On Line Determination of Deuterium in Hydrogen Water Exchange Reaction by Mass Spectrometry

J. D. Sharma, K. P. Alphonse, Sushama Mishra, S. A. Prabhu, Sadhana Mohan and V. K. Tangri
Heavy Water Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, INDIA
Email : jdsharma@barc.gov.in

Introduction

The Deuterium (D)/ Hydrogen (H) analysis at low Concentration is generally carried out by Mass Spectrometry. Mass Spectrometer is specially designed for the measurement of Mass 2 and 3 ratio. The Deuterium analysis of water and hydrogen in concentration range of a few ppm to about 1% plays an important role in the Heavy Water Production Plants [1]. For the enrichment of the Deuterium concentration in H₂O (l) by H₂ – H₂O exchange a catalyst is essential as reaction is relatively slow. Heavy Water Division has developed in house Platinum based catalyst for the isotopic exchange of Hydrogen and Water [2].

An on line Deuterium gas sampling system, which can directly be attached to Mass Spectrometer, was developed for carrying out the catalyst performance. Performance of the catalyst was studied in Static as well as in the Dynamic mode. Over all isotopic exchange reaction between Deuterated water and Ultra pure Hydrogen gas is taking place in the presence of the catalyst and ceramic raschig ring. Ceramic raschig rings act as hydrophilic agent where as, Platinum loaded on activated charcoal mixed with Teflon in raschig rings form behaves as hydrophobic catalyst [3,4]. Liquid water is converted to water vapour over hydrophilic packing and deuterium exchange between H₂O (v) and hydrogen gas is taking place over the catalyst surface.

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HDO + H_2 \leftrightarrow HD + H_2O
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Specific activity [5,6] of the catalyst kv* was calculated by knowing Deuterium concentration of H₂ gas and liquid water, weight of the catalyst, superficial gas velocity & liquid flow.
The upper limit of analysis is restricted to 1 % Deuterium concentration due to mass 4 interference and memory problem associated with higher deuterium concentration.

Experimental

[A] A double collector Mass Spectrometer indigenously manufactured by Technical Physics & Prototype Engineering Division of B.A.R.C, Mumbai was used for this work.

[B] Catalyst Preparation

Platinum loading on activated carbon was done by impregnation of carbon with chloroplatinic acid. After impregnation this was reduced with high purity Hydrogen gas at 350°C. This platinum loaded carbon was homogeneously mixed with Teflon and compacted to raschig ring form of size 6mmX6mmX3mm. The final composition of the catalyst is 0.1% Pt, 0.9% C, 99% Teflon.
[C] Static System

A static system made up of stainless steel was designed and fabricated in Heavy Water Division workshop for carrying out the isotopic exchange, to eliminate the problem of handling glass system as shown in figure-1.

![Stainless Steel Static Sample Bottle](image)

Fig-1. Stainless Steel Static Sample Bottle

The sample bottle shown in figure-1 was dried in an oven for 2 Hrs. at 110\(^0\) C and cooled down to room temperature. A known quantity of ceramic raschig ring and platinum loaded catalyst was taken inside the sample bottle. Ultra pure Hydrogen gas was taken at a pressure of 1.2 Kg/cm\(^2\) in the sample bottle after repeated flushing and evacuating the system. Isotopic purity of hydrogen gas was analyzed by Mass Spectrometer. 1.2 ml of Heavy Water (500 ppm) was injected into system and Deuterium concentration was analyzed on Mass Spectrometer at regular intervals. The time taken for half of the equilibrium concentration was measured from the plot of Time vs Deuterium concentration measured (Figure - 3) on Mass Spectrometer.

[D] Dynamic System

Catalyst column containing 50% each hydrophobic catalyst and ceramic raschig ring was (Figure-2) packed in the glass column. Heavy water (1000ppm) was passed downwards through the mixed bed and hydrogen gas saturated with water vapour was allowed to flow counter currently upwards. From the known deuterium (D) concentration of water entering the column at the top, D concentration of Hydrogen at top and bottom was analyzed on line with the help of mass spectrometer. Water enriched in deuterium concentration entering and leaving the column was separately analysed for their D/H ratios after converting into H\(_2\) over a furnace attached to the mass spectrometer.
From the static experiments it was found that $T_{1/2}$, the time taken to reach half the equilibrium concentration is 22 minutes (Figure-3) for 10 gms of catalyst.

The online static system developed for deuterium analysis in $H_2$ gas by Mass Spectrometry is easy to operate and no glass handling is involved. The quantity of gas required for mass spectrometric analysis is also reduced as the system was directly connected to mass spectrometer for analysis through narrow tubing. As sample volume drawn from the system for analysis is considerably reduced pressure drop in the reactor vessel is also reduced.

Results & Discussion

The catalyst activity was measured in dynamic system as follows:
The specific activity of the catalyst was measured as the overall gas-phase volume transfer rate $kv^*$ given in the s$^{-1}$.

$$ kv^* = \frac{F}{H} \times \frac{NTU}{NTU} $$

Where $F$= superficial hydrogen flow rate in m/s.

$H$= height of catalyst bed in m

$NTU$= No. of transfer units in the bed,

$$ NTU = \frac{(y_b - y_t)}{(y_b - y_b^*)} \times \frac{(y_t-y_t^*)}{(y_t-y_t^*)} \ln \frac{(y_t-y_t^*)}{(y_t-y_t^*)} $$

$y$ = the atom fraction of D in the Hydrogen gas,

The subscript t and b refers to the top and bottom of exchange column and the superscript (*) denotes the D conc. in the hydrogen in equilibrium with the water. The value of $y^*$ is calculated from the exact relation

$$ x \times \frac{y^*}{\alpha - x (\alpha - 1)} $$

Where $x$ = the atom fraction of D in the water

$\alpha$ = seperation factor

The specific activity of the catalyst ($kv^* = 0.02$s$^{-1}$) prepared in our Division is found to be in comparable with similar catalysts.

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**References**