

APCAT 2205

Simultaneous dehydrogenation of organic compounds and hydrogen removal by hydride forming alloys

W.J.T.M. Appelman, M. Kuczynski¹ and G.F. Versteeg*²

Twente University of Technology, Department of Chemical Engineering, P.O. Box 217, 7500 AE Enschede (Netherlands)

(Received 25 June 1991, revised manuscript received 11 October 1991)

Abstract

The applicability of hydrogen-absorbing metals in dehydrogenation reactions was investigated. Based on thermodynamic considerations, operating ranges were defined within which an increase of the reactant conversion can be achieved owing to an in situ hydrogen removal by the alloy. Low plateau pressures (e.g. < 0.01 MPa) at high temperature (e.g. > 473 K) are required for economic applications. An (economic) improvement of the alkane-to-alkene conversion does not seem feasible owing to the extreme pressure and temperature conditions. In the present study as a model system, 2-propanol was dehydrogenated in a batch process at 473 K and 0.1–1.0 MPa over a Cu/CuO catalyst in the presence of an excess amount of Mg_{2.4}Ni. The hydride forming metal alloy appears to be able to affect the hydrogen balance of the experimental system owing to absorption or desorption. However, an unexpected catalytic effect of the metal hydride was observed towards condensation reactions. Owing to the loss in selectivity, Mg_{2.4}Ni, is not applicable for an improvement of the dehydrogenation processes for secondary alcohols.

Keywords: copper/copper oxide, dehydrogenation, hydride-forming alloys, hydrogen removal, magnesium-nickel alloy, 2-propanol dehydrogenation.

INTRODUCTION AND SCOPE

Reactions between hydrogen and metals have been known for a long time. Owing to this reactivity of hydrogen towards metals it is possible to produce metal hydrides by means of an exothermic and reversible hydrogenation reaction.

The ability of hydride-forming alloys to absorb and desorb large quantities of hydrogen at a relatively constant hydrogen pressure seems very attractive in applications for hydrogen storage and purification. A substantial R&D effort has been invested in the past 20 years to develop economic storage and purification systems. An example of hydrogen storage is the use of metal-hy-

¹Present address: DSM Research BV, P.O. Box 18, 6160 MD Geleen, Netherlands.

²Present address: Chera BV, Anna Bijnsstraat 24, 7552 NC Hengelo, Netherlands, tel. (+31-74)431279, fax. (+31-74)500832.

hydride containers in vehicles using hydrogen as fuel [1]. For purification purposes an interesting continuous process with a circulating hydride-slurry has been proposed [2]. Another property of hydride forming alloys, the large heat effect of the reaction, can be exploited in heat pump applications [3].

Most hydride forming alloys contain metals like nickel, copper and cobalt which are catalytically active towards hydrogenation and dehydrogenation reactions. For instance Imamura et al. [4-7] showed that secondary alcohols can be dehydrogenated by Nd_2Co_7 and Sm_2Co_7 ; however, these alloys had to be pretreated in order to obtain a Raney-type surface on the alloy. In fact, numerous catalysts used in chemical processes involving hydrogen as a reactant are able to form hydrides. Hydrogen transfer and activity, however, is limited to the vicinity of the catalytically active sites and hence the hydride capacity was not exploited to affect the macroscopic hydrogen fluxes or mass balances.

Besides possible catalytic properties, hydride forming alloys can be used to fix the hydrogen partial pressure at a desired, nearly constant level during hydrogenation or dehydrogenation reactions of organic compounds. In this way a shift of the equilibrium conditions can be realized. The idea to apply these alloys in systems with chemical reactions was originally proposed by Fanelli et al. [8]. Their idea was to introduce a sufficiently large hydrogen absorption capacity into the reaction zone of a dehydrogenation process. The hydrogen is removed from the reaction mixture and higher degrees of conversion could be realized owing to the shift in the equilibrium composition.

