that would be necessary for initiation of catalysis by alkane protonation. Inasmuch as WZ catalysts are some four orders of magnitude more active than zeolites for alkane isomerization [43], it is clear that there is no one-to-one correlation between acid strength of WZ and its catalytic activity. We therefore infer that although the acidity of WZ catalysts is important in alkane conversion catalysis, the reaction is most likely initiated by a reaction other than protonation of the alkane by the catalyst or a species formed from it.

4.2. Redox properties

Temperature-programmed reduction (TPR) has been used to monitor the reduction of W^{6+} in WZ and Pt-promoted WZ [44,45]. The reduction is presumably facilitated by the delocalization of the net negative charge onto the polyoxotungstate clusters. The reduction of W^{6+} in these clusters on WZ catalysts promoted with platinum was also demonstrated by titrations with H_2, O_2, and CO [31]. The addition of platinum leads to lower reduction temperatures, evidently because of spillover of hydrogen adatoms (formed by H_2 dissociation on platinum) onto condensed WO_x clusters. The accommodation of a proton by electron abstraction from a hydrogen atom and charge delocalization on an extended WO_x network was proposed [31,46], which may lead to structures suggestive of tungsten bronzes, such as $(H^+)_x[(W^{5+})_x(W^{6+})_{n-x}O_{3n}]^{x-}$. The necessary condition for the formation of a bronze is the existence of polyoxoanion clusters.

We investigated the reduction in H_2 of 19WZ and 1Pt19WZ by EPR spectroscopy (Fig. 2) [47,48]. The results of Fig. 2 show that W^{5+} can be detected on 19WZ after reduction at 470 K and higher temperatures [47], whereas the maximum possible degree of reduction of the platinum-promoted catalyst is achieved even at room temperature [48]. Reduced tungsten sites were also detected on WZ when NO was used as an IR probe molecule; the results show that the reductive treatment of the unpromoted WZ catalyst at

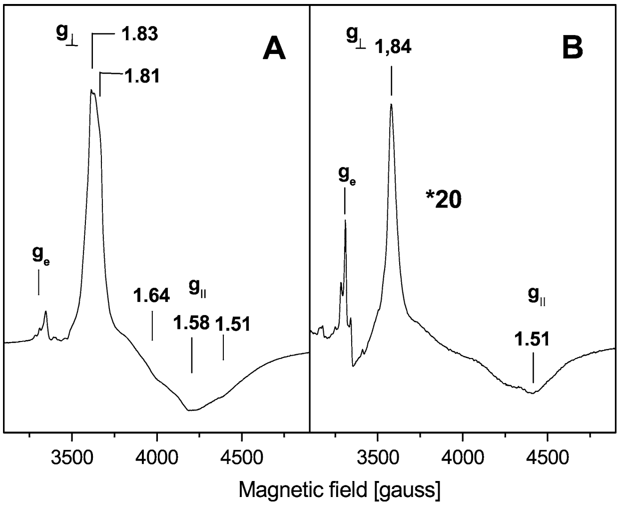


Fig. 2. EPR spectrum of (A) platinum-promoted and (B) platinum-free tungstated zirconia catalysts, reduced at 473 K.

---

[4] The in situ titration experiments were carried out with pyridine [37a] or ammonia [37b] as probe molecules, determining the total number of acid sites but not providing information about their strengths.

temperatures above 523 K leads to the formation of W^{5+}- and W^{4+}-containing centers [49].

The formation of W^{5+} centers is accompanied by the creation of new OH groups, as evidenced by IR spectra [47,48]. Although these Brønsted acid sites are conventionally considered to be active reaction centers [50], low-temperature CO adsorption measurements indicate that the strengths of Brønsted acid sites on reduced catalysts are lower than those characteristic of the oxidized catalyst [47]. This finding is not unexpected, as it is well known that the acid strength of inorganic oxyacids depends on the oxidation state of the central atom [51].

