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# Role of spill-over hydrogen in the hydrogenolysis of neopentane

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## Abstract

A series of Pt/LTL zeolite catalysts with varying Pt loading and support acidity was studied by hydrogen temperature-programmed desorption (TPD) and reaction of neopentane and propane. Specific desorption peaks in the TPD were associated with hydrogen spilled-over onto the support. The ability of the spilled-over hydrogen to migrate on the support surface was limited to approximately 35 nm from the platinum cluster. Saturation capacity for spilled-over hydrogen was related to the support acidity/basicity, with a maximum of about  $10^{18}$  atoms/m<sup>2</sup> for the most acidic support studied. Spilled-over hydrogen was inert to oxygen treatment at 100°C, and did not contribute to catalytic activity for neopentane or propane conversion. Instead, hydrogenolysis TOF and the amount of spilled-over hydrogen were mutually dependent on support acidity/basicity. Both declined with increasing K/Al ratio of the support, and continued to decline even for basic supports with K/Al ratios greater than 1. The continued decline in activity for K/Al > 1 indicates that the metal–support interaction is not dependent on acidic hydroxyls.

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## 1. Introduction

Since first described by Kuriacose [1], the phenomenon which has come to be known as spill-over has been the subject of numerous studies. Reviews on the subject were published in 1973 [2], 1980 [3], 1983 [4], 1986 [5], and 1990 [6]. One of the properties which has been attributed to spilled-over hydrogen is the ability to enhance catalytic activity. Khoobiar [7] studied the dehydrogenation of cyclohexane to benzene over admixtures of Pt/alumina and unpromoted alumina and reported reaction rates higher than expected based on the amount of platinum in the reactor. The enhanced rate was attributed to dehydrogenation of cyclohexane

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on the unpromoted alumina surface, followed by 'reverse spill-over', i.e. migration of the resulting hydrogen to the platinum, where it was desorbed. Similarly, Sancier [8], and later, Antonucci et al. [9] reported similar rate enhancements for benzene hydrogenation over mixtures of metal-promoted and unpromoted alumina. This reaction was also proposed to occur on the unpromoted alumina surface, in this case between spilled-over hydrogen and adsorbed benzene. Increased reaction rates have also been reported for ethylene hydrogenation in the presence of spilled-over hydrogen [10–12]. For ethylene hydrogenation, it was suggested that the spilled-over hydrogen does not just combine stoichiometrically with the ethylene, but that it forms catalytic centers which were capable of multiple turnover cycles [11,12]. Other authors, however, observed no activity enhancement attributable to spilled-over hydrogen [13,14], and suggested that the alumina diluent might act as a scavenger for impurities.

The presence of spilled-over hydrogen on the support can be detected and quantified using temperature-programmed desorption (TPD). Kramer and Andre [15], studying Pt/alumina, identified a hydrogen desorption peak at around 450°C which was assigned to spilled-over hydrogen. A similar desorption peak was also observed on pure alumina when hydrogen was dissociated upstream of the catalyst bed by a high frequency discharge. This showed not only that hydrogen could be 'spilled-over' to the alumina surface without the need for a metal, but that it could also be *desorbed* without the need for a metal. Moreover, the desorption occurred at the same temperature, regardless of whether or not the platinum was present. This study provided the first evidence that desorption of hydrogen can occur following a pathway other than 'reverse spill-over'.

In a recent study, Miller et al. [16] showed that large amounts of spilled-over hydrogen are present on zeolites, on alumina, and on silica supports and that desorption of the spilled-over hydrogen can be identified in TPD profiles by multiple desorption peaks. The total amount of spilled-over hydrogen was much larger on acidic supports, exceeding 4 hydrogen atoms per platinum atom. It was also shown that hydrogen spill-over was reduced on a catalyst which had been treated at high temperatures. It was suggested that spilled-over hydrogen was stabilized by surface hydroxyl groups, which are removed during any high temperature treatment, and that desorption of spilled-over hydrogen occurs as a result of dehydroxylation of the support.