The idea to use hydride forming alloys in dehydrogenation reactions will be developed on in the present study. Attention will be paid to chemical and thermodynamic aspects of the "in situ" use of metal hydrides in reacting systems.

Dehydrogenation reactions

Dehydrogenations of organic compounds form an important group of industrial processes. The reactions are endothermic equilibrium reactions with a small value for the equilibrium constant K_r . These unfavourable thermodynamics result in operating conditions which are characteristic for dehydrogenation processes. High reactor temperatures are required for a satisfactory high value for K_r and low process pressures are applied for the same reasons. Furthermore, large amounts of heat have to be supplied to the reaction zone and therefore multi-tubular reactors are frequently used for dehydrogenation reactions [9]. Rehydrogenation of the products must be prevented so the residence time in the reaction zone is limited.

In view of these problems "in-situ" removal of the hydrogen produced during a dehydrogenation reaction by absorption in hydride forming alloys might be interesting, aiming at an improvement of the performance of dehydrogenation processes. Provided the process conditions enable the alloy to absorb signifi-

cant amounts of hydrogen, the introduction of an alloy into a dehydrogenation reaction system will directly affect the overall thermodynamics. The equilibrium conversion increases because the hydrogen is removed and the total number of molecules in the mobile phase remains constant enabling higher operating pressures. The heat released in the metal–hydrogen reaction is used “in situ” for the dehydrogenation reaction, resulting in a small overall heat effect leading to a less critical temperature control. Also possible rehydrogenation will be prevented to a considerable extent.

Thermodynamics

For thermodynamic reasons, only a correctly selected combination of a dehydrogenation reaction with a hydride forming alloy will result in the absorption of the produced hydrogen. In order to achieve absorption, the hydrogen pressure in the reaction mixture must exceed the equilibrium pressure of the alloy. An operating range can be defined in which this thermodynamic condition for a dehydrogenation/absorption system is fulfilled. This operating range can be visualised in a pressure–temperature diagram and is defined by two relations describing hydrogen pressures. The lower limit is described by the equilibrium pressure of the metal hydride. The upper limit describes the maximum hydrogen pressure that can be created in a given dehydrogenation reaction without hydride being present. For the combinations of hydride forming alloys and dehydrogenation reactions that are selected on this thermodynamic criterium, the shift in the equilibrium composition can be calculated.

Dehydrogenations are endothermic equilibrium reactions, generally represented by:



with the following expression for the equilibrium constant $K_r(T)$:

$$K_r = \frac{a_B^{\nu_2} \cdot a_{H_2}^{\nu_3}}{a_A^{\nu_1}} = \exp\left(\frac{\Delta S_r}{R} - \frac{\Delta H_r}{RT}\right) \quad (2)$$

Hydrogen reacts with hydride forming alloys according to a reversible and exothermic reaction, generally represented by:



Commonly, the alloys undergo a phase change from the α - to the β -phase during the absorption of hydrogen. The relation between the plateau pressure at which the change takes place and the temperature can be approached with eqn. (4), derived from the Gibbs-energy function:

$$K_m = \frac{a_{\text{MH}_2}}{a_M \cdot a_{\text{H}_2}^{x/2}} = \frac{1}{P_{\text{H}_2}^{x/2}} = \exp\left(\frac{\Delta S_m}{R} - \frac{\Delta H_m}{RT}\right) \quad (4)$$

In order to enable an alloy to absorb hydrogen, the hydrogen partial pressure has to exceed the equilibrium pressure. This condition can easily be checked by comparing the maximum (= equilibrium) pressure that can be obtained in a dehydrogenation reaction with the equilibrium pressure of the alloy. The maximum hydrogen pressure in a dehydrogenation reaction can be estimated from the expression for the equilibrium constant, eqn. (2).