EPR experiments have shown that the redox ability of WZ catalysts is sufficient to initiate a homolytic cleavage of C–H bonds in alkanes. Exposure of a WZ catalyst to *n*-pentane at 523 K led to the formation of W^{5+} species and organic radicals on the surface [47]. The formation of organic radicals also occurred when WZ catalysts interacted with other hydrocarbons, including benzene [52,53] and cycloalkanes [53]. We therefore infer that one-electron transfer, although it is not regarded as a step in the catalytic cycle, can initiate catalysis by a process that leads to the formation of the carbenium ion chain carriers [47], as also occurs in acidic solutions [54]. We emphasize that a strong redox reactivity is necessary but not sufficient for the catalytic activity of WZ; the need for a balanced combination of acidic and redox properties has been asserted for both SZ [55] and WZ catalysts [56].

The complex EPR signal shown in Fig. 2 contains several components. An anisotropic signal (at $g_{\perp} = 1.84$ and $g_{\parallel} = 1.51$) was observed at 77 K after reduction of the catalyst at 470 K. We suggested that this signal is associated with coordinatively unsaturated earlier W^{5+} centers produced on the catalyst surface, as it appears even at low reduction temperatures and is sensitive to O_2 [47]. More recent EPR experiments showed, however, that this signal remains in fact almost unaffected by O_2. In contrast, the most prominent signal component (at $g_{\perp} = 1.83$ and $g_{\parallel} = 1.58$, with other components appearing at $g_{\perp} = 1.84$ and 1.81 and $g_{\parallel} = 1.64$ and 1.51) characterizing W^{5+} centers in different, environments are affected.

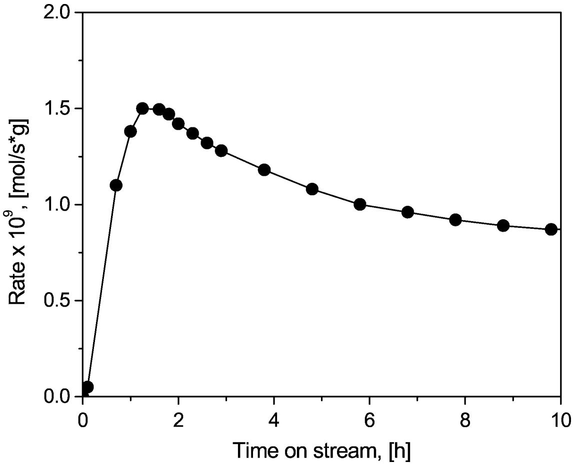
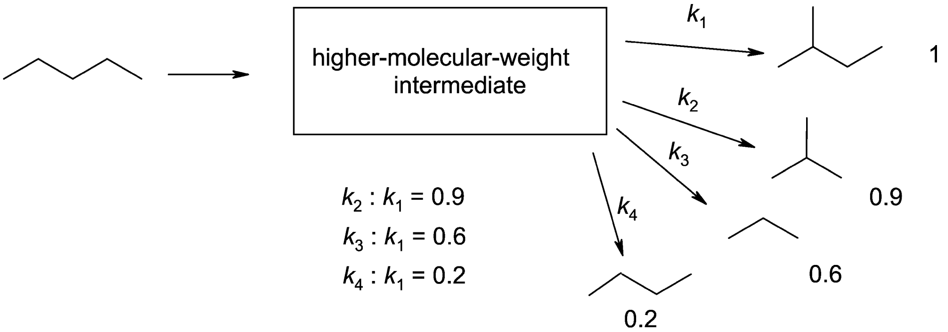


Fig. 3. Catalytic activity of unpromoted WZ during the isomerization of *n*-pentane in a flow reactor at 523 K.