It has been observed that the activity for hydrogenolysis is higher for metals on acidic supports than on neutral or basic supports [17–19]. It is widely believed that the increased activity is due to modification of the supported metal through interaction with the support [17–20]. As discussed above, larger amounts of spilled-over hydrogen are present on acidic supports than on neutral or basic supports. Since spilled-over hydrogen has been proposed to form reactive centers on the support, it might be surmised that the enhanced activity of metals on acidic supports is a result of the participation by spilled-over hydrogen, and not a modification of the metal itself. It is this hypothesis which shall be tested in the present study.

## 2. Experimental

All catalysts were prepared using Linde LTL zeolite. The acidity of the K-LTL zeolite support was varied by either impregnating with  $\text{KNO}_3$  or exchanging with ammonium nitrate to give K/Al ratios ranging from 0.61 to 1.33. All LTL zeolites were calcined at  $400^\circ\text{C}$  and analyzed for K and Al. Support samples are designated LTL(*x.xx*), with *x.xx* representing the K/Al molar ratio. Platinum was impregnated using an aqueous solution of tetraammine platinum(II) nitrate, followed by drying at  $125^\circ\text{C}$ .

$\text{H}_2$ -TPD profiles were obtained after initial in situ reduction for 1 h or 5 h at  $300^\circ\text{C}$ . Sample size was 0.5–0.6 g. Following reduction, samples were cooled to ambient temperature in flowing hydrogen. TPD profiles were obtained in flowing  $\text{N}_2$ . The temperature was ramped at  $10^\circ\text{C}$  per minute up to  $700^\circ\text{C}$ , then held for 1 h. Oxygen treatments were done in the TPD apparatus by first reducing at  $300^\circ\text{C}$ , cooling to  $100^\circ\text{C}$  under flowing  $\text{H}_2$ , purging with  $\text{N}_2$ , then flowing dry air for 1 h at  $100^\circ\text{C}$ . After purging and cooling to ambient under flowing  $\text{N}_2$ , a standard TPD experiment was carried out. TPD of zeolites without platinum give flat lines with no peaks.

The conversion of neopentane was conducted at  $325$ – $350^\circ\text{C}$  at atmospheric pressure in a fixed-bed reactor using 1.25 vol.-% neopentane in  $\text{H}_2$ . Conversion of propane was conducted at  $400^\circ\text{C}$  in the same apparatus using 3.78 vol.-% propane in  $\text{H}_2$ . The catalyst was pre-reduced at the reaction temperature, and conversion was adjusted to between 0.5 and 5% by varying space velocity. Catalyst loadings were between 0.01 and 0.5 g. The specific activity of Pt/LTL(1.33) was too low to measure at the same temperatures as the more active catalysts. Therefore, the activities for both Pt/LTL(1.19) and Pt/LTL(1.33) were determined at higher temperatures ( $475^\circ\text{C}$  for neopentane and  $550^\circ\text{C}$  for propane), and the activity of Pt/LTL(1.33) at the lower temperature was estimated assuming the same activity ratio with Pt/LTL(1.19) at the lower temperature as was observed at the higher temperature. TOF was calculated based on volumetric  $\text{H}_2$  chemisorption as molecules/s/surface Pt atom. Selectivity is calculated on a molar basis as the percent of the converted neopentane which is converted to isopentane (isomerization) and isobutane plus methane (hydrogenolysis).

## 3. Results and discussion

### 3.1. Hydrogen chemisorption

Measured H/Pt ratios were, in some cases, lower than the 1.0 expected for well-dispersed catalysts (Table 1). However, EXAFS measurements on similarly-prepared catalysts consistently find average coordination numbers ranging from 4–6, which correspond to an average particle size of 6–10 atoms [16,19,21–23]. We

Table 1  
Quantities of hydrogen desorbed by TPD<sup>a</sup>

Catalyst (K/Al ratio)	Total	Chemisorbed <sup>b</sup> (Peak I)	Interfacial (Peak II)	Spillover (Peaks III and IV)
0.5% Pt/LTL(0.61)	15.2	0.53	0.5	14.2
1.0% Pt/LTL(0.61)	10.8	0.70	0.4	9.7
1.5% Pt/LTL(0.61)	9.0	0.81	0.5	7.7
3.0% Pt/LTL(0.61)	5.2	0.67	0.4	4.1
1.0% Pt/LTL(0.83)	6.0	0.81	0.5	4.7
1.0% Pt/LTL(0.93)	3.1	0.85	0.4	1.9
1.0% Pt/LTL(0.96)	3.0	0.89	0.4	1.7
1.0% Pt/LTL(1.19)	1.4	1.15	0.3	0.1
1.0% Pt/LTL(1.33)	1.1	0.57	0.5	0.0

<sup>a</sup> H/Pt atomic ratio.

