Use of Hydride-forming Metals as Renewable Chemical Reagents: the Dehydrogenation of Isobutane to Isobutene

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The conversion of isobutane into isobutene was accomplished over hydride-forming metals (Ti) and alloys (TiVFe); the dehydrogenation could be carried out in a cyclic manner.

Metals and intermetallic compounds having the ability to dissolve large amounts of hydrogen are unique materials with properties of great potential value.[1] The use of these materials as H_2 storage media has long been recognized and much research to date has been directed towards development of practical fuel storage systems.[1—4]

The chemical use of these materials has received much less attention. Since hydrogen is involved in many industrial chemical and petrochemical processes, exploration of these unique materials in such applications is warranted. Potential chemical applications include use of hydrogen dissolving metals and alloys as catalysts and as renewable chemical reagents. Several examples relating to catalytic hydrogenations are known.[5—7]

The present work concerns the use of a hydrogen dissolving metal or alloy to drive an otherwise thermodynamically unfavourable reaction. The metal or alloy is used initially in the unhydrided state. Formation of the metal hydride provides negative free energy for the desired reaction, equation (1).

$$C_nH_{2n+2} + \underbrace{M \rightarrow C_nH_{2n} + MH_2}_{-H_2} \qquad (1)$$

Dehydrogenation reactions are frequently thermodynamically unfavourable at moderate temperatures. In practice, O_2 is often employed to drive the reaction through formation of H_2O. The same can be accomplished by forming metal hydride and the absorbed H_2 can either be recovered in a subsequent regeneration cycle or utilized in a hydrogenation.[5] To the authors' knowledge, this application has not appeared in the literature.

As an example, conversion of isobutane into isobutene in the presence of titanium (and other species) was examined as a model system on which to test the concept, equation (2).†

$$\text{i-}C_4H_{10}(g) + Ti(s) \rightarrow \text{i-}C_4H_8(g) + TiH_2(s) \qquad (2)$$

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† The dehydrogenation reactions were carried out in a 1.27 cm (1/2″) outer diameter stainless steel tubular reactor shaped in the form of a 'U'. The catalyst was supported on a stainless steel porous disc which was welded into one of the arms of the reactor. The reaction temperature was monitored by a thermocouple inserted into the bed. Hydrocarbons were passed through a silica gel–molecular sieve dryer and oxygen trap before entering the reactor. The effluent from the reactor was fed directly into a gas chromatograph. Hydrocarbon products from the isobutane reaction were analysed (flame-ionisation detector) by means of a Durapak on Porasil C (Supelco) column in series with a Carbopack/0.19% picric acid (Supelco) column at 343 K. The catalyst was either an intimate mixture made from 2.25 g Pt on Al_2O_3 catalyst (5 wt.% Pt, Engelhard 14772) and 3.48 g Ti powder or comprised 3.5 g $(Ti_{0.7}V_{0.3})_{0.9}Fe_{0.1}$ (325 mesh).

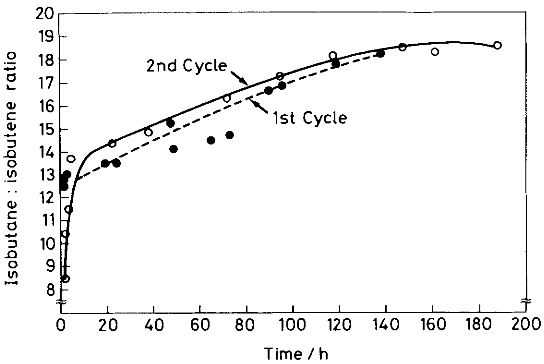

Figure 1. Dehydrogenation of isobutane to isobutene at 641 K over Pt/Al_2O_3–Ti catalyst. Isobutane: isobutene ratio as a function of time.

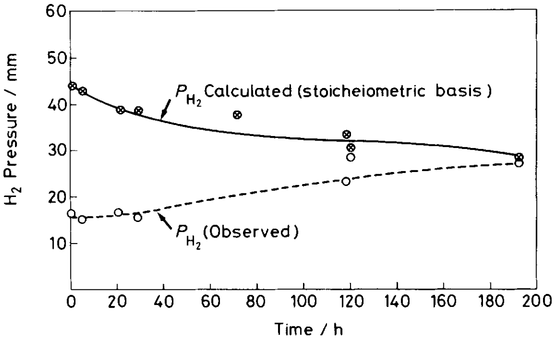

Figure 2. Comparison of observed and calculated H_2 in the reactor effluent from dehydrogenation of isobutane at 641 K. Pt/Al_2O_3–Ti catalyst. Second cycle.

At 25 °C the free energy of formation (kcal mol^{-1})‡ of the various compounds are: −4.99 for i-C_4H_{10}(g),[8a] +13.88 for i-C_4H_8(g),[8b] and −20.6 for TiH_2.[9] Thus, the standard free energy change for reaction (2), $\Delta\bar{G}°$, is −1.7 kcal at 25 °C. As the temperature is raised, $\Delta\bar{G}°$ becomes more negative and the reaction more favourable.