5. Catalysis

5.1. Unpromoted WZ catalyst

The catalytic reactions of *n*-pentane summarized below were carried out at a standard temperature of 523 K and atmospheric pressure in flow reactors. The unpromoted WZ catalyst develops a low activity (characterized by conversions ⩽ 1% under the conditions of our experiments). The rate of the total *n*-pentane conversion depends strongly on the time-on-stream (TOS) in a once-through flow reactor, as shown in Fig. 3. (Similar behavior is observed for SZ.) Initially, the catalytic activity is indistinguishable from zero [24], increasing with TOS through a maximum (during the induction period), followed by rapid deactivation until low but nearly stable activity is attained. The selectivity for isopentane formation remains essentially constant at about 30% under our conditions, with the products isobutane, propane, and *n*-butane and traces of unsaturated hydrocarbons also being observed. Although the overall activity of the catalyst is strongly dependent on TOS, the ratio of the product concentrations remains nearly constant, as indicated in Scheme 1 ([isopentane]:[isobutane]:[propane]:[*n*-butane] = 1:0.9:0.2:0.6).



Scheme 1. Proposed reaction scheme for the isomerization of alkanes on unpromoted WZ catalyst.

Because the catalytic activity was essentially negligible initially, we infer that the catalytically active sites were created from the reactants and catalyst during the induction period; a key question is what are they? We suggest that they are not simple acidic sites, as the product distribution cannot be explained by the classical monomolecular or bimolecular carbenium ion mechanisms that have usually been suggested for alkane isomerization on catalysts with classic proton–donor sites responsible for the catalysis. The lack of variation of the product distribution with time-on-stream suggests that isomerization and cracking reactions have a common intermediate. Because simple monomolecular or bimolecular mechanisms are unlikely, we suggest an intermediate with a carbon number greater than 5, which might form by oligomerization and condensation reactions during the induction period.

UV–visible [57] and Raman [58] spectra of the working catalyst show clearly that several types of surface-bound organic species form during the induction period of the n-pentane reaction, and these might be related to the postulated intermediate. Raman spectra also show the formation of pregraphitic carbon. The formation of these surface species, however, does not correlate with the development of catalytic activity, and the carbon deposits likely contribute to the deactivation of the catalyst [58]. The UV–visible spectra reveal the growth of bands at ca. 398, 434, 530, and 620 nm, corresponding to multisubstituted polyalkenyl species [57].

It has been suggested that unsaturated organic cations promote cracking in liquid acids [54], giving product distributions similar to ours. Similar species have also been observed on sulfated zirconia during the isomerization of butane and correlated with the catalytic activity [59]. We infer that these species (which likely include a variety of components) incorporate the postulated high-molecular-weight intermediate. The induction period can therefore be explained by the slow formation of the organic surface species that are responsible for the formation of the observed catalytic reaction products on the unpromoted WZ catalyst.

The following questions remain: How is the catalytic cycle initiated, and how is the alkane initially activated to form the observed high-molecular-weight species? EPR spectra [47] showed that during the interaction of the catalyst with the hydrocarbon in the absence of H_2, coordinatively unsaturated surface W^{5+} centers formed. Organic radicals were observed to form simultaneously [47]. We infer then that the (slight) reduction in the tungsten phase was accompanied by oxidation of the alkane and that activation of alkanes proceeds via a redox initiation step that involves the abstraction of two electrons and one proton that are transferred to the tungsten phase, leading to the formation of W^{5+} centers and OH groups.

Table 3
Comparison of the catalytic performance of platinum-promoted tungstated zirconia and comparison with Pt-free material

Catalyst	H_2 in feed?	Maximum activity ($\mathrm{mol\,s^{-1}\,m^2}$)	Selectivity (%)
WZ	Yes	8.0×10^{-10}	~ 30
	No	3.0×10^{-10}	40–60
PtWZ	Yes	(4.8×10^{-8})[a]	95
	No	2.4×10^{-9}	15–35

[a] Equilibrium conversion.