Let us consider the simple dehydrogenation reaction:



Assuming that all the components in the reaction behave as ideal gases, the maximum pressure of component A in the gas phase is defined by its vapour pressure and eqn. (6) can be derived:

$$P_{\text{plateau}} \leq (P_{\text{H}_2})_{\text{equilibrium}} = \sqrt{K_r(T) \cdot P_{v,A}(T)} \quad (6)$$

This correlation defines the range in which dehydrogenation with simultaneous absorption of hydrogen into the alloy is possible. From Fig. 1 it can be concluded that the absorption capacity at the plateau pressure of $\text{Mg}_{2.4}\text{Ni}$ cannot be used to absorb hydrogen from propane or methanol dehydrogenation. For ethanol and 2-butanol dehydrogenation the equilibria can be shifted favourably. The lower and upper limits of the lines describing the maximum hydrogen pressures in Fig. 1 for the different reactants represent the conditions at the boiling point at 1 bar and the critical point conditions of the pure reactant respectively.

At equilibrium conditions for both the dehydrogenation reaction and the

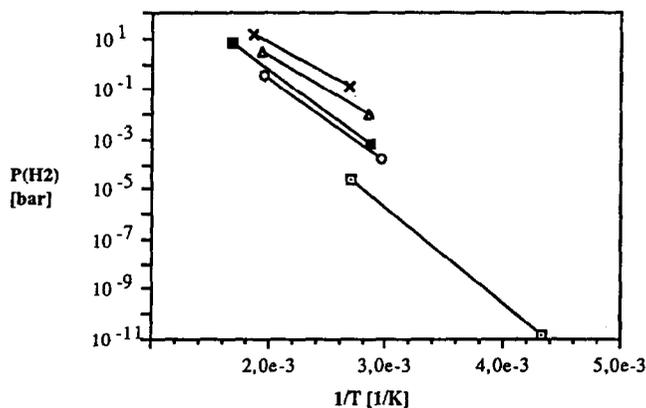


Fig. 1. Operating ranges for some selected organic compounds with $\text{Mg}_{2.4}\text{Ni}$. (□) Propane, (○) methanol, (△) ethanol, (×) sec. butyl alcohol, (■) $\text{Mg}_{2.4}\text{Ni}$.

reaction of hydrogen with the hydride forming alloy, the relative reactant conversion can be expressed as a function of operating pressure and temperature. In Table 1 the conversion expression is presented for reactors with constant volume and constant pressure, the latter e.g. corresponding to a continuously operated chemical convertor. It should be noted that owing to the instantaneous removal of hydrogen by the alloy the equilibrium conversion has become independent from the operating pressure.

In Fig. 2 the conversion at equilibrium for the dehydrogenation reaction of 2-propanol to acetone is given as a function of temperature for three different initial 2-propanol pressures. The lines start at the actual boiling temperatures of 2-propanol. Also in Fig. 2 the equilibrium line under simultaneous removal of hydrogen by virtual unlimited capacity of $Mg_{2.4}Ni$ is presented. This equilibrium is independent of the reactor pressure, see Table 1; therefore within the defined operating range it can be represented by one single line.

TABLE 1

Conversion as function of pressure and temperature

	Constant volume	Constant pressure
Without absorption	$\zeta = \frac{-K_r + \sqrt{K_r^2 + 4K_r \cdot P_{A_0}}}{2 \cdot P_{A_0}}$	$\zeta = 1 - \frac{P_{A_0} - 2 \cdot P_B}{P_{A_0} - P_B}$ with $P_B = -K_r + \sqrt{K_r^2 + K_r \cdot P_{A_0}}$
With absorption	$\zeta = 1 - \frac{P_{e,m}}{P_{e,m} + K_r}$	$\zeta = 1 - \frac{P_{e,m}}{P_{e,m} + K_r}$