<sup>b</sup> From static hydrogen chemisorption measurements.

have also examined similarly-prepared catalysts by TEM, observing few, if any Pt particles larger than the detection limit of about 10 Å [23,24]. While the measured H/Pt values would seem to indicate much larger particles, such large particles would be clearly visible by TEM, and this size is well outside the error limit of our EXAFS measurements. Given the agreement between the EXAFS and TEM results, we conclude that the Pt particles are, in fact, quite small, and reside within the pores of the zeolite.

### 3.2. TPD experiments

The effect of increasing Pt loading on TPD profiles following 1 h reduction is shown in Fig. 1. Peaks I and II are assigned to hydrogen chemisorbed on the Pt surface and hydrogen in the metal–support interface, respectively, while peaks III and IV represent hydrogen spilled-over onto the support [16]. Peaks I and II are associated with the Pt and increase with Pt loading. The area of peak I approximates the H/Pt ratios obtained by H<sub>2</sub> chemisorption.

The total amount of spilled-over hydrogen (peaks III and IV) increases more or less linearly at low Pt loadings (Fig. 2 and Table 1), then levels off, approaching a value of about 7.3 cm<sup>3</sup>/g of catalyst. TPD profiles of the 0.5% and 3.0% Pt samples after 5 h reduction were identical to those after 1 h reduction, showing that hydrogen uptake is complete after 1 h, even though, at least in the 0.5% Pt case, the total amount of spilled-over hydrogen is well below the saturation capacity of the support. These observations suggest a model in which hydrogen is dissociated on the platinum particles, spills over to the support and migrates to a nearby accepting site. The spilled-over hydrogen saturates the support surface in the vicinity of the platinum particle, but is limited in the distance it can migrate. As platinum loading is increased, these areas coalesce, eventually forming a completely saturated surface. This model leads to the following expression:

$$\ln\left(1 - \frac{H}{H_{\text{sat}}}\right) = -A \cdot N_{\text{Pt}}$$

where  $H$  is the coverage of spilled-over hydrogen,  $H_{\text{sat}}$  is the saturation coverage,  $A$  is the area around the Pt cluster which is covered to saturation, and  $N_{\text{Pt}}$  is the density of platinum clusters. Although platinum particle sizes were not measured for the samples used in this study, EXAFS analysis of similarly-prepared catalysts have shown platinum particle sizes of 6–10 atoms [16,19,21–23], and an average of 8 atoms/cluster is assumed. Other structural parameters for LTL are: 16.4 T/1000 Å<sup>3</sup>, 386 m<sup>2</sup>/g, 2.11 g/cm<sup>3</sup> [25,26]. Fitting the data to this model yields:

$$H_{\text{sat}} = 9.9 \times 10^{17} \text{ atoms/m}^2$$

$$A = 1.7 \times 10^{-16} \text{ m}^2/\text{cluster}$$

The saturation coverage of  $9.9 \times 10^{17}$  atoms/m<sup>2</sup> is equivalent to approximately 1.8 H atoms/unit cell. Similar coverages have been found on alumina [16]. This value is two orders of magnitude higher than the  $10^{16}$  atoms/m<sup>2</sup> typically reported for spill-over capacity [12,15,27]. However, these earlier studies were carried out on catalysts which had been calcined at relatively high temperatures, and/or reduced at high temperatures. The capacity of a support to accept spilled-over hydrogen is greatly reduced by dehydroxylation during high temperature treatments [16]. The catalysts used in the present study were precalcined at 400°C and reduced at only 300°C. Furthermore, the capacity for spilled-over hydrogen we obtained is

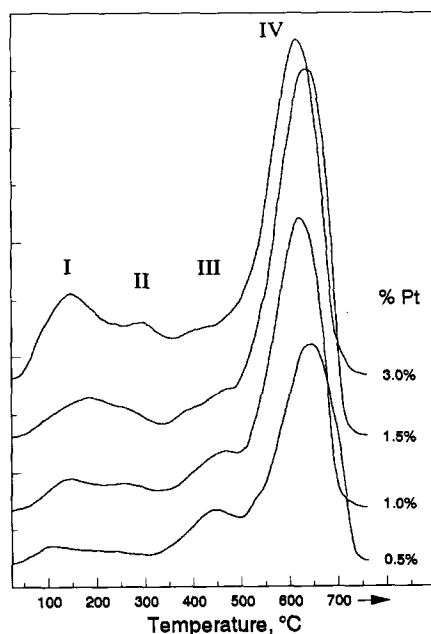


Fig. 1. Effect of increasing Pt loading in TPD of Pt/LTL(0.61).