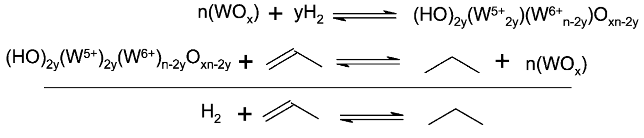
The formation of bronzelike surface clusters, such as $(H^+)_x[(W^{5+})_x(W^{6+})_{n-x}O_{3n}]^{x-}$, has been suggested [25,47]. The formation of these clusters could, for example, occur via a dehydrogenation step followed by a protonation of the resulting alkene on a Brønsted acid site. Consistent with this suggestion, the reaction products were found to contain small amounts of alkenes, and—further bolstering the suggestion—we observed that in fact under conditions comparable to those of the isomerization reaction the WZ catalyst hydrogenates propene [57]. The alkenes may undergo oligomerization and condensation to form the proposed high-molecular-weight reaction intermediate and other hydrocarbon deposits shown in Scheme 1.

Although the activation of alkanes with the formation of unsaturated intermediates is evidently plausible and consistent with the data, alternatives, discussed earlier [47] cannot be ruled out.

5.2. Platinum-promoted WZ catalysts

Promotion of WZ catalysts by noble metals such as platinum dramatically improves their activity and selectivity for n-pentane isomerization. The improvement is only marginal in the absence of H_2, but it becomes significant when H_2 is co-fed with the reactant. The conversion increases to more than 56% under our standard conditions, with only little deactivation, and the selectivity for isopentane reaches nearly stable values of about 95% [57]. The conversion to isopentane reaches a value near the equilibrium value (the $i\text{-}C_5/(i\text{-}C_5 + n\text{-}C_s)$ ratio is $\geqslant 0.59$, compared to a theoretical value of 0.61 [5]). The side products differ markedly from those observed with the unpromoted catalyst. Methane and butanes (as well as ethane and propane) are formed in equimolar ratios [57], suggesting that side products result from direct hydrogenolysis of C_5 species, likely on platinum surfaces [14]. Transmission electron micrographs showed that the platinum dispersion in our catalyst was high, perhaps even atomic, with only few, barely detectable platinum clusters being present. We suggest that the side products originate from these minority platinum clusters.

The performance of the unpromoted catalyst in comparison with the platinum-promoted WZ catalyst is summarized



Scheme 2. Proposed reaction scheme for the isomerization of alkanes on Pt/WZ catalyst.

in Table 3. The results emphasize the effects of H_2 and the promotion by platinum and suggest that the complex mechanism that is inferred to be operative on the WZ catalyst is essentially suppressed on the platinum-containing catalysts in the presence of H_2, when a fast and selective monomolecular isomerization reaction takes over. The desorption of products formed from the branched carbenium ion or alkene is thought to be facilitated by the presence of reactive spill over hydrogen, with simultaneous reoxidation of W^{5+} to W^{6+}, as indicated in Scheme 2.

EPR spectra [48] show that reduction of the polyoxotungstate clusters is strongly enhanced by the platinum (vide supra), which should have a favorable effect on the adsorption/desorption rates of alkanes and unsaturated surface species and result in a strong decrease in the concentration/lifetime of the latter. Consequently, the unsaturated surface species have less opportunity to undergo secondary reactions to form higher-molecular-weight deposits, and the highly selective and fast monomolecular isomerization becomes dominant. This interpretation had been proposed earlier by Iglesia et al. [17] and Barton et al. [46].

This picture constitutes a bifunctional mechanism in the sense that both acidic and metallic functions are involved. However, it differs from the classical bifunctional mechanism according to which platinum's role is simply to catalyze dehydrogenation [4,14]. Instead, we infer that alkane molecules are activated by dehydrogenation on the polyoxotungstate clusters via a redox process, and the protonation of the resulting alkenes occurs on the oxidic components of the catalyst that incorporate acidic sites. Desorption may then occur via deprotonation and hydrogenation. We also propose that the function of the highly dispersed platinum is to facilitate the dissociative chemisorption of H_2 and that it does not interfere significantly in the hydrocarbon transformations, as this would not allow the extremely high isopentane selectivities. The low activity for hydrogenolysis is attributed to the small number of platinum clusters in the catalyst.

5.3. Platinum- and iron-promoted WZ catalysts (PtFeWZ)

We investigated the effect of addition of small amounts of iron salts during the synthesis of WZ catalysts [22]. In accordance with previous investigations [20], the iron promotion in the absence of platinum had no positive effect on the catalytic performance; the FeWZ catalysts were essentially inactive.