The theoretical i-C_4H_{10} : i-C_4H_8 equilibrium ratio, without removal of H_2, is 19 : 1 (5.3% conversion) at 641 K and 101.3 kPa (1 atm) pressure. An initial modest enhancement of isobutene above the theoretical value was achieved at 641 K and 90 h^{-1} space velocity over a mixture of 5% platinum on alumina and titanium. The Pt/Al_2O_3 served as the catalyst while Ti functioned as an H_2 absorber. Titanium alone showed no catalytic activity.§ In the first cycle, a ratio of 12.5 : 1 (7.4% conversion) was observed initially, the ratio increasing toward the theoretical 19 : 1 value as the Ti became saturated with H_2. Following regeneration of the Ti, by removal of H_2 at 873 K and 0.1 Pa pressure, an initial i-C_4H_{10} : i-C_4H_8 ratio of 8.6 : 1 (10.4% conversion) was observed, which again increased toward 19 : 1.

These results are presented graphically in Figures 1—3. Figure 1 shows the ratio i-C_4H_{10} : i-C_4H_8 with respect to time for two cycles carried out as discussed above. Note that the initial activity in the second cycle is significantly higher than the activity obtained at the beginning of the first cycle. This is attributed to disintegration of the Ti powder and creation of an increased surface area induced by the first hydrogenation–dehydrogenation cycle. The attrition of metal powders, as a result of the action of hydrogen, is a well known process in metallurgy.[2—4]

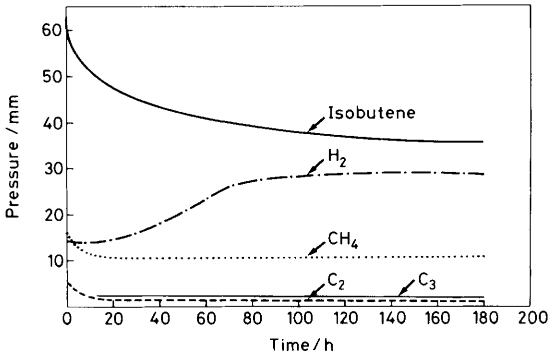

Figure 3. Products from dehydrogenation of isobutane at 641 K. Pt/Al_2O_3–Ti catalyst. Second cycle.

Throughout the run, H_2 was never completely removed from the reaction mixture, its concentration increasing with time as the Ti capacity became exhausted. The amount of H_2 in the reactor effluent varied inversely with the isobutene produced, a result opposite to that expected in the absence of metal hydride formation. The amount of H_2 observed *vs.* the amount expected, without Ti present, is shown in Figure 2. The difference in the two curves represents the amount absorbed by the Ti. Note that the two curves coalesce as the Ti becomes saturated. The H_2 recovered during regeneration corresponded to TiH as the composition of the titanium hydride produced. Good agreement was obtained between the measured and calculated quantity of H_2 absorbed. The recovered H_2 amounted to 86% of the value calculated by graphical integration of the data in Figure 2.

Some hydrogenolysis (CH_4, C_2H_6, C_3H_8) and isomerization (n-C_4H_{10}) products, as expected for a Pt/Al_2O_3 catalyst, were observed in addition to the isobutene.

Following an initial surge, the hydrogenolysis products quickly levelled out to concentrations remaining independent of time. The time profiles of the various products are shown in Figure 3.

The intermetallic compounds, $Ti_{0.63}V_{0.27}Fe_{0.1}$ and $Ti_{0.63}V_{0.225}Fe_{0.1}Pt_{0.045}$ were tried in hopes of avoiding the use of a separate catalyst. Unlike Ti alone, the materials showed some, albeit weak, activity (<1% conversion) for isobutane dehydrogenation. In contrast to the Pt/Al_2O_3 plus Ti system, hydrogen was not detected in the gas phase during the reaction at 623 K. The hydrogen was recovered quantitatively from the metal at 763 K in a subsequent cycle.

Finally, regeneration could also be effected by H transfer. Thus, at 473 K, butadiene was saturated stoicheiometrically by (Ti–V–Fe)H. Significantly, these reactions can be operated consecutively with a feed of 0.1% C_4H_6 in i-C_4H_{10} providing butane at 473 K while isobutene is desorbed at 598 K. As above, a mixture with Pt on alumina increased conversion, but at the expense of selectivity (i-C_4H_8 : n-C_4H_{10} >100 for $Ti_{0.63}V_{0.27}Fe_{0.1}$ *vs.* 15 for $Ti_{0.63}V_{0.27}Fe_{0.1}$ + Pt/Al_2O_3; in the absence of intermetallic species, the ratio was 5 for Pt/Al_2O_3 alone).

In our view, at least two plausible mechanisms can account for the overall process: capture of molecular or spillover (atomic) hydrogen, *i.e.*, $Pt/Al_2O_3 + i\text{-}C_4H_{10} \rightarrow (H)Pt/Al_2O_3 \rightarrow (H)/Al_2O_3 \rightarrow TiH_n$. The latter ultimately derives from

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‡ 1 kcal = 4.18 kJ.

§ Similarly Zr, for which ΔG_F ZrH_2 = −29.3 kcal mol^{-1}, is inactive alone.

dissociatively chemisorbed isobutane while the former results from H atom recombination and release to the gas phase. Whereas the spillover mechanisms cannot be ruled out by the data the appearance of H_2 early in the reaction (Figure 2) suggests that the molecular hydrogen capture mechanism is operating solely or competitively. Since the dissociation pressure of hydrogen over titanium at the reaction temperature used is much lower than that observed, the overall efficiency is controlled by the rate of hydrogen uptake by the metal. This suggests that the use of a fast hydriding alloy, displaying a low dissociation pressure over a wide composition range, would result in improved yields.

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