

## The Role of Spillover Hydrogen in the Hydrogenolysis of Neopentane

J. T. Miller<sup>1</sup>, F. S. Modica<sup>1</sup>, B. L. Meyers<sup>1</sup>, and D. C. Koningsberger<sup>2</sup>

<sup>1</sup>AMOCO Research Center  
150 W. Warrenville Rd.  
Naperville, IL 60566-7011

<sup>2</sup>Laboratory of Inorganic Chemistry and Catalysis  
Debye Institute  
University of Utrecht  
P.O. Box 80083  
3508 TB Utrecht, The Netherlands

### INTRODUCTION

There is considerable evidence for the spillover of hydrogen species by supported metals, and this subject has been thoroughly reviewed (1,2). Depending on the nature of the support and the pretreatment conditions, spilled-over hydrogen may be catalytic or may activate the support to become catalytic (3-7).

It is well known that the hydrogenolysis activity is higher for noble metals on acidic supports compared to non-acidic supports (8). In a recent study, the amount of spilled-over hydrogen was also shown to be higher for platinum on acidic supports and, generally paralleled the propane hydrogenolysis TOF (9).

In this study, two series of catalysts were investigated: one with varying platinum loading on an acidic support, and another with constant platinum loading and varying zeolite acidity. Comparison of the neo-pentane hydrogenolysis TOF shows that while activity correlates with the amount of spilled-over hydrogen, the spilled-over hydrogen sites are not catalytic and are not re-

sponsible for the large differences in hydrogenolysis rates.

### EXPERIMENTAL

The acidity of the K-LTL zeolite support was varied by either impregnating with KNO<sub>3</sub> or exchanging with ammonium nitrate to give K/Al ratios ranging from 0.61 to 1.33. All LTL zeolites were calcined at 400°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 tetraamine platinum (II) nitrate, followed by drying at 125°C.

H<sub>2</sub> TPD were obtained after an initial reduction at 300°C. The temperature was ramped at 10°C per

minute up to 700°C, then held for 1 hr.

The conversion of neo-pentane was conducted at atmospheric pressure in a fixed-bed reactor using 1.25 vol% neo-pentane in H<sub>2</sub>. The catalyst was pre-reduced at the reaction temperature, either 325 or 350°C, and conversion was adjusted to between 0.5 and 5% by varying space velocity. The specific activity of Pt/LTL(1.33) was too low to measure at 350°C. Therefore, the activities for both Pt/LTL(1.19) and Pt/LTL(1.33) were determined at 475°C, and the activity of Pt/LTL(1.33) at 350°C was estimated assuming the same ratio with Pt/LTL(1.19) at 350°C as was observed at 475°C. TOF was calculated based on volumetric H<sub>2</sub> chemisorption.

### RESULTS

#### Hydrogen Temperature Programmed Desorption (H<sub>2</sub>-TPD)

The H<sub>2</sub>-TPD profiles for varying Pt loadings on LTL(0.61) are shown in Figure 1, with the integrated areas of the TPD peaks given in Table 1. As observed previously, broad overlapping hydrogen desorptions are observed at 150 (Peak I) and 275°C (Peak II). These peaks are due to chemisorbed hydrogen (Peak I) and hydrogen trapped in the metal-support interface (Peak II) (9-10). Additionally, higher temperature desorptions are present at 475°C (Peak III) and 625°C (Peak IV). These higher temperature peaks are due to desorption of hydrogen which was spilled-over onto the support during reduction (9-10). While all four peaks increase in size with increasing Pt loadings, there are changes in the relative sizes of these peaks. Both the