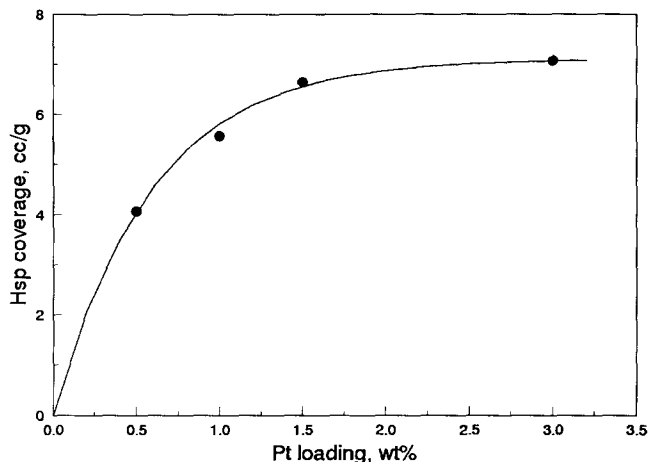


Fig. 2. Amount of spilled-over hydrogen as a function of Pt loading. Symbols represent measured values; line represents model fit. See text for explanation of model.

well below the surface oxygen density of ca.  $4 \times 10^{19}$  atoms/m<sup>2</sup>, demonstrating that only about 2–3% of the surface oxygen atoms in LTL(0.61) are capable of holding spilled-over hydrogen atoms.

At 0.5% Pt, spilled-over hydrogen totals about 14.2 H atoms per platinum atom or 114 atoms per 8-atom cluster. Even at this low Pt loading, coverage by spilled-over hydrogen is more than half the saturation coverage (see Fig. 2). The maximum area around a Pt cluster saturated by spilled-over hydrogen (*A*) was estimated above to be about  $1.7 \times 10^{-16}$  m<sup>2</sup>. This area in LTL corresponds to about 96 unit cells. Zeolite LTL has a unidimensional pore structure, with a unit cell dimension in the *c* axis of 0.75 nm. Ninety-six unit cells in LTL amounts to more than 70 nm of pore length. Typical zeolite crystallites were cylindrical, and approximately 150 nm in both diameter and length. On an atomic scale, this represents a prodigious distance for the hydrogen to travel, but is too small to indicate significant crossing of zeolite particle boundaries, and is much less than the value of 0.5 mm reported by Sancier [8].

The effect of support acidity on the amount of spilled-over hydrogen is shown in Fig. 3. Peaks I and II, which are associated with hydrogen in contact with Pt, did not change, while peaks III and IV, which represent spilled-over hydrogen, increased with increasing support acidity. The amount of spilled-over hydrogen was too small to be measured on LTL(1.33), while Pt on LTL(0.61) spilled-over 5.6 cm<sup>3</sup>/g or about  $7.8 \times 10^{17}$  H atoms/m<sup>2</sup>. The association between spilled-over hydrogen capacity and the number of support hydroxyl groups is evident in Fig. 4. The number of tetrahedral Al atoms not compensated by K cations (Al–K) is a measure of, although not necessarily equal to, the number of acidic hydroxyls on the surface. The slope of the line in Fig. 4 is 0.37, indicating that at 1% Pt loading, 0.37 spilled-over hydrogen atoms are held for each uncompensated framework aluminum atom. However, at 1% Pt, the support surface is only about 77% saturated

