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HYDROGEN STORAGE VIA POLYHYDRIDE COMPLEXES

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Abstract

The reversible dehydrogenation of $NaAlH_4$ is catalyzed in toluene slurries of the $NaAlH_4$ containing the pincer complex, $IrH_4\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$. The rates of the pincer complex catalyzed dehydrogenation are about five times greater those previously found for $NaAlH_4$ that was doped with titanium through a wet chemistry method. Homogenization of $NaAlH_4$ with 2 mole % $Ti(OBu^n)_4$ under an atmosphere of argon produces a novel titanium containing material. TPD measurements show that the dehydrogenation of this material occurs about 30 °C lower than that previously found for "wet" titanium doped $NaAlH_4$. In further contrast to "wet doped" $NaAlH_4$, the dehydrogenation kinetics and hydrogen capacity of the novel material are undiminished over several dehydriding/ hydriding cycles. Rehydrogenation of the titanium doped material occurs readily at 170 °C under 150 atm of hydrogen. TPD measurements show that about 80% of the original hydrogen content (4.2 wt %) can be restored under these conditions.

Introduction

For decades, hydrogen has been targeted as the utopian fuel of the future due to its abundance and environmental friendliness. A major difficulty in the utilization of hydrogen as a fuel is the problem of onboard hydrogen storage. High pressure and cryogenic hydrogen storage systems are impractical for vehicular applications due to safety concerns and volumetric constraints. This has prompted an extensive effort to develop solid hydrogen storage systems for vehicular application. Metallic hydrides (Sandrock et al.

1992; Sandrock 1995), activated charcoal (Carpetis and Peshka, 1980; Agarwal et al., 1987) and carbon nanotubules (Dillon et al., 1997) have been investigated as hydrogen carriers. Unfortunately, despite decades of extensive effort, especially in the area of metallic hydrides, no material has been found which as has the combination of a high gravimeteric hydrogen density, adequate hydrogen dissociation energetics, and low cost required for commercial vehicular application (Suda and Sandrock, 1994).

The dehydrogenation of $NaAlH_4$ is known to occur by a multistep process involving the reactions seen in equations 1 and 2 (Dymova, 1975). This process is thermodynamically

$$3\ NaAlH_4 \text{ ---------->} Na_3AlH_6 + 2\ Al + 3\ H_2 \qquad (1)$$

$$Na_3AlH_6 \text{ ---------->} 3\ NaH + Al + 3/2\ H_2 \qquad (2)$$

favorable at moderate temperatures. However, it is characterized by very slow kinetics (Dymova, 1975) and reversibility only under severe conditions (Dymova, 1974). Thus despite favorable thermodynamics and a high available hydrogen weight percentage, $NaAlH_4$ has generally been precluded from consideration as a potential hydrogen storage material and there has been very little effort to develop this material as a hydrogen carrier. This thinking has been changed recently by Bogdanovic and Schwickardi. Their pioneering study demonstrated that upon doping with selected titanium compounds, the dehydrogenation of anionic aluminum hydrides could be kinetically enhanced and rendered reversible under moderate conditions (Bogdanovic and Schwickardi, 1997). These findings represent a breakthrough in the application of this class of hydrides to hydrogen storage. However, further kinetic enhancement of the dehydriding and rehydriding processes are required to produce a material which is suitable for practical vehicular applications. Also the hydrogen capacity of Bogdanovic's material diminished upon extended cycling. It is therefore necessary to find improved catalysts of increased stability.

We are developing $NaAlH_4$ based hydrogen storage materials which contain catalytic additives. The polyhydride complex, $IrH_4\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ was found to be an unusually robust and active catalysts for the reversible dehydrogenation of cycloalkanes to arenes (Gupta et al, 1997). This suggested that it might act as a catalyst for the reversible dehydrogenation of $NaAlH_4$. We have also explored the effect of variation in the method of the introduction of titanium to this host material.

Results

Pincer Complex Catalyzed Dehydrogenation of $NaAlH_4$.

