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Isotopic Exchange between Hydrogen and Water over Plain and Hydrophobized Nickel–Chromia Catalysts

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Isotope exchange between hydrogen and deuterated water has been studied in gas phase as well as in liquid phase using nickel–chromia catalyst. The optimum chromia content in the oxide was found to be 15 mole%. Hydrophobized catalyst could be prepared by hydrogen reduction of nickel oxide–chromium oxide powder treated with phenyl trimethoxy silane. The hydrophobic layer did not alter the gas phase kinetics and was observed to promote H–D exchange between hydrogen and liquid deuterated water. Counter-current exchange studies carried out up to 90 days have demonstrated the stability of the catalyst and capability for repeated use. The hydrophobic layer was stable in water pressurized up to 10^6 Pa and at temperatures up to 373 K. On the basis of gas phase kinetic studies an activation energy of 16.0 ± 1.8 kJ/mole has been observed for hydrophobized catalyst. © 1992 Academic Press, Inc.

1. INTRODUCTION

Hydrogen–water isotopic exchange reaction has long been considered as the one to provide a possible breakthrough for an economic process for the production of heavy water (*1*, *2*) because of high separation factor for the exchange reaction (separation factor at 30°C = 3.5). The reaction suffers from slowness (*3*, *4*) in the absence of a catalyst. Two catalysts known to be quite active for this exchange reaction are platinum and nickel–chromia. Although of comparable activity, these are active essentially in gas phase. A process based on these catalysts would thus entail large energy input and large plant size and be uneconomical.

Development of a catalyst that would retain its activity in water is highly desirable (*5*). The development of a hydrophobized platinum catalyst by Stevens (*6*) was a useful step in this direction; however, this catalyst was not found to be sufficiently stable in a bithermal system (*7*). Further, the platinum-based catalyst becomes easily poisoned with NH_3, CO, H_2S, etc. About 15 to 20 thousand mole of hydrogen feed must be processed to produce 1 mole of heavy water and the problem of catalyst poisoning can be serious.

Nickel–chromia catalyst is likely to be less vulnerable to impurities, it can be more easily regenerated than platinum-based catalyst (*8*), and it costs several times less. No research work is reported to develop a hydrophobized nickel–chromia catalyst.

Experimental work on nickel–chromia catalyst included the preparation, hydrophobization, physicochemical characterization, and evaluation of the capability for promoting H–D exchange reaction, in the gas phase as well as in the liquid phase.

2. MATERIALS

Heavy water having 99.5 mole% D_2O was diluted with distilled water to obtain deuterated water having 5.26, 1.999, and 0.115 mole% D_2O.

The chemicals used in all these investigations were of the analytical grade. Hydrogen gas of analytical grade was purified by being passed over noble metal-based deoxocatalyst for the conversion of traces of oxygen

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to water and silica gel as well as molecular sieves for the removal of water. Organosilicon compounds were taken from a sister laboratory dealing with the synthesis of silicon compounds. These included phenyl ethyl triethoxy silane (PETES), phenyl trimethoxy silane (PTMS), phenyl ethyl trimethoxy silane (PETMS), and vinyl triethoxy silane (VTES).

3. CATALYST PREPARATION AND HYDROPHOBIZATION

A homogeneous mixture of nickel and chromium carbonates was prepared by coprecipitation in accordance with the procedure of Taylor (*8*). The precipitate was washed, dried, crushed, and calcined in air at 615 K to obtain nickel oxide–chromium oxide powder.

Nickel oxide–chromium oxide powders having 10 to 70 mole% chromium oxide were prepared in 100-g batch sizes. For obtaining hydrophobized powder, 40 ml of 20% solution of alkoxy silane in benzene was taken and mixed with 20 g of the oxide powder. The slurry was kept overnight in an open container and then dried in an air oven at 383 K for 6 hr. In a few cases the powder was dried in a closed system to collect the volatile products.

The catalyst (plain as well as hydrophobized) was prepared by reducing the oxide powder with hydrogen at 600 K. The catalyst was rapidly oxidized if exposed to air.