In the presence of H_2, however, the performance of the PtFeWZ catalyst is remarkably improved. Under identical reaction conditions, the PtFeWZ(N) catalyst (prepared from $Fe(NO_3)_3$) shows an n-pentane conversion rate ($5 \times -10^{-8}\ \mathrm{mol\,s^{-1}\,m^{-2}}$) comparable to that of the PtWZ catalyst, but the PtFeWZ(S) catalyst (prepared from $FeSO_4$) shows a markedly increased rate ($9 \times 10^{-8}\ \mathrm{mol\,s^{-1}\,m^{-2}}$). Furthermore, there is an important effect of the iron promotion on the isopentane selectivity of the catalysts. Whereas the PtWZ catalyst is characterized by a nearly stable selectivity of about 95%, the PtFeWZ(S) catalyst develops a selectivity, increasing with TOS, of up to 98%, and PtFeWZ(N) shows a stable selectivity greater than 99%. All three catalysts are characterized by nearly stable conversions in the flow reactor, and only the PtFeWZ(S) catalyst deactivated (but very slowly).

The enhanced activity of the PtFeWZ(S) catalyst may be attributed, at least in part, to the presence of ${SO_4}^{2-}$ groups on the surface (one thinks of the SZ catalysts). Experiments with a catalyst synthesized by coimpregnation with $(NH_4)_2SO_4$ and the tungsten precursor component clearly showed enhanced activity, but the catalyst suffered from fast deactivation. The iron promotion in the case of PtFeWZ(S) appears to stabilize the sulfate groups on the surface.

Independent of the iron salt that was used, the selectivity of the catalysts is strongly enhanced by iron, indicating that promotion by the iron itself leads to this improvement.

As the remaining 5% of the products formed in the presence of the PtWZ catalyst are mainly hydrogenolysis products, they are likely formed on the surface of platinum clusters, and the suppression of the formation of these side products on the PtFeWZ catalyst might be a consequence of the suppression of the formation of metallic platinum by the promoter iron. Furthermore, the redox properties of the Fe^{3+}/Fe^{2+} pair might be involved and could influence the reducibility of the tungsten phase.

6. Perspective and outlook

The motivation for the development of strong solid acid catalysts was technological, driven by environmental concerns. The key initial discovery of sulfated zirconia was made in industry and reported in a patent [6]. The initial interpretations of the catalytic action were simplified, and the development of more-intricate interpretations rested on the foundation of spectroscopic characterizations of the catalyst, with data representing catalysts in the working state being especially important. As is common in catalyst development, improvement in catalysts were made by addition of components to the base catalyst. The "promoted" catalysts that work best incorporate not only tungstated zirconia but also platinum, iron, and possibly sulfate, and they benefit greatly from operation in the presence of H_2. The chemistry is clearly related to the chemistry of classical acid–base catalysis and to classical bifunctional catalysis, but it is subtly different and essentially new.

The insights that led to the interpretation of the performance of these new catalysts (which are no doubt subject to revision and improvement) are based on the following:

- Classical ideas of acid–base catalysis, including physical organic chemistry of acidic solutions, specifically including their redox properties.

- Surface structures of the catalysts developed from the concerted application of various spectroscopic methods.
- Spectroscopic evidence of minor products, specifically free radicals, indicating the role of redox reactions.
- Understanding of the reactivity of surface species based on solid-state chemistry (e.g., bronzes).
- Measurements of catalyst performance in flow systems, including analysis of minor reaction products and observation of catalyst break-in and deactivation.
- The combination of reaction experiments and spectroscopy of the catalysts.

Additional important questions remain to be answered. What makes zirconia a seemingly unique support material? Polyoxotungstate species are formed on various other supports, but the resultant catalysts are less active and selective (or not active at all). Is it the property of zirconia to form the most active tungstate phase on the surface that makes it so good? If so, why? Two- and three-dimensional polyoxotungstate clusters are also formed on TiO_2 [29a,29b] and tungstated titania is indeed catalytically active [29c], although inferior to tungstated zirconia. Is zirconia really unique, or can the presumed active-phase–support interaction be reproduced on other supports?