The pincer polyhydride complex, $IrH_4\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ examined as a catalyst for the dehydrogenation of $NaAlH_4$. As seen in Figure 1, hydrogen is evolved from toluene slurries of the $NaAlH_4$ containing the pincer catalyst at rates about five times greater those found $NaAlH_4$ which was doped with an equimolar amount of titanium through the method of Bogdanovic (Bogdanovic and Schwickardi,, 1997).

Preparation of the Novel Titanium Containing Material.

Freshly recrystallized $NaAlH_4$ was added to prescribed amounts of $Ti(OBu^n)_4$ under an atmosphere of argon. The originally colorless mixture was homogenated using a mortar and pestle until it become red-violet. The resulting paste was visually very distinct from the brown powders obtained through Bogdanovic's procedure for producing titanium doped materials. Elemental analysis showed that only trace amounts of carbon are present in this material.

We examined the dehydrogenation of this novel material in the solid state. Clearly the material produced by this method exhibits catalytic effects which are an order of magnitude improved over the materials originally prepared by Bogdanovic or those containing the polyhydride catalyst.

Thermal programmed (TPD) measurements.

TPD measurements were made on samples of undoped $NaAlH_4$ (**1**); $NaAlH_4$ which was doped with titanium through the Bogdanovic method (**2**); and $NaAlH_4$ which was doped with titanium through the method described above. Excellent agreement was found among samples of 2 and 3 which were prepared independently. The data obtained for **2** is also consistent with the finding of Bogdanovic. The TPD measurement of samples of the three different materials are plotted in Figure 2. While the catalytic effect of titanium is evident for both **2** and **3**, the temperature of dehydrogenation of **3** is seen to be 30 °C lower than that of **2**.

A priori, it seemed possible that the differences observed in the dehydriding behavior of **2** and **3** were simply due to variation in the level of titanium loading in the two materials. In order to probe this possibility, independent TPD measurements were made on samples of **2** and **3** which were prepared using 1.0, 2.0, and 4.0 mol % $Ti(OBu^n)_4$ respectively. As seen in Figure 3 variation in the amount of $Ti(OBu^n)_4$ used in the preparation showed little effect on the dehydrogenation temperature. However, increasing the titanium content of the material does show the expected gravimetric effect of lowering the H/M wt %. These results indicate that only a fraction amount of titanium introduced into the materials is catalytically active. Furthermore, there is clearly a significantly larger amount of catalytically active titanium in **2** than **3**. However, we can not say at this point why the dry doping method is more effective than the wet doping method for the generation of the active titanium sites. It is possible that the action of wet doping method is restricted to the surface of the hydride while the dry doping method introduces active titanium sites in the bulk. Thus our homogenization technique may be crudely equivalent to ball milling of the material.

Cycling Studies

Since the reversibility is a requirement for most applications, the behavior of rehydrogenated samples were investigated. In an initial set of experiments, samples were rehydrided under 1600 psi of hydrogen pressure at 200 °C. Under these conditions, only about 40% of the hydrogen in the original material is replaced at the moderate hydrogen pressure. TPD measurements were then made on the rehydrided samples. Figure 4 shows the percentage of hydrogen desorbed from the samples as a function of temperature, considering the desorbed hydrogen at the first cycle to be 100%. The uptake is clearly less than found in the original sample showing that only partial hydrogenation could be obtained under this conditions. The second dehydriding cycle of **3** occurs at nearly the same temperature observed for the first. This sharply contrasts the dehydriding behavior of **2** for which dehydriding occurs at a significantly higher temperature, closer to that of **1**, in the second cycle.

In a second set of experiments, samples were rehydrided at 150 atm and 170 °C. As seen in Figure 5, TPD measurements show that about 80% of the original hydrogen content (4.2 wt %) of **2** and **3** can be restored under these conditions. However, unlike the Bogdanovic material, **2**, for which the capacity drops to 3.8 wt % on the second cycle, no loss of hydrogen capacity was observed for our novel material, **3** through the 5 dehydrogenation/rehydrogenation cycles. Also TPD studies show that the dehydrogenation temperature of **2** drifts back toward that of **1** on cycling. A 10 °C rise in is observed for second cycle alone. The dehydrogenation temperature of **3**, on the other hand, remains constant through the first 5 cycles.