4. PHYSICOCHEMICAL CHARACTERIZATION

4.1. X-Ray Diffraction

The X-ray diffraction pattern of the samples was recorded on a Siemens diffractometer using Cu$K\alpha$ radiation ($\lambda = 0.15418$ nm). Nickel oxide–chromium oxide powders of all compositions were found to be amorphous in nature.

4.2. Surface Area

Total surface areas and pore size distributions of various powders were measured by multipoint BET method using He + N_2 gas mixtures (*9*). A Quantasorb instrument from M/S Quantachrome Corporation was used for this purpose. Surface areas of the plain oxide powders ranged between 150 and 275 m^2/g with a broad peak around 15 to 30 mole% Cr_2O_3. Surface areas of the plain catalyst ranged between 150 and 225 m^2/g with a broad peak for powders having 30 to 50 mole% Cr_2O_3. In the case of hydrophobized oxide powder/catalyst, surface area was measured only for materials having 15 mole% Cr_2O_3. For the hydrophobized oxide powder the surface area dropped to 16 m^2/g probably due to the presence of hydrophobizing reagent. The surface area of the hydrophobized catalyst was 130 m^2/g, which is in the same range as that observed for the plain catalyst.

The pore size distribution of plain as well as hydrophobized oxide powder was bimodal with smaller pores in the range 1.5 to 2.0 nm diameter and larger pores of 3.0 to 4.5 nm diameter indicating that the catalyst would be microporous in nature.

4.3. Hydrogen Adsorption

Hydrogen adsorption/desorption by the catalyst, at room temperature (299 K), was studied using a volumetric setup similar to that used for surface area measurements. Hydrogen pressures from 2.5 to 22.5 kPa were used to obtain isotherms that were found to be linear beyond hydrogen pressure of 5.0 kPa. The linear portion of the desorption isotherm was extrapolated to zero pressure for obtaining the amount of hydrogen chemisorbed on the dispersed nickel atoms (*10*). Nickel metal surface area was calculated by assuming that (i) there is a monolayer of hydrogen, (ii) one atom of hydrogen is bonded to one atom of nickel, and (iii) one atom of nickel occupies an area of 6.76×10^{-20} m^2. For plain catalyst the variation of metal surface area was studied as a function of Cr_2O_3 content and the values ranged between 10 and 20 m^2/g with a broad peak for compositions having 10 to 30 mole% Cr_2O_3. For hydrophobized catalyst having 15% Cr_2O_3 the metal surface area was identical to that of plain catalyst.

From the metal surface area, percentage metal dispersion (%*D*) was calculated as

$$\%D = \frac{\text{Hydrogen atoms adsorbed per gram of catalyst}}{\text{Nickel atoms present in per gram of catalyst}} \times 100$$

The values of percentage metal dispersion varied from 1 to 4 with a peak at 15 mole% Cr_2O_3. The nickel crystallite size, calculated using the formula $d(\text{nm}) = 80/\%D$ (*11*), was 20 nm for catalyst with 15 mole% Cr_2O_3.

4.4. *Water Adsorption*

Water adsorption by plain and hydrophobized catalyst having 15 mole% Cr_2O_3 was determined at 299 K by equilibrating with water vapor at a pressure of 0.13 to 2.8 kPa. The studies were carried out in a quartz spring thermobalance in which 500 mg of the oxide powder was taken, reduced with hydrogen at 600 K, and cooled under vacuum to 299 K. The thermobalance was then momentarily connected to an evacuated water container kept at 299 K in which water vapor was at a pressure (p_0) of 3.36 kPa. The pressure p of water vapor in equilibrium with the catalyst was measured with a manometer after the catalyst weight became constant. Different values of p/p_0 were obtained by changing the duration for which the sample was connected to the source of water vapor. At values of p/p_0 ranging from 0.1 to 0.5 the quantity of water adsorbed by plain as well hydrophobized catalyst increased from about 20 mg/g at $p/p_0 = 0.1$ to 70 mg/g at $p/p_0 = 0.5$. Thereafter, water absorption increased linearly with increasing p/p_0 for the hydrophobized catalyst and exponentially for the plain catalyst. This indicated that, whereas monolayer adsorption takes place on the hydrophobized catalyst, multilayer adsorption takes place on plain catalyst beyond $p/p_0 = 0.5$.