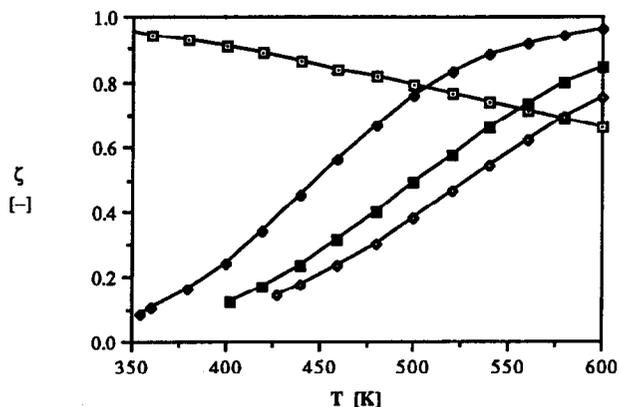


Fig. 2. Shift in equilibrium conditions for the 2-propanol/ $Mg_{2.4}Ni$ system. (\square) With absorption, (\blacklozenge) 1 bar, (\blacksquare) 5 bar, (\diamond) 10 bar.

EXPERIMENTAL

The main purpose of the experiments was to demonstrate that the absorption capacity of an alloy can be used to remove hydrogen produced by a dehydrogenation reaction. Also it was attempted to show that the thermodynamics described in the previous section can predict the shift in equilibrium conversion. In the experiments, a gas-phase equilibrium reaction was carried out in a batch reactor. In two series of reference experiments possible catalytic properties of the reactor and the catalyst selected were tested. The dehydrogenation of 2-propanol to acetone was selected as the model reaction. The favourable equilibrium of this reaction results in relatively high hydrogen pressures during the dehydrogenation. The hydride forming alloy selected for the experiments was $\text{Mg}_{2.4}\text{Ni}$, supplied by Hystor (Hystor 301), because of its sufficiently low plateau-pressures at high temperatures, see Fig. 1.

Powdered CuO was selected as a suitable catalyst for the model reaction as suggested by Cunningham et al. [10,11]. The active sites on this catalyst are formed by combinations of Cu^{I} and Cu^{II} valences. Moreover, the catalyst's activity is relatively insensitive to prereducations or preoxidations because the actual surface is formed during the reaction. This property is very important as the catalyst must be insensitive to the activation procedure of the alloy.

All experiments were carried out at 473 K and an initial 2-propanol or acetone pressure of about 7 bar. Under these conditions both the CuO catalyst and the $\text{Mg}_{2.4}\text{Ni}$ were reported to be active [10,11]. Theoretically the equilibrium conversion for a selective dehydrogenation of 2-propanol under these conditions can be increased from 32% to 82%.

Experimental setup

The reactor used was a stirred vessel operated batchwise at constant temperature. The $\text{Mg}_{2.4}\text{Ni}$ and/or the CuO catalyst were enclosed in a cylindrical annulus between the inside of the stainless-steel autoclave wall and a porous cylinder placed coaxially in the reactor. The distance between the reactor wall and the filter was $1 \cdot 10^{-3}$ m, the inside diameter of the reactor was $4 \cdot 10^{-2}$ m. The mean pore diameter of the sintered steel filter element was about $1 \cdot 10^{-6}$ m. The reactor volume of $2.25 \cdot 10^{-4}$ m³ was maintained at a constant temperature by means of electrical heating.

The hydrogen supply section was suited for the activation and characterisation of the alloy and the preparation of the catalyst. Well defined amounts of hydrogen could be fed to the reactor via known buffer volumes connected to pressure transducers, the pressures could be recorded. The gas temperature in the buffer volumes was measured by means of thermocouples. The reactor temperature was measured and recorded via thermocouples in the gas-phase and in the annulus.

The reactants in the model reaction, 2-propanol or acetone, were injected by means of a syringe. The needle is inserted via a septum and a valve, the reactant is injected into the bottom of the reactor, from where it is expected to evaporate within a few seconds.

The reactor pressure was measured and recorded via a pressure transducer. The experiments were evaluated based on the pressure recorded during the reaction and gas-chromatographic analyses of the reaction products after they were condensed in the cold trap placed outside the reactor.