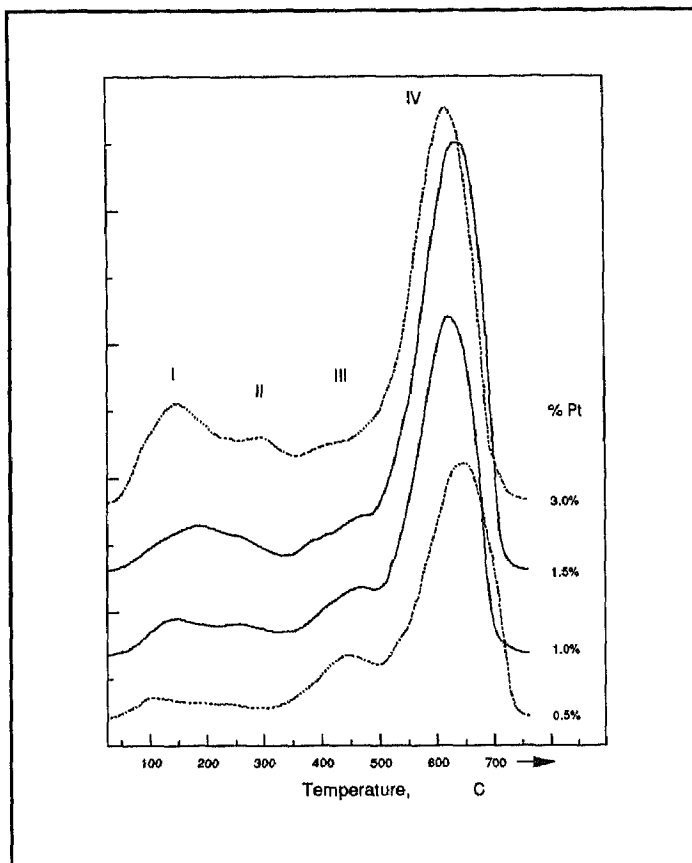


Figure 1. TPD of Pt/LTL (0.61) with various Pt loadings as indicated.

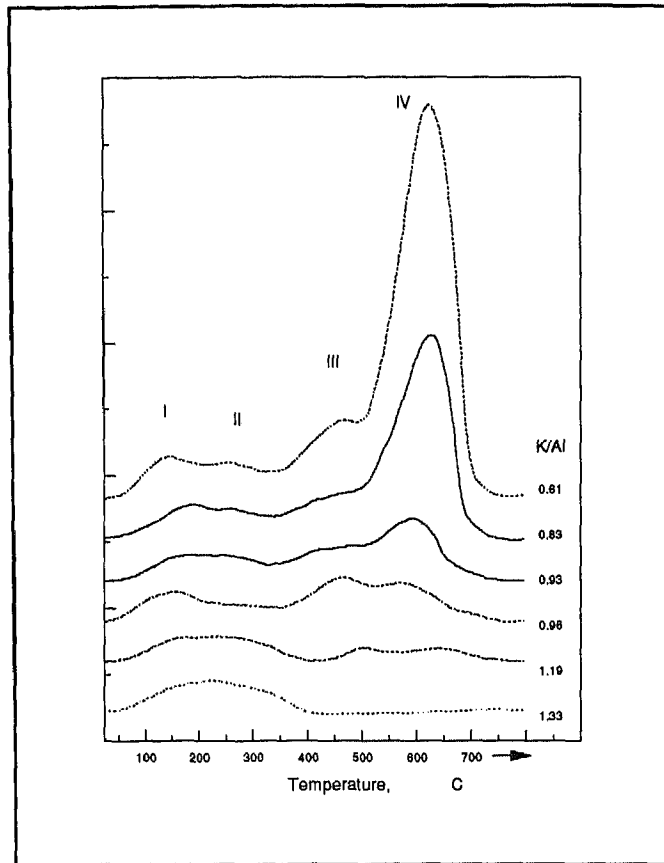


Figure 2. TPD of Pt/LTL with various levels of ion-exchange (K/Al as indicated).

chemisorption and interfacial hydrogen peaks increase in proportion to the Pt loading, as would be expected. The higher temperature peaks increase more slowly, suggesting that the ability of the support to accept spilled-over hydrogen may be approaching saturation.

The effect of changing support acidity on the amount of hydrogen spillover is shown in Figure 2 and Table 1. Peaks I and II do not change with support acidity, and this is consistent with their assignment as being due to hydrogen associated with the platinum. As the K/Al ratio is increased from 0.61 (acidic) to 1.33 (basic), the quantity of spilled-over hydrogen (Peaks III and IV) decreases dramatically. On acidic supports the quantity of spilled-over hydrogen approaches 10 times the amount of chemisorbed hydrogen, while on basic supports we observe virtually no spilled-over hydrogen.