Effect of presaturation of nickel sites with hydrogen on water adsorption by plain catalyst was also studied. For this, freshly prepared plain catalyst, after being cooled to 299 K in vacuum, was first equilibrated with hydrogen at a low partial pressure of 13 Pa. Subsequently water adsorption studies were carried out for values of p/p_0 ranging from 0.1 to 0.5. It was observed that preadsorption with hydrogen decreased uptake of water by about 15% throughout the range of water vapor pressure used in the study.

5. H/D ISOTOPE EXCHANGE

5.1. *Gas Phase Reaction*

Transfer of deuterium from deuterated water to hydrogen in the gas phase was studied in a fixed-bed integral flow reactor made from a glass tube of 15 mm diameter and 350 mm length. Fifteen milligrams of plain nickel oxide–chromium oxide powder or 19 mg of hydrophobized oxide powder was mixed with water to make a slurry, which was coated on 2 g of 3-mm-diameter glass balls. Careful control was required on the amount of catalyst used in these studies since increase of the quantity of catalyst increased the steady-state value of D/H. The coated glass balls were loaded in the central 20-mm zone of the reactor and 135 mm on either side was filled with plain Raschig rings. The reactor was heated in a furnace and its temperature at the central part measured with a chromel–alumel thermocouple. The oxide powder was converted to the catalyst by reduction with H_2 at 600 K and the reactor cooled to the temperature of investigation, which ranged from 383 to 428 K. Hydrogen at a flow rate of 380 ml/min was then bubbled through two bubblers containing deuterated water (1.999 mole% D_2O) and maintained at a fixed temperature to obtain the desired partial pressure of water in the gas phase. This gas was preheated to the reaction temperature before entering the reactor. After isotope exchange the gas was passed through two liquid nitrogen-cooled traps to remove water and sampled at various time intervals for analysis of the resultant D/H mole ratio. The analysis was carried out mass spectrometrically using an instrument with double collector facility and

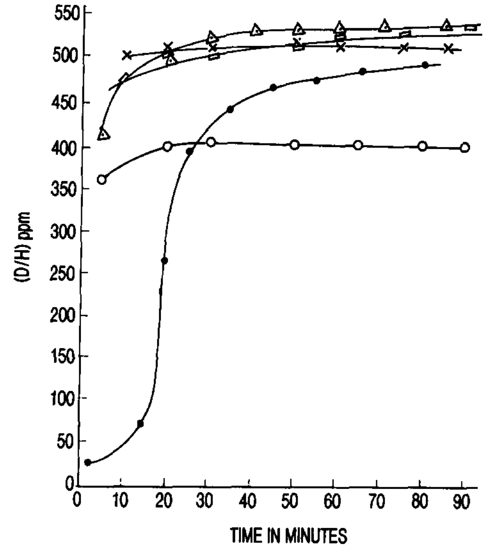

FIG. 1. Gas phase exchange characteristics of plain and hydrophobized nickel–15 mole% chromia catalyst. (●) Plain catalyst at 388 K; □ plain catalyst at 408 K; (△) plain catalyst at 428 K; (○) hydrophobized catalyst at 383 K; (×) hydrophobized catalyst 403 K.

exclusively devoted to D/H analysis. This instrument (Model TPPED-660) was manufactured by an instrumentation group of the research center.

The effect of temperature on the exchange capability of nickel–15 mole% chromia plain and hydrophobized catalyst is presented in Fig. 1.

It is seen that the plain and hydrophobized catalysts have similar efficacy for gas phase reaction and the reaction attains a steady-state after some time. The efficacy of reaction also increased with increasing temperature.

5.2. Gas Phase Kinetics

Kinetics of the gas phase reaction, with plain and hydrophobized catalyst, was studied in the manner described in Section 5.1 except that the hydrogen flow rate was enhanced to 840 ml/min. The temperature of the deuterated water bubblers was varied between 301 and 306 K and that of the catalyst between 383 and 508 K.