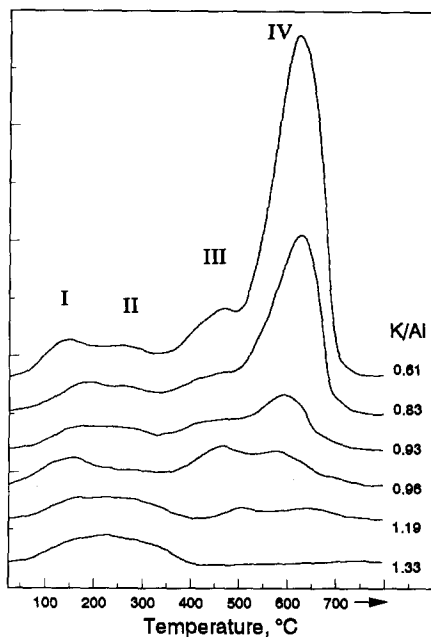


Fig. 3. Effect of increasing acidity in TPD of 1% Pt/LTL.

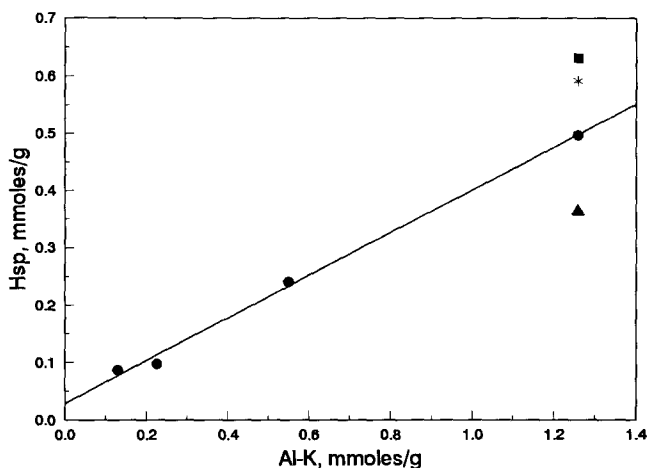


Fig. 4. Relationship between the amount of spilled-over hydrogen and the number of acidic hydroxyls. Al-K is the molar concentration of tetrahedral Al minus K cations, and is used as an indicator of the number of acidic hydroxyl groups. Line is best linear fit through 1% Pt points. (▲) 0.5% Pt, (●) 1.0% Pt, (\*) 1.5% Pt, (■) 3.0% Pt

by spilled-over hydrogen. Thus, saturation capacity corresponds to about 0.48 spilled-over hydrogen atoms per uncompensated framework aluminum atom.

The intercept of the fitted line is close to, but slightly above zero. Also, Pt on supports with  $K/Al > 1$  continue to hold a small amount of spilled-over hydrogen, although their ability to do so continues to decline with potassium addition above

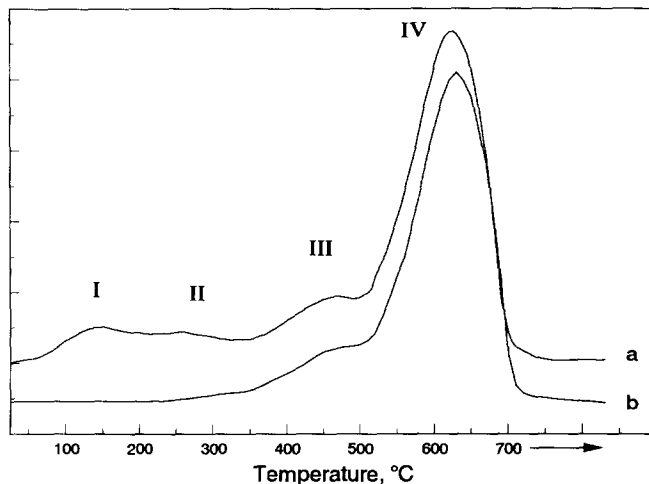


Fig. 5. TPD of 1% Pt/LTL(0.61) after (a) 300°C reduction; (b) 300°C reduction followed by dry air at 100°C.

K/Al of 1. This implies that other, non-acidic hydroxyls may also hold spilled-over hydrogen. The TPD profiles show two peaks attributed to spilled-over hydrogen: a small one (peak III) at about 450°C and a much larger one (peak IV) at about 625°C. The area of peak III is difficult to quantify, but qualitatively, this peak seems to decline more slowly with increasing potassium loading than peak IV. The size of peak IV on LTL(0.61) is consistent with the holding of spilled-over hydrogen on acidic hydroxyls, while peak III may represent spilled-over hydrogen held in non-acidic hydroxyl groups, or possibly silanol groups.