Conclusion

The polyhydride pincer complex and titanium doping have been observed to catalyze the dehydrogenation kinetics of $NaAlH_4$. The greatest catalytic effect was observed for $NaAlH_4$ in which titanium was induced through a solid state method. These results demonstrate the catalytic effect of titanium dopants first reported by Bogdanovic was only a starting point and that further improvement of the kinetics of the reversible dehydriding of $NaAlH_4$ is possible. Furthermore, we have shown that it is possible to introduce catalysts into $NaAlH_4$ such that enhanced dehydrogenation kinetics and the attainable hydrogen capacity are undiminished over several dehydriding/ hydriding cycles.

Future Work

The material will be monitored through 100 dehydrogenation/rehydrogenation cycles in order to determine its long term stability. The equilibrium hydrogen pressures and other thermodynamic parameters will be determined from PCT curves obtained at 100 °C above. The kinetics of the dehydrogenation at these temperatures will also be determined with more precision that our preliminary data allows. We will continue to modify the hydride system and study the dehydriding kinetics of the resulting materials.

References

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FIGURE CAPTIONS

Figure 1. Dehyrogenation of $NaAlH_4$ at 120 °C.

Figure 2. Thermal programmed desorption (2 °C min^{-1}) of hydrogen from undoped, wet titanium doped, and dry titanium doped $NaAlH_4$.

Figure 3. Thermal programmed desorption (2 °C min^{-1}) of hydrogen from samples of dry titanium doped $NaAlH_4$ prepared from 1, 2, and 4 (0.5x, x, and 2x) mol % $Ti(OBu^n)_4$.

Figure 4. Thermal programmed desorption (2 °C min^{-1}) of hydrogen from dry titanium doped $NaAlH_4$ following one dehydrogenation/rehydrogenation cycle. 100 % corresponds to the amount of hydrogen released in the first dehydrogenation.

Figure 5. Thermal programmed desorption (2 °C min^{-1}) of hydrogen from dry and wet titanium doped $NaAlH_4$ after 3 cycles of dehydrogenation/rehydrogenation.