RESULTS

Alloy characterisation and reference experiments

$\text{Mg}_{2.4}\text{Ni}$ was characterised by determining the maximum absorption capacity and the plateau pressure as a function of temperature. The maximum amount of hydrogen absorbed in the activated alloy was 10 mol H_2 /kg $\text{Mg}_{2.4}\text{Ni}$. This is 59% of the theoretical amount of hydrogen that can be absorbed in $\text{Mg}_{2.4}\text{NiH}_4$. The plateau pressure as a function of temperature was determined by measuring the equilibrium pressure at half the absorption capacity. The results of these measurements in the range 467–473 K are in agreement with the data supplied by Huston and Sandrock [12] who characterized a large number of hydride forming metal alloys supplied by Hystor.

Two sets of reference dehydrogenation experiments were carried out in order to test the reactor and the filter element on catalytic effects towards the reactants and to test the CuO catalyst.

In the catalytic activity tests, the injection of 3.5 ml ($4.6 \cdot 10^{-2}$ mol) of 2-propanol resulted in a reactor pressure of 7.1 bar. The amount of reactor contents that could be condensed in the cold trap varied between 2.15 and 2.25 gram (3.6 to $3.8 \cdot 10^{-2}$ mol). With the ideal-gas law and the reactor volume of $2.25 \cdot 10^{-4}$ m³ an amount of $4.1 \cdot 10^{-2}$ mol 2-propanol in the gas phase was calculated. The deviations were a result of losses during the injection and condensation steps; the pressure in the reactor can be reproduced within ± 0.2 bar. From these experiments it could be concluded that the reactor and the filter element were not active towards the reactants even after several hours.

For the experiments with the CuO catalyst, one batch of 10.0 g CuO powder ("Baker" grade) was placed in the annulus. The equilibrium system was approached with both acetone/hydrogen and 2-propanol as feed. All reference experiments on the CuO catalyst were carried out using the same batch of catalyst. In Fig. 3 the pressure recordings for some experiments with 2-propanol are presented, the notation B1, B2 and B4 refers to the sequence of the experiments. The differences between the B1, B2 and B4 must be attributed to small changes in activity and/or selectivity of the CuO catalyst during the first experiments. From the results of these reference experiments it was concluded that equilibrium was approached from both the hydrogenation and de-

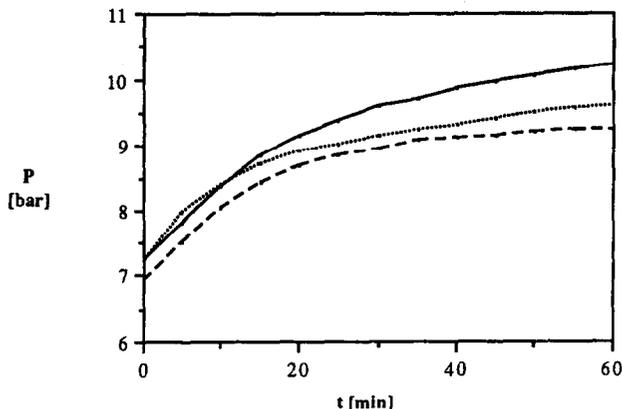


Fig. 3. Reference experiments with CuO catalyst, with 2-propanol as feed. (—) B1, (·····) B3, (-----) B4.

hydrogenation side. The values for the equilibrium constant varied from 2.1 for the first experiment to about 1.2 for following experiments e.g., B3 and B4. The GC analyses of the condensed reaction products showed that only small amounts of an additional component are formed, so the CuO catalyst itself is very selective. No analysis of the gas phase was carried out.

The insensitivity of the CuO catalyst to the reducing atmosphere in which the $Mg_{2.4}Ni$ was activated was confirmed by reducing the same batch of catalyst for four hours at 2.5 bar of hydrogen at 473 K. The equilibrium constants calculated from the experiments with the reduced catalyst were lower compared to the previous constants. This might be caused by the parallel dehydration reaction from 2-propanol to propene [10,11]. Also small amounts of some polymeric component could be detected. The catalyst appeared to withstand the activation conditions of the alloy and to remain selective.