#### Neo-Pentane Hydrogenolysis

Analysis of the reaction products at conversions from 0.5 to 5.0% by the Delplot method (11) indicated that methane, ethane, propane, isobutane and isopentane were primary reaction products. The initial selectivity was obtained by extrapolation of these plots to zero conversion. The selectivities were not affected by either the platinum loading or the acidity/basicity of the support. Selectivity to isopentane (isomerization selectivity) was 22%.

The activities for neo-pentane conversion are shown in Figure 3. The TOF for Pt/LTL(0.61) was unaffected by the platinum loading from 0.5 to 3.0 wt% Pt. Over this same range, the amount of spilled-over hydrogen decreased from 14.2 to 4.1 hydrogen atoms per platinum atom.

Although the platinum loading had no effect on the TOF, changes in the acidity/basicity were accompanied by large changes in the specific activity. TOF was highest for Pt/LTL(0.61), but decreased only slightly upon increasing the K/Al ratio to 0.83. Unexpectedly, small additional increases in K/Al resulted a rapid decline in activity. Addition of alkali beyond the stoichiometric ion-exchange capacity results in a continuing decrease in TOF by several orders of magnitude.

#### DISCUSSION

At high platinum loadings the total amount of spilled-over hydrogen for LTL(0.61) asymptotically approaches a saturation coverage of about  $5 \times 10^{14}$  atoms/cm<sup>2</sup>. This capacity is much smaller than the surface oxygen density of ca.  $1 \times 10^{16}$  atoms/cm<sup>2</sup>, showing that only about 5% of the surface oxygens in

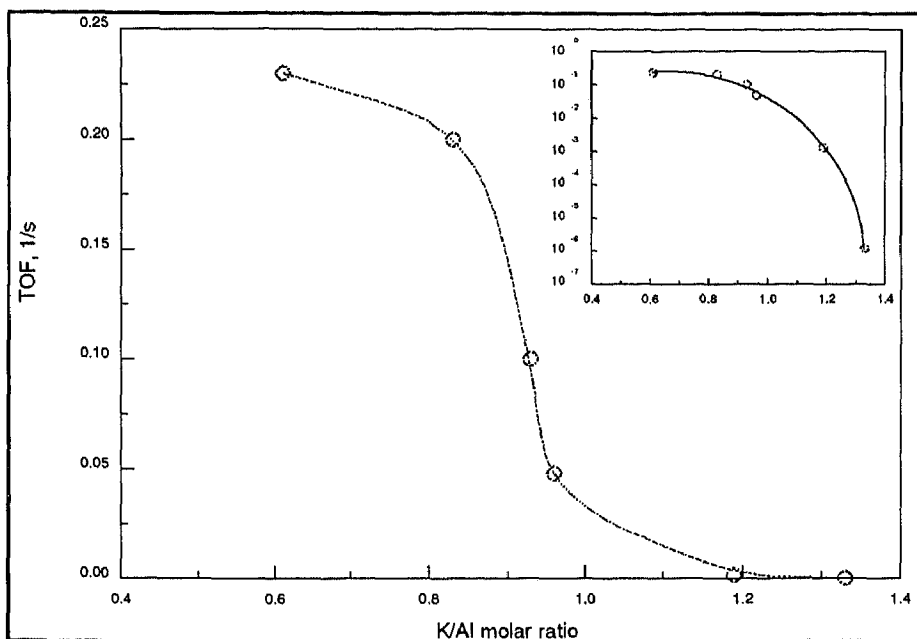


Figure 3. Effect of support acidity on activity of supported platinum. Inset shows same data as semi-log plot.

LTL(0.61) are capable of holding a spilled-over hydrogen atom. Furthermore, the capacity of the support for spilled-over hydrogen declines with potassium exchange, and is directly proportional to the number of framework aluminum atoms minus the number of potassium atoms. This strong correlation of spillover capacity with acidity suggests that the primary support site for spilled-over hydrogen is the acidic hydroxyl.

While the total amount of spilled-over hydrogen increased with platinum loading, the ratio of spilled-over hydrogen to platinum atoms decreased substantially. Over this same range, however, the hydrogenolysis TOF was unchanged. This indicates that the spilled-over hydrogen does not generate catalytic centers, nor does it increase the activity of the platinum clusters.