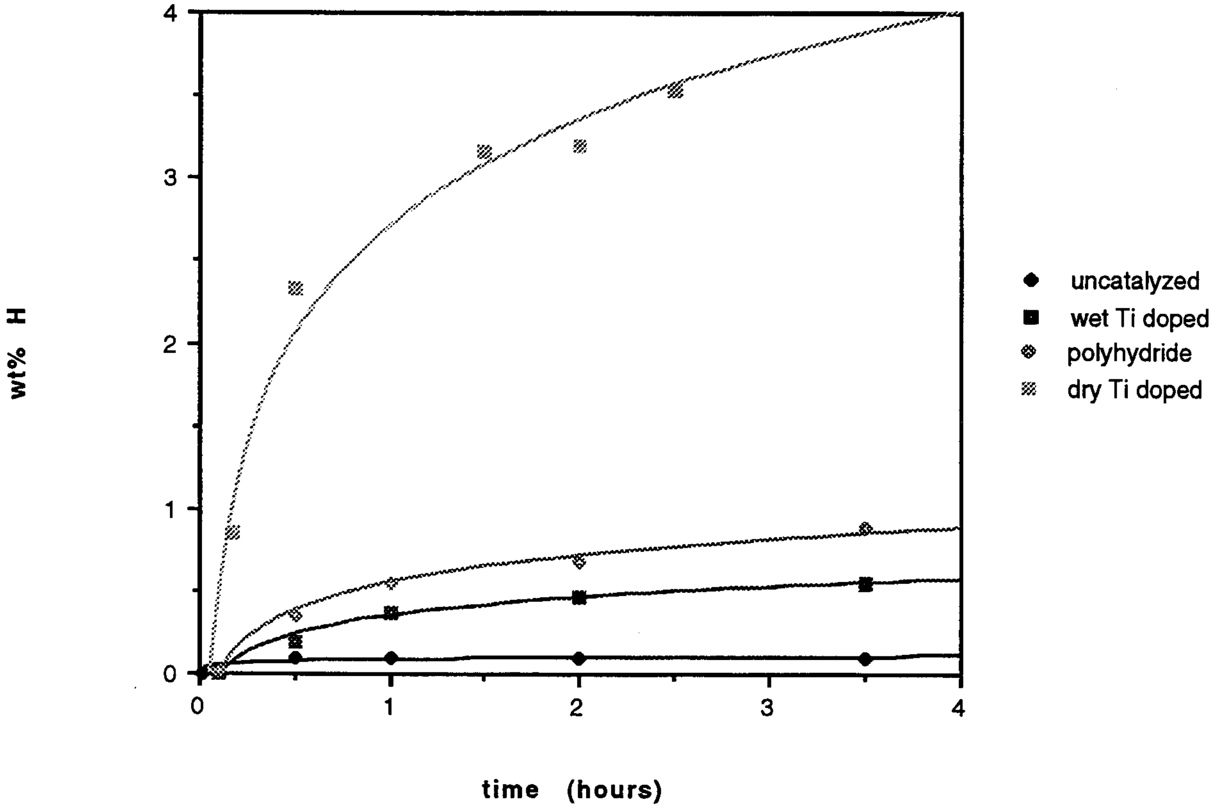

4
3
2
1
0
wt% H
0
1
2
3
4
time (hours)
● uncatalyzed
■ wet Ti doped
▨ polyhydride
▨ dry Ti doped