The procedure suggested by Sagert *et al.* (*12*) was used for the data analysis. The rate coefficient, K (HD mole g^{-1} s^{-1}) of the catalyst was calculated by the following equation, which is valid for D_2O concentration less than 5%.

$$K = \frac{F}{W(\alpha + \tau)} \ln \frac{n_e - n_0}{n_e - n},$$

where F is the flow rate of hydrogen in mole per second, α is the reciprocal of the equilibrium constant of the reaction: $HDO + H_2 \rightarrow H_2O + HD$, τ is the ratio of partial pressures of hydrogen and water, W is the weight of the catalyst in grams, n_0, n are the D/H mole ratios in feed and product hydrogen streams, and n_e is the D/H mole ratio expected at equilibrium = $(N_0 + \tau n_0)/(\alpha + \tau)$ (*13*), where N_0 is the deuterium concentration of the water vapor from the saturator. The value of α was calculated (*14*) from

$$\text{Log}_{10}\alpha = 205/T(K) - 0.129.$$

The specific rate K_s (HD mole m^{-2} s^{-1}) was calculated by normalizing the rate coefficient K for metal surface area of the catalyst. Duplicate measurements were carried out at each temperature and the specific rates obtained for plain and hydrophobized catalysts are given in Table 1. It is seen that the specific rates for the hydrophobized catalyst at each temperature are higher than those for the plain catalyst. Figure 2 shows the specific rates and absolute reaction temperatures fitted to an Arrhenius expression: $K_s = A \cdot e^{-E/RT}$, where A and E are preexponential factor and activation energy, respectively. The values of correlation coefficients for the least-squares lines of the plain and hydrophobized catalysts are, respectively, 0.979 and 0.929. The values of activation energy, E, for plain and hydrophobized catalysts are (20.5 ± 1.3) kJ/mole and (16.0 ± 1.8) kJ/mole, respectively. The values of preexponential factor, A, for plain and hydrophobized catalysts were found out to be $(1.33 \pm 0.12) \times 10^{-2}$ mole m^{-2} s^{-1} and $(5.51 \pm 0.57) \times 10^{-3}$ mole m^{-2} s^{-1}, respectively.

TABLE 1

Gas Phase Kinetic Data for Hydrogen–Water Isotopic Exchange Reaction over Plain and Hydrophobized Nickel–15 mole% Chromia Catalyst (Conc. of Deuterium in Water: 1.999 mol%)

Temperature (K)		D/H mole ratio in hydrogen $\times 10^6$	K_s
Main bubbler	Reactor		HD Mole $m^{-2} s^{-1} \times 10^5$
	Plain catalyst (15 mg)		
301.0	383.0	229.0,225.0	2.12, 2.07
304.4	403.0	271.5,256.5	2.60, 2.41
305.0	433.0	460.0,445.0	5.43, 5.17
305.5	460.0	535.0,545.0	6.80, 7.02
306.0	483.0	590.0,580.0	7.85, 7.63
306.0	508.0	650.0,650.0	9.31, 9.31
	Hydrophobized catalyst (19 mg)		
301.5	384.0	234.0,241.0	2.88, 3.00
302.0	406.0	335.0,343.0	4.85, 5.02
303.0	429.0	425.0,446.0	6.79, 7.33
303.5	449.0	498.0,500.0	8.66, 8.72
304.0	470.0	505.0,513.0	8.68, 8.91
304.0	493.0	525.0,530.0	9.25, 9.10
303.0	508.0	596.0,599.0	12.16,12.29

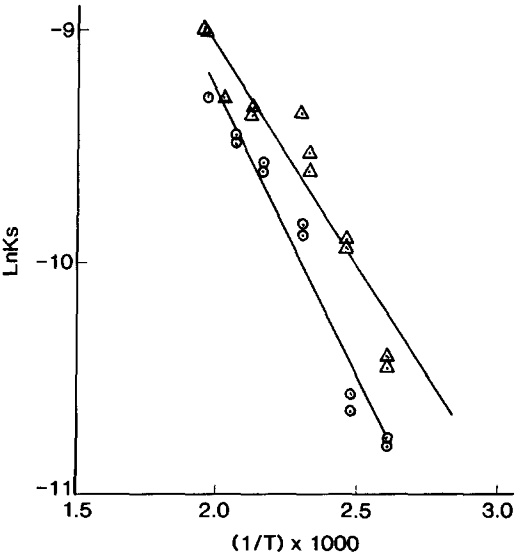

FIG. 2. Arrhenius plot for plain and hydrophobized nickel–chromia catalyst. (○) Plain catalyst, (△) hydrophobized catalyst.