A further issue that requires extensive research is the elucidation of the function of the iron promoter. Are the redox properties of the Fe^{3+}/Fe^{2+} couple involved? Do the iron centers possibly act as anchoring sites for platinum, thus stabilizing a high dispersion? Does iron play a catalytic role, or does it instead act as a stoichiometric reactant, perhaps involved in an initiation step? Is it a redox initiator? Currently we have evidence that the addition of iron has no detectable positive effect on the catalytic performance of platinum-free WZ [20]. We therefore infer that the effect of iron on the platinum-containing catalyst is caused by a synergistic action of the two promoters. In addition to the remaining problems, one can also ask: Is iron unique or do other additives act comparably or even better?

The answers to some of those questions may require more than the capabilities of today's spectroscopic and catalytic investigations, and new techniques, such as molecular modeling, may be helpful. Theoretical investigations have already been reported [60], and more are needed. Work with structurally well-defined model catalysts might also be of value.

We believe that catalysts closely related to the ones described here may find industrial application. Tungstated zirconia-supported catalysts have already received wide attention from both the industrial and academic sectors, but more work is needed to improve their performance. Several trends of development can be suggested on the basis of what is now known.

- Improvements in activity of WZ catalysts are needed to maximize the yields of desired products. Presently we are able to reach near-equilibrium conversions to branched alkenes at temperatures above 523 K; catalysts with increased activities would allow operation at lower temperatures and allow higher yields of isoalkanes under equilibrium conditions. This goal might be achieved by improvements in the promotion of WZ, which by itself is not highly active, perhaps by inclusion of additional elements, such as noble metals and transition metals.
- Second, more fine-tuning of WZ catalysts is in order: such parameters as the amount and the nature of promoters, preparation procedures, and noble metal dispersion and accessibility have been shown to be important and need to be optimized. Improvements should not only lead to better overall catalytic performance of WZ, they should also make the catalysts more affordable.
- Third, WZ catalysts may find industrial application for reactions apart from alkane conversions. A number of reports and patents dealing with new applications of WZ catalysts have already appeared.

Acknowledgments

We thank Prof. M. Che for his interpretation of the EPR spectra. This research was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 338) and the Fonds der Chemischen Industrie. P.L. and B.C.G. are indebted to the Alexander-von-Humboldt-Foundation for research fellowships.

References

[1] P.J. Kuchar, J.C. Bricker, M.E. Reno, R.S. Haizmann, Fuel Process. Technol. 35 (1993) 183.

[2] (a) B.W. Burbridge, J.K.R. Rolfe, Hydrocarbon Process. Petrol. Refiner 45 (1966) 168;
(b) D.H. Belden, Petrol. Refiner 35 (1956) 149.

[3] (a) H.W. Kouwenhoven, W.C. van Zijll Langhout, Chem. Eng. Progr. 67 (1971) 65;
(b) H.W. Kouwenhoven, W.C. van Zijll Langhout, Oil Gas J. March 8 (1971) 44.

[4] J.G. Santiesteban, D.C. Calabro, C.D. Chang, J.C. Vartuli, T.J. Fiebig, R.D. Bastian, J. Catal. 202 (2001) 25.

[5] S.T. Sie, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 4, Wiley–VCH, Weinheim, 1997, p. 1998.

[6] V.C.F. Holm, G.C. Bailey, US Patent 3,032,599, 1962.

[7] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. 851 (1980).

[8] T. Yamaguchi, K. Tanabe, J. Phys. Chem. 90 (1986) 4794.

[9] C.-Y. Hsu, C.R. Heimbuch, C.T. Armes, B.C. Gates, J. Chem. Soc. Chem. Commun. 1992 (1645).