Figure 1

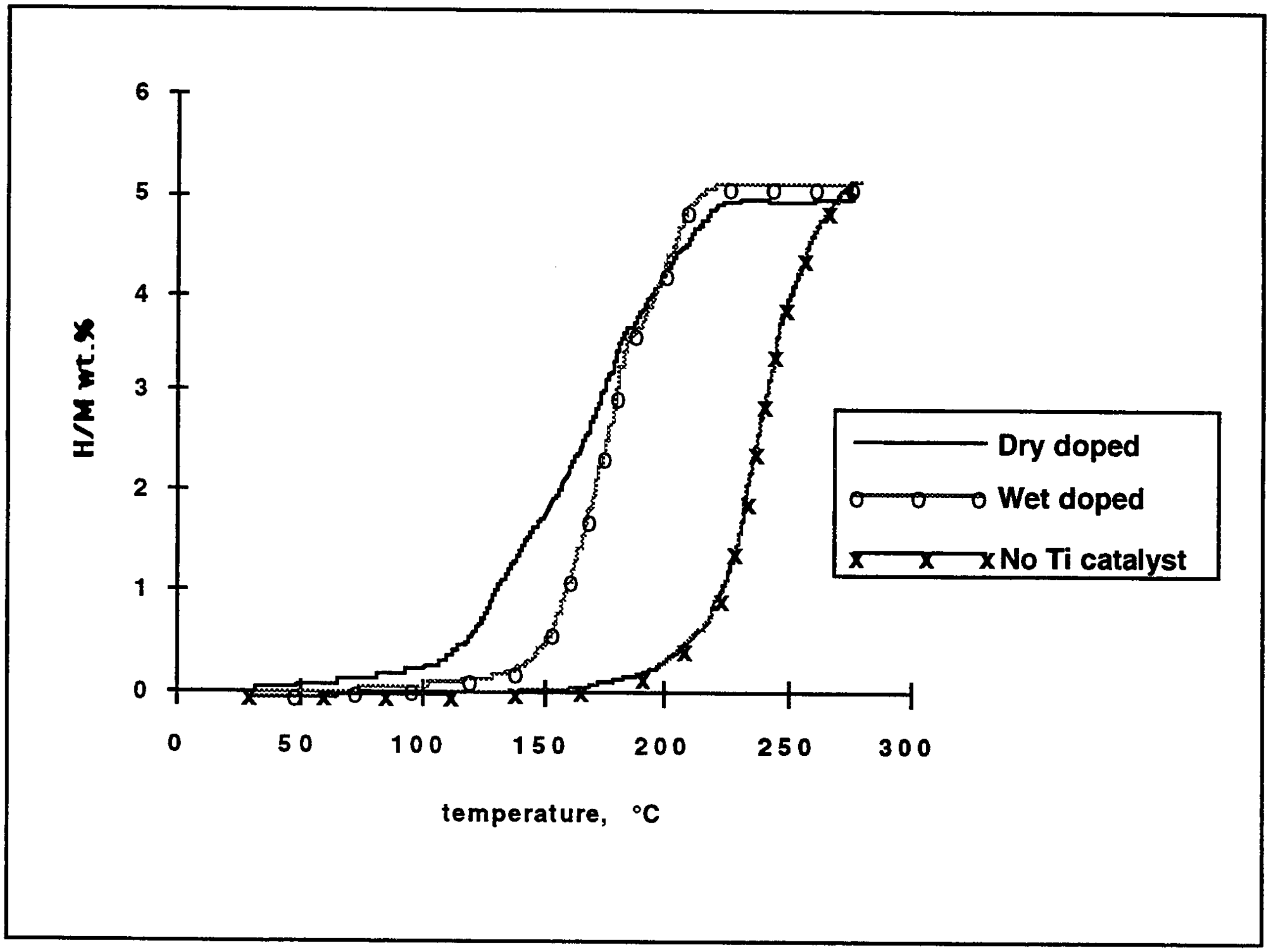

6
5
4
3
2
1
0
H/M wt.%
0
50
100
150
200
250
300
temperature, °C
Dry doped
Wet doped
No Ti catalyst