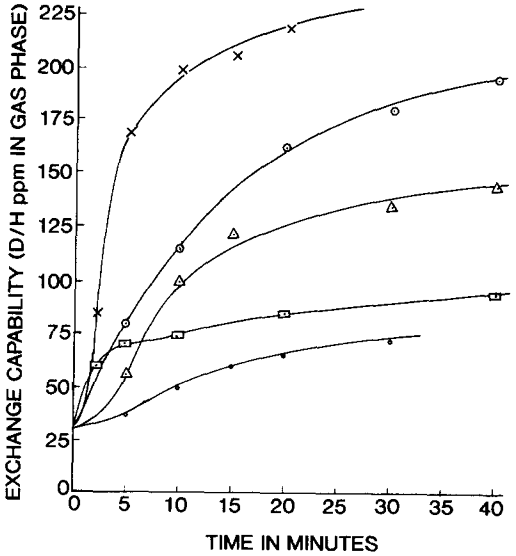

FIG. 3. Liquid phase hydrogen–water isotopic exchange studies on nickel–15 mole% chromia catalyst hydrophobized with various organosilicon compounds. (●) Plain and hydrophobized with (□) vinyl triethoxy silane, (△) phenyl ethyl trimethoxy silane, (○) phenyl ethyl triethoxy silane and, (×) phenyl trimethoxy silane.

5.3. Gas–Liquid Isotopic Exchange Studies in Static Reactor

The efficacy of different alkoxy silanes to hydrophobize nickel–chromia catalyst was studied by equilibrating hydrogen with deuterated water (0.115 mole% D_2O) in a 40-mm-diameters closed glass vessel of 200-ml capacity. About 200 mg of plain or hydrophobized oxide powder (15 mole% Cr_2O_3) was taken in this vessel, reduced with hydrogen at 600 K, and cooled under vacuum. The reactor was filled with hydrogen and 5 ml of deuterated water added. Equilibration was carried out by shaking for periods ranging from 5 to 40 min at 305 K. After each equilibration hydrogen was sampled and replaced by fresh hydrogen. The isotopic ratios D/H obtained as a function of contact time are plotted in Fig. 3 for catalysts hydrophobized with different alkoxy silanes. The results show that the catalyst hydrophobized with phenyl trimethoxy silane is superior to the catalysts treated with the other

TABLE 2

Gas–Liquid Isotope Exchange Studies in a Static Reactor

Amount of catalyst = 200 mg
Reaction temperature = 305 K
Expected equilibrium D/H in gas phase: 329.3 ppm

Time of sampling (min)	D/H concentration in hydrogen phase (ppm)			
	Sample 1	Sample 2	Sample 3	Sample 4
5	153.0	115.7	117.0	40.8
10	185.0	137.2	135.0	44.2
15	201.2	189.4	182.5	58.5
20	215.2	—	—	60.8
30	282.8	252.0	255.0	78.7
40	—	—	—	98.5
45	—	279.5	280.3	—
50	—	—	—	100.1

Note. Sample 1, catalyst prepared from normal hydrophobized oxide powder. Sample 2, catalyst prepared from hydrophobized oxide powder subjected to 3.3×10^6 Pa pressure. Sample 3, catalyst prepared from hydrophobized oxide powder refluxed at 373 K in water. Sample 4, catalyst prepared from hydrophobized oxide powder equilibrated with liquid water at 508 K and 3.3×10^6 Pa hydrogen pressure.

three alkoxy silanes. Subsequent investigations were therefore carried out by using catalyst hydrophobized with PTMS. Typical results for a sample are presented in Table 2.