[10] (a) V. Adeeva, J.W. de Haan, J. Jänchen, G.D. Lei, V. Schünemann, L.J.M. van de Yen, W.M.H. Sachtler, R.A. van Santen, J. Catal. 151 (1995) 364;
(b) E.J. Hollstein, J.T. Wei, C.-Y. Hsu, US Patent 434,743, 1989.

[11] (a) P.G. Blomuel, C.D. Gosling, S.A. Wilcher, US Patent 5,763,713, 1998;
(b) C. Gosling, R. Rosin, P. Bullen, Petrol. Technol. Q. 55 (1997/1998).

[12] G. Larsen, E. Lotero, R.D. Parra, L.M. Petkovic, H.S. Silva, S. Radhavan, Appl. Catal. A 130 (1995) 213.
[13] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. 1259 (1988).
[14] J.C. Yori, C.R. Vera, J.M. Parera, Appl. Catal. A 163 (1997) 165.
[15] J.M. Grau, J.C. Yori, J.M. Parera, Appl. Catal. A 213 (2001) 247.
[16] S.L. Soled, W.E. Gates, E. Iglesia, US Patent 5,422,327, 1995.
[17] E. Iglesia, D.G. Barton, S.L. Soled, S. Miseo, J.E. Baumgartner, W.E. Gates, G.A. Fuentes, G.D. Meitzner, Stud. Surf. Sci. Catal. 101 (1996) 533.
[18] (a) C.D. Chang, S. Han, R.A. Morrison, J.G. Santiesteban, US Patent 5,992,643, 1993;
(b) C.D. Chang, J.G. Santiesteban, D.L. Stern, US Patent 6,080,904, 1996.
[19] M. Scheithauer, R.K. Grasselli, H. Knözinger, Langmuir 14 (1998) 3019.
[20] M. Scheithauer, R.E. Jentoft, B.C. Gates, H. Knözinger, J. Catal. 191 (2000) 271.
[21] (a) C.D. Chang, C.T. Kresge, J.G. Santiesteban, J.C. Vartuli, US Patent 6,124,232, 1998;
(b) J.G. Santiesteban, D.C. Calabro, C.D. Chang, J.C. Vartuli, T.J. Fiebig, R.D. Bastian, J. Catal. 202 (2001) 25.
[22] S. Kuba, B.C. Gates, P. Vijayanand, R.K. Grasselli, H. Knözinger, Chem. Commun. 321 (2001).
[23] (a) F. Lange, J. Mater. Sci. 17 (1982) 255;
(b) R.G. Silver, C.J. Hou, J.G. Ekert, J. Catal. 118 (1989) 400.
[24] M. Scheithauer, T.K. Cheung, R.E. Jentoft, R.K. Grasselli, B.C. Gates, H. Knözinger, J. Catal. 180 (1998) 1.
[25] D.G. Barton, M. Shtein, R.D. Wilson, S.L. Soled, E. Iglesia, J. Phys. Chem. B 130 (1999) 630.
[26] J.R. Sohn, M.Y. Park, Langmuir 14 (1998) 6140.
[27] M. Valigi, D. Gazzoli, I. Pettiti, G. Mattei, S. Colonna, S. De Rossi, G. Ferraris, Appl. Catal. A 231 (2002) 159.
[28] D.S. Kim, M. Ostromecki, I.E. Wachs, J. Mol. Catal. A 106 (1996) 93.
[29] (a) F. Hilbrig, H.E. Göbel, H. Knözinger, H. Schmelz, B. Lengeler, J. Phys. Chem. 95 (1991) 6974;
(b) S. Eibl, B.C. Gates, H. Knözinger, Langmuir 17 (2001) 107;
(c) S. Eibl, R.E. Jentoft, B.C. Gates, H. Knözinger, Phys. Chem. Chem. Phys. 2 (2000) 2565.
[30] F. Hilbrig, H. Schmelz, H. Knözinger, J. Catal. 180 (1998) 1.
[31] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal. 181 (1999) 57.
[32] I.E. Wachs, F.D. Hardcastle, in: Specialist Periodical Reports: Catalysis, Vol. 10, Royal Chem. Society, Cambridge, UK, 1993, p. 102.