Figure 2

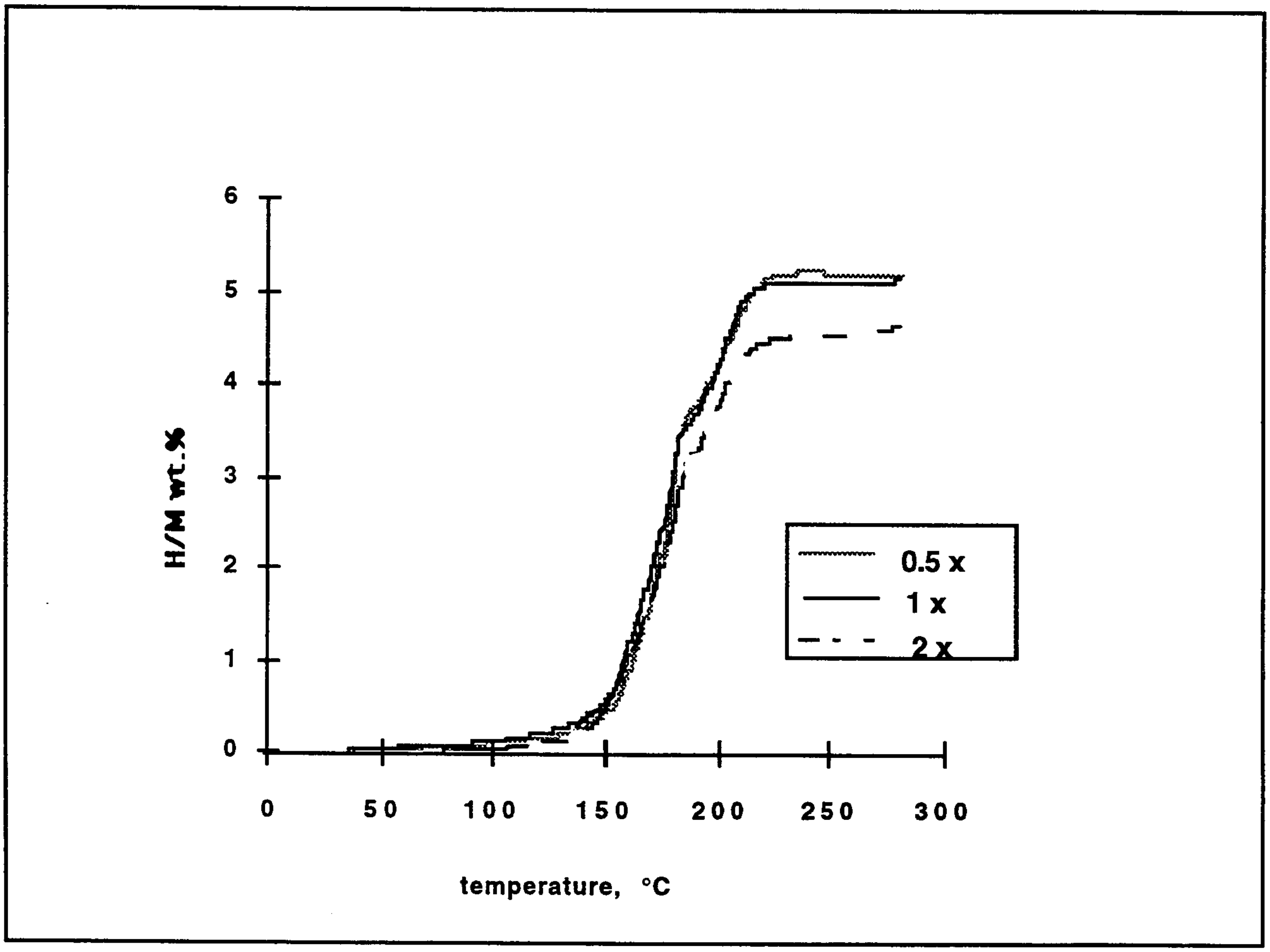
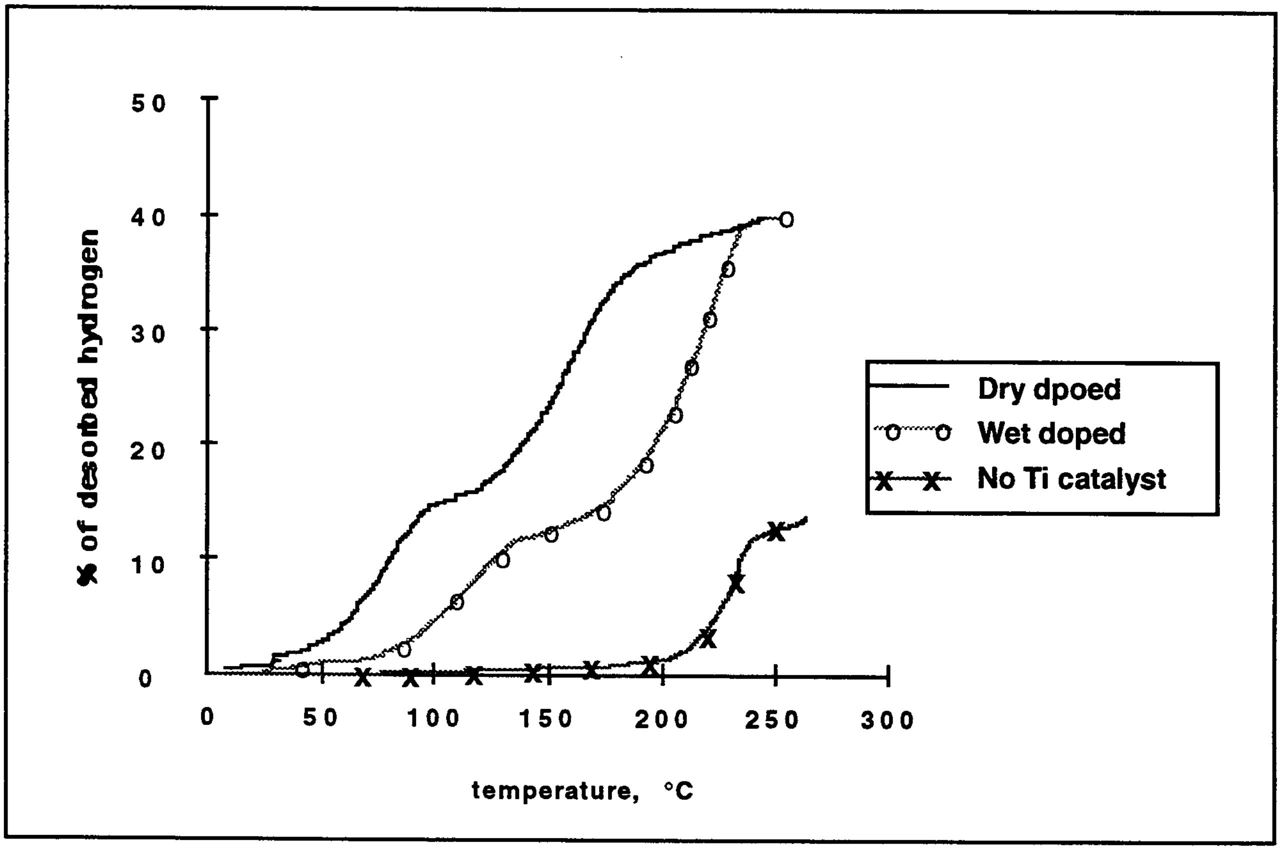