The stability of the coating of alkoxy silanes on the precursor oxide to pressurization was checked by mixing the oxide with water and subjecting it to 3.3×10^6 Pa of hydrogen pressure for 48 h. Refluxing the oxide powder with boiling water for about 100 h was also carried out to study stability of this coating at 373 K. In order to infer the efficacy of the catalyst for gas–liquid isotope exchange at 508 K, the highest temperature used for gas phase studies, the oxide powder was treated with water at 508 K under a hydrogen pressure of 3.3×10^6 Pa in an autoclave. After these treatments, the oxide slurries were filtered and dried. In each case about 200 mg of the treated powder was transferred to the static reactor and tested for its efficiency of promoting isotopic exchange as described in the previous paragraph. The results of these studies are presented in Table 2. It is seen from the table that the values of D/H in the gas phase for treated samples 2 and 3 are only marginally less than those of sample 1. However, D/H for sample 4 are substantially lower indicating partial loss of the hydrophobic layer.

5.4. Gas–Liquid Counter-Current Isotopic Exchange Studies

Counter-current gas–liquid exchange studies were conducted in a glass column shown in Fig. 4. The central zone of this column was packed with 50 g of crushed pellets (2.4 to 4.6-mm size) of the hydrophobized oxide powder (15 mole% Cr_2O_3) mixed with porcelain rings. The oxide pellet pieces were reduced with hydrogen at 600 K and the catalyst stored after stabilizing against rapid reaction with air by first injecting small doses of air and then with hydrogen bubbled through deuterated water. Prior to each exchange study the catalyst was heated at 373 K under a hydrogen flow of 1 liter/min for 3 h to reduce the partially oxidized catalyst. During the exchange reaction, hydrogen gas at flow rates varying from 165 to 650 ml/min

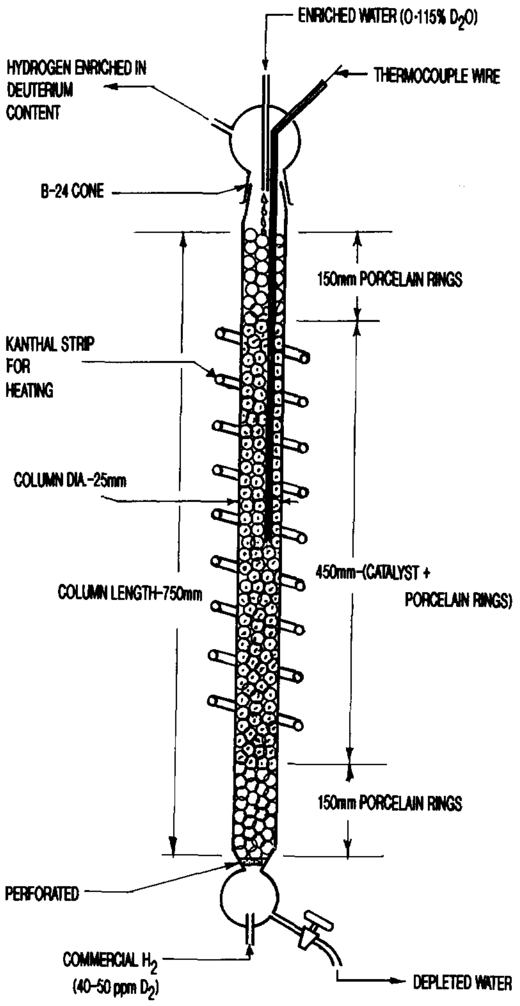

FIG. 4. Schematic diagram of the hydrogen–water isotopic exchange glass column.

TABLE 3

Exchange Reaction Study in a Glass Column with Counter-current Flow of Hydrogen and Water

Hydrogen flow rate ml/min	D/H concentration in the gas phase (ppm)		Period after reduction (*d*)
	Extraction column	Back extraction column	
165	235.0	—	0
330	200.0	—	0
650	187.2	—	0
165	240.0	—	7, 15, 30, or 90
330	202.0	66.1	90

Note. Conc. of deuterium in water, 0.115 mol%. Flow rate of deuterated water, 1.7 ml/min. Conc. of deuterium in hydrogen, 30 ppm (mole ratio). Flow rate of natural water, 1.4 ml/min. Operating temperature, 303 K.