In a previous study, it was shown that spilled-over hydrogen is stable, as long as the support hydroxyls remain intact [16]. The reaction of oxygen with various types of hydrogen is shown in Fig. 5. Oxygen reacts rapidly with both the chemisorbed hydrogen (peak I) and the interfacial hydrogen (peak II). Hydrogen in contact with the platinum is very reactive. In contrast, oxygen did not react with spilled-over hydrogen (peaks III and IV). If spilled-over hydrogen is unable to react with oxygen, it seems unlikely that it could react with hydrocarbons.

### 3.3. Hydrogenolysis of neopentane and propane

Analysis of the reaction products for neopentane conversions between 0.5 to 5.0% by the Delplot method [28] indicated that methane, isobutane and isopentane were primary reaction products. Ethane and propane, which were detected at low conversion, were produced by hydrogenolysis of a small amount of n-butane present as an impurity in the neopentane feed.

The effect of Pt loading on TOF for neopentane conversion over Pt/LTL(0.61) is shown in Table 2. As discussed above, the ratio of spilled-over hydrogen on the support to the number of Pt atoms ( $H_{sp}/Pt$ ) decreased from 14.2 to 4.1 for this series. If spilled-over hydrogen generated reaction centers on the support, the TOF,



Table 2  
TOF for neopentane conversion

Catalyst (K/Al ratio)	neoPentane TOF ( $s^{-1}$ )	Hydrogenolysis selectivity (%)	Propane TOF ( $s^{-1}$ )
0.5% Pt/LTL(0.61)	$1.3 \times 10^{-1}$ <sup>a</sup>	78	
1.0% Pt/LTL(0.61)	$1.0 \times 10^{-1}$ <sup>a</sup>	78	
1.5% Pt/LTL(0.61)	$1.3 \times 10^{-1}$ <sup>a</sup>	78	
3.0% Pt/LTL(0.61)	$8.0 \times 10^{-2}$ <sup>a</sup>	78	
1.0% Pt/LTL(0.61)	$2.3 \times 10^{-1}$ <sup>b</sup>	82	$3.5 \times 10^{-1}$ <sup>d</sup>
1.0% Pt/LTL(0.83)	$2.0 \times 10^{-1}$ <sup>b</sup>	89	
1.0% Pt/LTL(0.93)	$1.0 \times 10^{-1}$ <sup>b</sup>	84	
1.0% Pt/LTL(0.96)	$4.8 \times 10^{-2}$ <sup>b</sup>	77	
1.0% Pt/LTL(1.19)	$1.3 \times 10^{-3}$ <sup>b</sup>	76	$2.8 \times 10^{-2}$ <sup>d</sup>
1.0% Pt/LTL(1.33)	$1.2 \times 10^{-6}$ <sup>c</sup>		$4.0 \times 10^{-5}$ <sup>e</sup>

<sup>a</sup> Determined at 325°C.

<sup>b</sup> Determined at 350°C.

<sup>c</sup> Estimated at 350°C from determination at 475°C.

<sup>d</sup> Determined at 400°C.

<sup>e</sup> Estimated at 400°C from determination at 550°C.

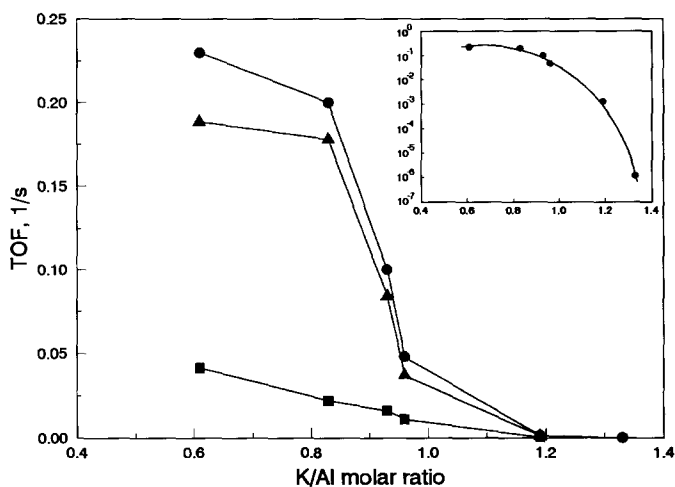


Fig. 6. Effect of support acidity on neopentane hydrogenolysis and isomerization activity for Pt/LTL. Inset shows total TOF as semi-log plot. (■) Isomerization TOF, (▲) hydrogenolysis TOF, (●) isomerization + hydrogenolysis TOF