Figure 3



50
40
30
20
10
0
% of desorbed hydrogen
0
50
100
150
200
250
300
temperature, °C
Dry dpoed
Wet doped
No Ti catalyst

Figure 4

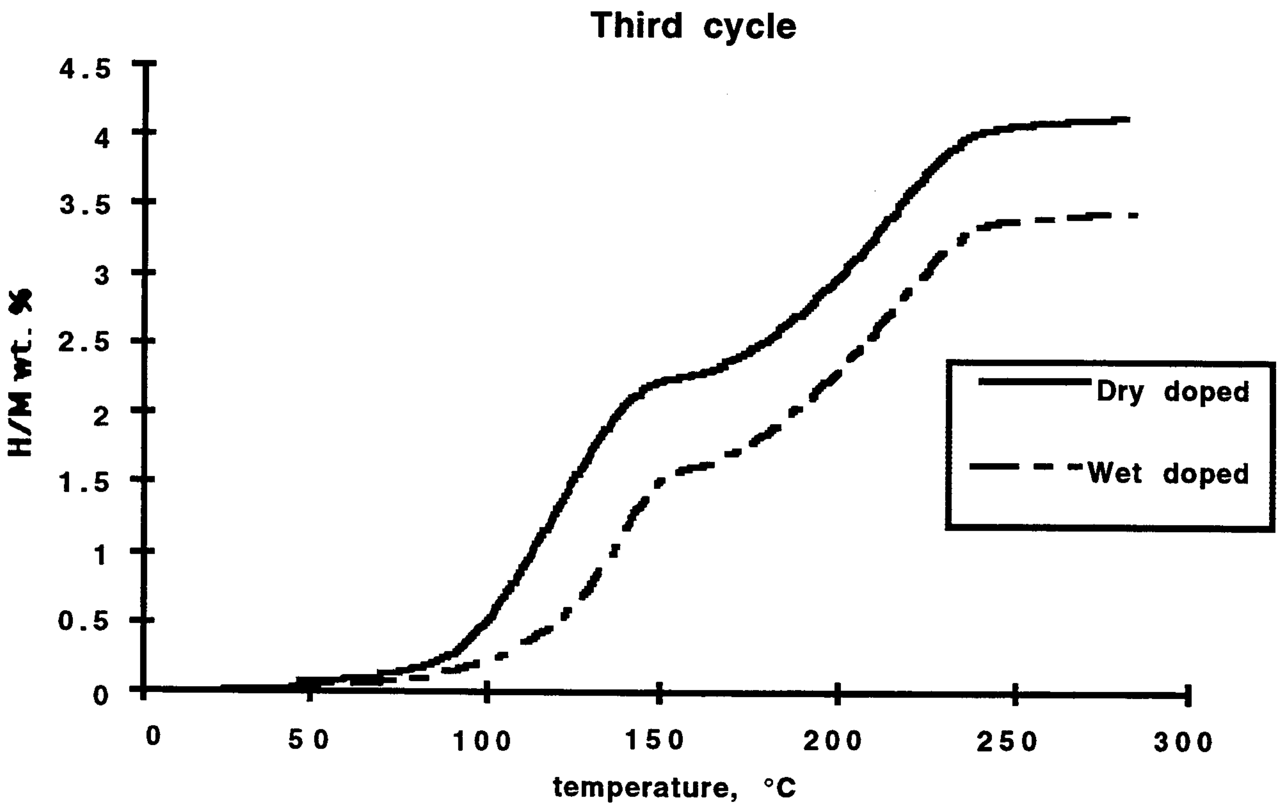

Third cycle
H/M wt. %
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
50
100
150
200
250
300
temperature, °C
Dry doped
Wet doped

Figure 5