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 (12). Alternatively, the higher activity with acidic supports could result from adsorption of feed poi-

sons by the acidic support (13), 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(1.19) before and after reaction of neo-pentane shows no change whatsoever in the fraction of exposed metal atoms. 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.

Although spilled-over hydrogen does not directly influence activity, both increase with increasing support acidity. There is considerable evidence indicating that the electronic properties of the metal can be modified by interaction with the support (14). Platinum on acidic supports is believed to be "electron deficient", and generally displays higher catalytic activity than on non-acidic supports (8, 15). In this study, we have shown that specific activity continues to decrease for K/Al ratios larger

Table 1.  
Quantities of Hydrogen Desorbed by H<sub>2</sub>-TPD<sup>1</sup>

Catalyst (K/Al ratio)	Total	Chemisorbed <sup>2</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(0.81)	10.8	0.70	0.4	9.7
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>1</sup> Values reported as H/Pt molar ratios.

<sup>2</sup> Values determined from volumetric chemisorption.

than 1.0, where acidic hydroxyls are not present, and that the metal-support interaction, therefore, 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. Spilled-over hydrogen, while also dependent on support acidity, does not generate catalytic centers nor does it affect catalyst activity.

## 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 correlation suggests that spilled-over hydrogen may be held at or near these acidic hydroxyl groups. Although there is a general trend of increasing hydrogenolysis TOF with the increasing amounts of spilled-over hydrogen, there is no causal relationship. Spillover sites do not form catalytic centers, nor do they enhance hydrogenolysis activity. Differences in specific activity resulting from

changes in the support acidity/basicity are due to modification of the electronic properties of the supported metal. These electronic changes, however, do not alter the reaction selectivity.

## LITERATURE CITED

- (1) Bond, G. C., Spillover of Adsorbed Species; *Studies in Surface Science and Catalysis*, 17; G. M. Pajonk, S. J. Teichner and J. E. Germain, eds., Elsevier, 1 (1983).
- (2) Conner, C. W., Jr., Pajonk, G. M. and Teichner, S. J., *Adv. Catal.*, 34, 1 (1986).
- (3) Sinfelt, J. M. and Lucchesi, P. J., *J. A.C.S.*, 85, 3365 (1963).
- (4) Lacroix, M., Pajonk, G. M. and Teichner, S. J., *Bull. Soc. Chim. Fr.*, 94, pp (1981).
- (5) Sermon, P. A. and Bond, G. C., *J. Chem. Soc., Farad. Trans.*, 76, 889 (1980).
- (6) Fujimoto, K., Masamizu, K., Asaoka, S. and Kunigi, T., *J. Chem. Soc. Jpn.*, VV, 1062 (1976).
- (7) Khoobiar, S., *J. Phys. Chem.*, 68, 411 (1964).
- (8) Dalla Betta, R. A. and Boudart, M., *Proc. 5th Int. Cong. on Catal.*, 2, 1329 (1973).
- (9) Miller, J. T., Meyers, B. L., Modica, F. S., Vaarkamp, M., and Koningsberger, D. C., *J. Catal.*, submitted.
- (10) Vaarkamp, M., Modica, F. S., Miller, J. T. and Koningsberger, D. C., *Catal. Lett.*, submitted.
- (11) Bhore, N. A., Klein, M. T. and Bischoff, K. B., *Ind. Eng. Chem. Res.*, 29, 313 (1990).
- (12) Parera, J. M., Traffano, E. M., Musso, J. C. and Pieck C. L., Spillover of Adsorbed Species; *Studies in Surface Science and Catalysis*, 17; G. M. Pajonk, S. J. Teichner and J. E. Germain, eds., Elsevier, 101 (1983).
- (13) Schlatter, J. C. and Boudart, M., *J. Catal.*, 24, 482 (1972).
- (14) Gallezot, P., *Catal. Rev. Sci. Eng.*, 20, 121 (1979)
- (15) Homeyer, S. T., Karpinski, Z., and Sachtler, W.M.H., *J. Catal.*, 123, 60 (1990)