Experiments with both catalyst and $Mg_{2.4}Ni$

For this group of experiments, a mixture of 8.3 g CuO and 16.7 g $Mg_{2.4}Ni$ was placed in the reactor. The $Mg_{2.4}Ni$ was activated and desorbed, and 3.5 ml of 2-propanol was injected. The pressure recording for this experiment is presented as line C in Fig. 4 and should be compared with reference experiment B (CuO catalyst only).

From Fig. 4 it can be seen that a substantial difference exists between the initial pressures after injection for B and C. Injection of 3.5 ml 2-propanol in the empty reactor resulted in an initial pressure of 7.1 bar. The initial pressure in B was also 7.1 bar but in experiment C an initial pressure of 6.0 bar was recorded. This deviation cannot be explained by assuming instantaneous adsorption of a monolayer of 2-propanol on the $Mg_{2.4}Ni$ surface.

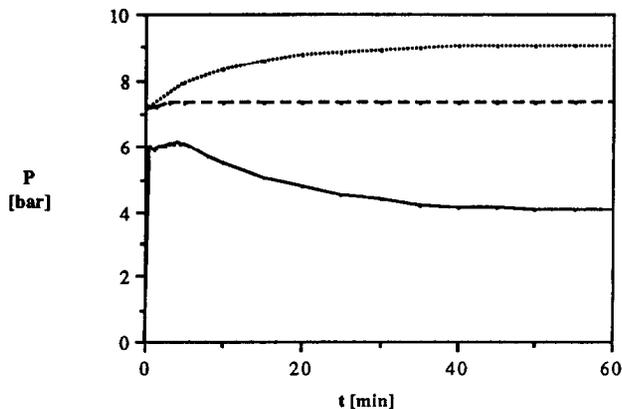


Fig. 4. Dehydrogenation of 2-propanol with CuO/Mg_{2.4}Ni. (—) C, (·····) B, (-----) E.

In case of a selective dehydrogenation reaction with immediate hydrogen removal, the predicted pressure recording should be a straight, horizontal line at a pressure level little above the sum of the initial 2-propanol pressure (7.1 bar) and the equilibrium pressure of the Mg_{2.4}Ni (0.2 bar) (line E in Fig. 4). The pressure recording for experiment C differed substantially from this prediction. After a (too low) initial pressure a second maximum occurred, next decreasing to an apparent equilibrium at 4.1 bar.

After 60 min the reaction was stopped and the reactor contents were condensed. The amount of condensed products was 0.85 g. The possible losses during injection or condensation are much too small to explain this large difference between the injected and condensed amounts. Gas-chromatographic analyses of the condensate showed that a large number of additional compounds is formed and therefore 2-propanol and/or acetone must also be consumed by parallel or consecutive polymerisation reactions induced by Mg_{2.4}Ni. The dehydrogenation of 2-propanol over CuO in the presence of Mg_{2.4}Ni turns out to lose its selectivity.

A probable explanation for the initial course of the pressure recording seems the dehydrogenation of 2-propanol followed by a polymerisation reaction of acetone. In that case the second maximum in the pressure recording is attributed to the hydrogen produced during the dehydrogenation and the subsequent pressure decrease is attributed to the polymerisation of the acetone. In a second experiment it was attempted to verify this hypothesis. After 3 min, as the pressure reached the second maximum, the reaction was stopped and 1.55 g of products were condensed. GC-analyses of the products showed a pattern similar to the GC-analyses of the first experiment; however, the peaks for the heaviest components were smaller.