was allowed to rise from the bottom and deuterated water (0.115 mole% D_2O) at a flow rate of 1.7 ml/min was allowed to trickle down from the top. In one experiment deuterium transferred to the hydrogen phase was back extracted using a second column in which enriched gas was equilibrated with ordinary distilled water. Deuterium contents in both enriched and depleted gas phases were determined by mass spectrometry and were taken as the measure of isotopic exchange efficiency. After starting the fluid flows the gas phase was sampled thrice at 2-h intervals. The D/H ratios in hydrogen were identical in the three samples taken during each experiment indicating attainment of steady state within 2 h. A few experiments were also carried out by storing the catalyst under hydrogen for 7 to 90 days followed by exchange studies. The results of all these studies are presented in Table 3. It is seen from the table that substantial enrichment of the gas phase takes place and the degree of enrichment is inversely proportional to the hydrogen flow rate. It is also seen that storage of the hydrophobized catalyst in hydrogen for periods up to 90 days did not lead to any deterioration of its performance. Back extraction of deuterium from the gas phase into the liquid has also been demonstrated.

The stability of the hydrophobic layer when the catalyst is subjected to high pressure was studied in a stainless-steel column. For this, the hydrophobized oxide powder (15 mole% Cr_2O_3) was pressed into pellets 10 mm long × 10 mm diameter and 850 g of these pellets were reduced in a glass column and stabilized. The catalyst, thus obtained, was transferred into a stainless-steel exchange column (50 mm diameter × 1000 mm height) under a water blanket, which was later drained off. The catalyst was then completely submerged in deuterated water containing 5.26% D_2O and the column pressurized with nitrogen for 1 to 4 days. The pressure was varied from 10^5 to 10^6 Pa. After this, the column was depressurized, deuterated water was drained off, and countercurrent exchange studies were carried out under ambient temperature and pressure with deuterated water (5.26% D_2O) and hydrogen. For hydrogen flow rates of 150 and 300 ml/min the D/H mole ratios in the product were respectively 340 and 200 ppm, irrespective of the magnitude of the pressure or the time for which the catalyst was pressurized.

6. DISCUSSION

Vapor phase D–H exchange studies on plain catalysts of various compositions revealed that compositions with 15–40 mole% Cr_2O_3 have relatively high catalytic efficiency. Fodor *et al.* (*15*) also report that catalyst with 15 mole% Cr_2O_3 gives a good performance. These observations are supported by the results of the physicochemical investigation. Surface area of the plain oxide powder displayed a peak for compositions having 15 to 30 mole% Cr_2O_3. Hydrogen adsorption by the plain catalyst displayed a peak for compositions having 10–30 mole% Cr_2O_3. Maximum metal dispersion was observed for the catalyst having 15 mole% Cr_2O_3. On the basis of these results one can infer that nickel–chromia catalyst with about 15 mole% Cr_2O_3 is best suited for H–D isotope exchange.

The addition of chromia has a promotional effect on the exchange activity of nickel. The present investigation shows that the exchange capability reaches its maximum when the chromia content is 15% and remains nearly constant up to 40%. Incorporation of a small percentage of chromia in the nickel matrix reduces the agglomeration tendency of nickel to form bigger crystallites. This indicates a structural promotional effect (*13*). Other mechanisms of promotion by chromia could be (i) Temkin's mechanism involving redox reactions at nickel sites and (ii) an exchange mechanism involving adsorption of hydrogen at nickel sites and water vapor on chromia sites. Sagert *et al.* (*12*) tried to understand the exact role played by chromia and the exact mechanism taking place on the catalyst. They investigated the specific rates of the exchange reaction on nickel promoted with 20% of the oxides of chromium, molybdenum, manganese, tungsten, and uranium. They concluded that Temkin's mechanism is predominant for molybdenum and tungsten oxide-promoted nickel catalysts, but the exchange mechanism is dominant for uranium and manganese oxide-promoted catalysts. In the case of chromia-promoted nickel catalyst, they proposed that both Temkin's mechanism and exchange mechanisms may be operative. In the present study on water adsorption it was seen that the quantity of water adsorbed on plain catalyst, particularly at lower partial pressures of water when monolayer adsorption is expected, is about 15% higher than on the catalyst having a monolayer of hydrogen. It was also seen from the surface area studies that metal surface area (22 m^2/g catalyst) is about 15% of the total surface area (145 m^2/g catalyst) of the catalyst. This indirectly indicates that nickel sites having hydrogen may not be taking part in water adsorption when hydrogen is already adsorbed. If Temkin's mechanism was valid then hydrogen should be replaced by water and water uptake should not be less for catalyst with preadsorbed hydrogen. It may be inferred that under actual operating conditions, when both hydrogen and water vapor are present, hydrogen is likely to be preferentially chemisorbed on nickel sites and water vapor on chromia sites. In such a case the exchange mechanism is more likely to promote the catalytic activity.