which is based on the number of exposed platinum atoms, should be higher for catalysts with higher  $H_{sp}/Pt$  ratios. Instead, the TOF for all the catalysts were all about  $0.1 \pm 0.03 s^{-1}$ . Selectivity was constant at 22% isomerization to isopentane and 78% hydrogenolysis. These results indicates that the spilled-over hydrogen had no effect on this reaction.

In contrast, support acidity had a large effect on activity and selectivity (Fig. 6 and Table 2). Isomerization TOF increased more or less linearly with decreasing K/Al ratio, while hydrogenolysis varied in a highly non-linear manner. Hydrogen-

olysis TOF was highest for Pt/LTL(0.61) and Pt/LTL(0.83), but decreased rapidly as the support approached neutrality. Addition of alkali beyond the stoichiometric ion-exchange capacity resulted in a continuing decrease in TOF by several orders of magnitude. Activity modification by K on the Pt surface can be ruled out, since EXAFS analyses have shown that there is no K in the first coordination shell of Pt [16]. The increase in hydrogenolysis selectivity with support acidity is consistent with what has been previously reported [29,30], although the highly non-linear behavior has not been previously reported. Propane hydrogenolysis showed similar trends in activity (Table 2). Equilibrium amounts of propene were formed in all cases, including the highest K/Al support, which shows that the platinum was accessible and that the low hydrogenolysis activity for this catalyst was not due to blockage of the pores by excess alkali.

It has been suggested that spilled-over hydrogen might affect catalytic activity indirectly. For example, it is possible that spilled-over hydrogen keeps the platinum surface clean by hydrogenation of coke precursors [31]. Alternatively, the higher activity with acidic supports could result from adsorption of feed poisons by the acidic support [14], also keeping the platinum surface clean. In either case, the lower activity for platinum on non-acidic supports would result from a reduction in the fraction of exposed metal surface by coking or adsorption of poisons. Measurement by CO chemisorption of exposed platinum surface of Pt/LTL(0.61) and Pt/LTL(1.19) before and after reaction of neopentane showed no change in the fraction of exposed metal atoms for either catalyst. The nearly 200-fold lower activity for Pt/LTL(1.19) compared to Pt/LTL(0.61) cannot, therefore, be a result of differences in the coverage of the metal surface by coke or poisons.

There is considerable evidence indicating that the electronic properties of the metal can be modified by interaction with the support [32,33]. Platinum on acidic supports is believed to be 'electron deficient', and generally displays higher catalytic activity than on non-acidic supports [17,18]. In this study, we have shown that specific activity continues to decrease for K/Al ratios larger than 1.0, where acidic hydroxyls are not present, indicating that the metal-support interaction does not require the presence of acidic hydroxyls. Rather, we conclude that the interaction is with the surface oxide layer, and that this interaction is dependent on the acidity/basicity of the support. While the details of how this interaction occurs are not yet understood, we propose that the observed activity differences result from a modification of the metal by interaction with the support.

#### 4. Conclusions

Platinum clusters are capable of spilling over large quantities of hydrogen onto the support. The capacity of the support is limited, and is proportional to the density of acidic hydroxyl groups. This relationship suggests that spilled-over hydrogen may be held at or near these acidic hydroxyl groups.

Spilled-over hydrogen appears to be relatively stable and unreactive — it does not react with gas-phase oxygen. It does not enhance catalytic activity for hydrogenolysis reactions, either by generating catalytic centers or itself reacting with hydrocarbons, nor does it act to keep the metal surface from coking. While there is a general correlation between specific activity and the amount of spilled-over hydrogen, this correlation is due to the mutual dependence of both specific activity and spill-over capacity on support acidity. The changes in specific activity observed for supports with differing acidity/basicity appear to be due to modification of the electronic properties of the supported metal. These changes result from interaction with the oxide surface, rather than interaction with acidic hydroxyls.

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