The catalytic activity of Mg_{2.4}Ni towards the polymerisation of acetone was studied in separate tests. After activation, the experimental setup was evacu-

ated and a volume of 3.5 ml of acetone was injected. A rapid decrease from an initial pressure of 5.9 bar to an apparent equilibrium at 1.6 bar was recorded, see Fig. 5. The pressure decrease is faster and attains a lower constant value than that obtained for the experiment with 2-propanol as feed. From GC-analyses it could be concluded that the same products were formed. After this experiment the absorption capacity of the $Mg_{2.4}Ni$ batch was reduced to 6 mol $H_2/kg Mg_{2.4}Ni$; this is 60% of the initial absorption capacity. This decrease seems irreversible as the capacity could not be restored after the usual activation procedure.

The observed polymerisation reaction can be either a pure catalytic effect or can be induced by a combination of catalysis and absorption capacity of the alloy. In order to check on these options, two experiments, with 2-propanol and acetone as feed, respectively, were carried out in the presence of only completely saturated $Mg_{2.4}Ni$.

The initial pressure with 2-propanol as feed was 7.7 bar. Based on the reference experiments an initial pressure of 8.1 bar was expected (7.1 bar 2-propanol plus 1 bar hydrogen). From this initial point the pressure started to increase up to 9.9 bar at 60 min. In the case of a selective dehydrogenation the pressure should reach an equilibrium at 10.0 bar. The reaction was stopped after 60 min and 0.45 g of reaction products were condensed. GC-analyses showed peaks at equal retention times as in the previous experiments; so the polymerisation reaction also occurred in this experiment. The initial pressure with acetone as feed was 5.9 bar while the predicted value was 8.1 bar. At the start a very rapid pressure decrease occurred and an apparent equilibrium at 2.7 bar after 10 min was reached (at a partial hydrogen pressure of 1 bar due to the saturated metal hydride). After 15 min an amount of 0.90 g of the condensate was collected. Again, from the GC-analyses it could be concluded that

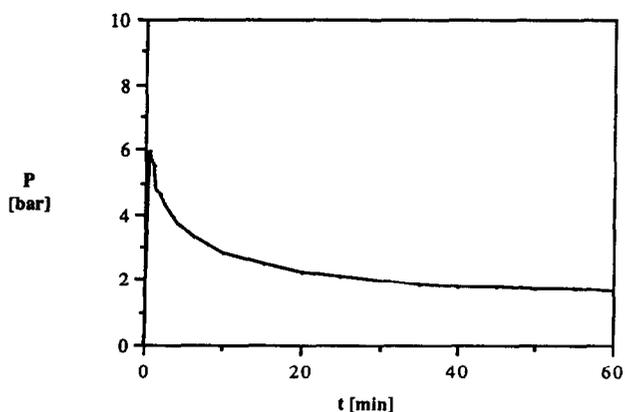


Fig. 5. Catalytic activity of $Mg_{2.4}Ni$ towards acetone.

the polymerisation products were formed. After this experiment the absorption capacity of $Mg_{2.4}Ni$ was reduced to 5% of the initial capacity.

DISCUSSION

The main objective was to demonstrate that the hydrogen-absorption capacity of $Mg_{2.4}Ni$ could be used to withdraw hydrogen in the 2-propanol/acetone system. Unfortunately, the shift in equilibrium could not be verified because a large number of additional products were formed. From the results it is evident that hydrogen was absorbed and desorbed in the course of the chemical conversion, so it appears in principle possible to remove or supply hydrogen in alcohol/ketone systems by means of a suitable alloy.

The reaction products were analyzed by a mass-spectrometric technique and it was concluded that the polymers were formed by a condensation reaction, in which the secondary carbon from a 2-propanol or acetone molecule was bonded to a primary carbon. This type of reaction is well known (e.g. aldol condensation reactions). The primary carbon can be part of a 2-propanol, acetone or polymer molecule. From the pressure recordings it is clear that the water molecules that are expected to be formed during condensation were removed from the gas phase. The oxidation of the $Mg_{2.4}Ni$ or the formation of $Mg(OH)_2$ would explain the decrease in absorption capacity during the experiments.