The new approach to hydrophobizing the catalyst assumed that the organosilicon compound will attach to the catalyst surface in such a way that the hydrophilic alkoxy groups would bind to the oxide surface by chemical interaction and the hydrophobic silanol groups would project outward. The analysis of the volatile products produced during the reaction of the oxide powder with alkoxy silanes revealed the presence of alcoholic species, which tends to support this reaction mechanism. Subsequent reduction of the oxide with hydrogen at 600 K does not impare the hydrophobic characteristics.

Hydrogen–deuterium exchange reaction requires that water be adsorbed on the catalyst surface, but if multilayer adsorption of water takes place then it poisons the catalyst. The aim of hydrophobization is to prevent the multilayer adsorption of water. Water adsorption isotherms of plain and hydrophobized catalyst clearly indicate monolayer water adsorption for the latter. Gas phase isotope exchange studies have revealed that the performance of the catalyst is not affected by hydrophobization. Successful use of the hydrophobized catalyst for gas–liquid exchange studies proves the efficacy of the hydrophobic treatment. For the sake of comparison, it is worthwhile to mention that in the gas phase, the specific rates respectively for unsupported platinum, pure nickel, and hydrophobized nickel–chromia catalyst are 3.3×10^{-4} (*16*), 1×10^{-8} (*10*), and 7.4×10^{-5} mole HD m^{-2} s^{-1} at 433 K.

The activation energy of both plain and hydrophobized catalysts agree within ±20%. Hence it can be concluded that hydrophobization treatment does not alter the basic mechanism of catalysis. In fact hydrophobization leads to marginal lowering of activation energy, which enhances the performances of the catalyst and leads to higher specific rates.

The tests for the stability of alkoxy silane coating on the oxide to boiling water as well as hydrogen pressure at ambient temperature have shown that this coating is quite stable as the catalyst obtained from this oxide had not lost its capacity to promote H–D exchange in the presence of liquid water. Gas phase isotopic exchange studies with plain and hydrophobized catalyst gave identical results up to 508 K. However, gas–liquid exchange studies with the catalyst obtained from the oxide powder treated with water at 508 K and 3.3×10^6 Pa hydrogen pressure indicated partial loss of hydrophobic layer.

Gas–liquid counter-current exchange studies in a glass column have shown promising results. It was seen that the hydrophobized catalyst did not degenerate even after 90 days under water. This may be attributed to the absence of multilayer adsorption of water on the coated catalyst surface.

Counter-current exchange studies carried out in the stainless-steel column, in which the catalyst could be subjected to prepressurization prior to exchange, have demonstrated the stability of the hydrophobic layer on the catalyst to pressure. This indicates the possibility of exploitation of hydrophobized nickel–chromia catalyst for H–D exchange.

7. CONCLUSIONS

(i) The nickel–chromia catalyst having 15% chromia results in an efficient H–D exchange.

(ii) Simple treatment of the nickel oxide–chromium oxide powder with phenyl trimethoxy silane followed by hydrogen reduction at 600 K yields the hydrophobized nickel–chromia catalyst.

(iii) The hydrophobic layer is basically stable at least up to 600 K, the temperature used for the oxide reduction. However, water at 508 K, along with the pressure required to keep it liquid, seems to damage this layer.

(iv) The hydrophobic layer is stable to pressures up to 10^6 Pa.

(v) The catalyst does not lose activity with storage or repeated use.

(vi) Isotope exchange between hydrogen adsorbed at nickel sites and water adsorbed at adjacent chromia sites appears to be responsible for the exchange reaction.

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