[33] D.C. Calabro, J.C. Vartuli, J.G. Santiesteban, Top. Catal. 18 (2002) 231.
[34] G. Fitzsimons, J.K.A. Clarke, M.R. Smith, J.J. Rooney, Catal. Lett. 52 (1998) 69.
[35] D. Farcasiu, A. Ghenciu, G.J. Miller, J. Catal. 134 (1992) 118.
[36] H. Knözinger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 2, Wiley–VCH, Weinheim, 1997, p. 707.
[37] (a) J.G. Santiesteban, J.C. Vartuli, S. Han, R.D. Bastian, C.D. Chang, J. Catal. 168 (1997) 431;
(b) C.D. Baertsch, S.L. Soled, E. Iglesia, J. Phys. Chem. B 105 (2001) 1320.
[38] T.-K. Cheung, B.C. Gates, Top. Catal. 6 (1998) 41.
[39] T.K. Cheung, J.L. d'Itri, B.C. Gates, J. Catal. 151 (1995) 464.
[40] F.T.T. Ng, N. Horvat, Appl. Catal. A 123 (1995) 197.
[41] (a) L.M. Kustov, V.B. Kazansky, S. Béran, L. Kubelkova, P. Jiru, J. Phys. Chem. 91 (1987) 5247;
(b) I. Mirsojew, S. Ernst, J. Weitkamp, H. Knözinger, Catal. Lett. 24 (1994) 235.
[42] K. Shimizu, T.N. Venkatraman, W. Song, Appl. Catal. A 224 (2002) 224.
[43] J.C. Vartuli, J.G. Santiesteban, P. Traverso, N. Cardona-Martinéz, C. Chang, S.A. Stevenson, J. Catal. 187 (1999) 131.
[44] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal. 181 (1999) 57.
[45] J.G. Santiesteban, D.C. Calabro, W.S. Borghard, C.D. Chang, J.C. Vartuli, Y.P. Tsao, M.A. Natal-Santiago, R.D. Bastian, J. Catal. 183 (1999) 314.
[46] D.G. Barton, S.L. Soled, E. Iglesia, Top. Catal. 6 (1998) 87.
[47] S. Kuba, P. Concepción Heydorn, R.K. Grasselli, B.C. Gates, M. Che, H. Knözinger, Phys. Chem. Chem. Phys. 3 (2001) 146.
[48] S. Kuba, R.K. Grasselli, M. Che, H. Knözinger, submitted.
[49] K. Hadjiivanov, P. Lukinskas, H. Knözinger, Catal. Lett. 82 (2002) 73.
[50] L.M. Petkovic, J.R. Bielenberg, G. Larsen, J. Catal. 178 (1998) 533.
[51] L. Pauling, in: 3rd ed., General Chemistry, 1979, p. 409.
[52] F.R. Chen, G. Coudurier, J.F. Joly, J.C. Vedrine, J. Catal. 143 (1998) 616.
[53] P. Lukinskas, F. Jentoft, P. Concepción Heydorn, K. Köhler, H. Knözinger, manuscript in preparation.
[54] D. Farcasiu, P. Lukinskas, J. Chem. Soc. Perkin Trans. 2 (1999) 2715, and references therein.
[55] D. Farcasiu, A. Ghenciu, Q.L. Li, J. Catal. 158 (1996) 116.
[56] A. Gutiérrez-Alejandre, A. Castillo, P. Ramírez, G. Ramis, G. Busca, Appl. Catal. A 216 (2001) 181.
[57] S. Kuba, R. Ahmad, P. Lukinskas, F. Jentoft, R.K. Grasselli, B.C. Gates, H. Knözinger, manuscript in preparation.
[58] S. Kuba, H. Knözinger, J. Raman Spectrosc. 33 (2002) 325.
[59] R. Ahmad, J. Melsheimer, F. Jentoft, R. Schlögl, manuscript in preparation.
[60] F. Haase, J. Sauer, J. Am. Chem. Soc. 120 (1998) 13503.