It appears that acetone is more active in the polymerisation reaction than 2-propanol. On the saturated $Mg_{2.4}Ni$ the initial pressure recorded with 2-propanol differs less from the expected value than the initial pressure after injection of acetone. The decrease in absorption capacity was observed especially after the experiments in which acetone was injected. From experiments it appears that the hydrogen present in the $Mg_{2.4}Ni$ plays an active role in the polymerisation reaction.

CONCLUSIONS

1. The possibility to improve on the degrees of conversion of dehydrogenation reactions has been studied theoretically and experimentally.
2. Based on equilibrium thermodynamics, operating conditions have been defined under which an improvement of the (equilibrium) conversion can be achieved. This operating range is determined by the equilibrium characteristics of the reaction, the saturated vapour pressures of the reactants and products and of the plateau pressure of the alloy.
3. The total system pressure does not affect the maximum possible degree of conversion for the constant volume systems.
4. The dehydrogenation of 2-propanol to acetone has been selected for experimental verification of the theoretical predictions. For dehydrogenation ex-

periments at 473 K, $Mg_{2.4}Ni$ appears to possess strong catalytic properties towards the condensation reactions of acetone and/or 2-propanol.

5. $Mg_{2.4}Ni$ is able to interchange the in-situ hydrogenation with reacting species. However, its activity rapidly decreases.

6. In a physical mixture of $Mg_{2.4}Ni$ and the Cu/CuO catalyst, the latter does not undergo any deactivation in the course of the reaction. Therefore it seems possible to apply mixed beds of catalyst and hydrides in potential industrial applications.

7. The deactivation of $Mg_{2.4}Ni$ is most probably caused by deposition of non-volatile condensation products forming a non-permeable diffusion layer at the surface.

8. Possible catalytic properties of the alloys must form an essential criterion in selecting suitable alloys for the equilibrium shift. For dehydrogenation of secondary alcohols the selectivity loss may appear prohibitive for the proposed in-situ hydrogen removal.

ACKNOWLEDGEMENTS

These investigations were financed by DSM. The authors wish to thank Prof. Dr. Ir. W.P.M. van Swaaij and Prof. Dr. J.R. Ross for their stimulating discussions and remarks.

REFERENCES

- 1 J.F. Nachman and D.A. Rohy, in T.N. Veziroglu, Proc. Int. Symp. on Metal Hydrogen Systems, Miami, 1981, Pergamon, Oxford, New York, 1982, pp. 557-600.
- 2 R.D. Holstvoogd, Ph.D. Thesis, University of Twente, The Netherlands, 1988.
- 3 I. Sheft and G. Lamich, in T.N. Veziroglu, Proc. Int. Symp. on Metal Hydrogen Systems, Miami, 1981, Pergamon, Oxford, New York, 1982, pp. 633-647.
- 4 H. Imamura, K. Yamada and S. Tsuchiya, Appl. Catal., 27 (1986) 243-256.
- 5 H. Imamura, K. Yamada, K. Nukui and S. Tsuchiya, J. Less Common Metals, 123 (1986) L1-L4.
- 6 H. Imamura, K. Yamada, K. Nukui and S. Tsuchiya, J. Chem. Soc., Chem. Commun., (1986) 367-368.
- 7 H. Imamura, T. Takada and S. Tsuchiya, Int. J. Hydrogen Energy, 13 (1988) 11-13.
- 8 A.J. Fanelli, A.J. Maeland, R.W. Armbrust and G. Rak, US Patent 4 675 465 (1987).
- 9 E.B.E. Leach (Editor), Applied Industrial Catalyses, Vol. II, Academic Press, New York, 1983, p. 150.
- 10 J. Cunningham, B.K. Hoodnett, M. Ilyas and E.L. Leahy, Faraday Disc. Chem. Soc., 72 (1981) 283-302.
- 11 J. Cunningham, G.H. Al-Sayyed, J.A. Cronin, C. Healy and W. Hirschwald, Appl. Catal., 25 (1986) 129-138.
- 12 E.L. Huston and G.D. Sandrock, J. Less Common Metals, 74 (1980) 435-443.