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Cracking of *n*-Hexane over NaX and a Series of NiX Catalysts

J. R. McLAUGHLIN AND C. G. POPE

University of Otago, Dunedin, New Zealand

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Catalytic cracking of *n*-hexane over NaX and various samples of the nickel-exchanged zeolite have been studied. NaX produced no significant reaction below 500°C, at which temperature reaction was only a little slower in the Pyrex reaction vessel containing no zeolite. NiX samples all caused appreciable reaction at 400°C. The only initial gas phase product was hydrogen, but methane was formed after an induction period. Samples of nickel zeolite which had previously been used as catalysts showed a rather similar rate of removal of hexane, but produced hydrogen and methane much more rapidly. Nickel metal was produced during the reaction, and it appears that methane was formed by the supported metal. The production of a carbonaceous residue shows little tendency to poison the catalyst, and adsorption capacity measurements suggest that the residue does not form a continuous layer over the catalyst. The initial chemisorption of hexane appears to occur on a relatively small number of preferentially exchanged nickel ions, which can each lead to the removal of many hexane molecules from the gas phase before losing their activity.

INTRODUCTION

There is now a considerable amount of evidence to show that the nature of the products obtained by cracking simple hydrocarbons over zeolite catalysts depends on the zeolitic cations present (*1–3*). Sodium zeolites are typically rather unreactive, and show product distributions attributable to a free radical mechanism. Replacement of some of the sodium ions by more strongly polarizing cations generally increases catalytic activity, and yields products more typical of a carbonium ion mechanism (*1*, *3*). As not all the cation sites are accessible to guest molecules in the zeolite cavities (*4*) and different intrinsic activities may well be associated with the different accessible sites, the catalytic activity may be expected to give information about the cation distribution. Tung and McIninch were able to show that their kinetic results for cracking reactions over CaY could be closely correlated with the reported cation distribution in the 100% exchanged zeolite which was obtained by X-ray methods, if it was assumed that the observed site preferences are the same in faujasite and zeolite Y, and that this also indicates the order in which sodium ions were replaced at the various sites during exchange. Typical microcrystalline molecular sieve preparations are not very suitable for X-ray determination of cation distribution (*4*, *5*) so that this type of comparison is often not possible. In any case, it is apparent that not all kinetic results can be so simply explained. Pope and Kemball (*6*) found that the catalytic activity of NiX in the exchange reaction between benzene and deuterium increased quickly to a constant level after only a very small amount of nickel had been introduced, and that further ion exchange had little effect. This result made it seem unlikely that arguments which consider all cation sites of a particular crystallographic type as equivalent can always be adequate.

This work was undertaken to find whether a cracking reaction over NiX would show the same pattern of activity. It was hoped that the possibility of discontinuous changes in the product distribution would aid the interpretation of the results.

Methods

A. *Materials*

A range of nickel-containing zeolites was prepared by ion exchange from the same bulk sample of binder-free Molecular Sieve Type 13X, manufactured by Linde, and marketed by B.D.H.Ltd. Batch No. 0003940. Our procedures closely followed those of Pope and Kemball (*6*). We use the nomenclature of Egerton and Stone (*4*) in calling, for example, a sample in which 20.5% of the exchangeable sodium ions have been replaced by nickel ions NiX–20.5. The starting material will be termed NaX.

No analysis was carried out for sodium in the exchange solutions, because it was felt that the much lower accuracy which could be achieved would make the results of little value. No significant pH change occurred, showing little or no exchangeable hydrogen was being replaced by nickel ions.

A sample of NaX which had been thoroughly washed with deionized, distilled water was analyzed for sodium, aluminum, silicon and water. This gave a unit cell composition of $Na_{81\pm2}\,(AlO_2)_{86\pm2}\,(SiO_2)_{106\pm2}\,(H_2O)_{263\pm2}$. Water content was estimated by assuming that material calcined to 1000°C was water free. These results are consistent with analytical data supplied by the Linde Corporation, as being typical of their product. The apparent Na^+ deficiency is presumably due to the presence of H^+ (or OH). The unit cell size, estimated from 16 diffraction lines in the range $2\theta = 35$ to 53°, and using the 222 and 200 lines from Analar NaCl as an internal standard, was 2.4960 nm, with a standard deviation of ±0.0007 nm. This also is consistent with the analytical data, although there are differences in reported correlations between cell size and composition (*7–9*).

The *n*-hexane was a standard sample obtained from the Chemical Standards Division of the National Physical Laboratory, England. It was degassed in the usual way by freezing, pumping, and melting. All other hydrocarbons, used in calibration, were CP grade reagents from the Matheson Company. Hydrogen was supplied by N.Z.I.G. Limited, and purified by passage through a palladium thimble. All these materials gave single peaks with the gas chromatography arrangements used in this work.

B. *Apparatus and Sampling*

The experiments were carried out with a conventional vacuum system, capable of sustaining a dynamic vacuum of about 10^{-3} N m^{-2} ($\sim 10^{-5}$ Torr). The zeolite sample (about 0.1 g) was placed in the bottom of a reaction vessel, volume ~200 cm^3, constructed so that a 1 mm capillary sampling lead extended into the center of the gas space, with its entrance about 5 cm above

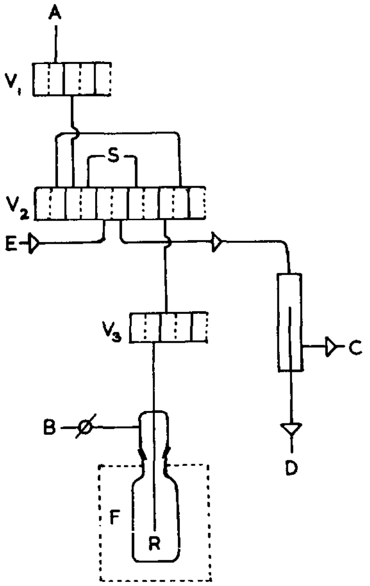

FIG. 1. Schematic diagram showing sampling arrangements: A, Outlet to vacuum line; B, To dosing line; C, Splitter outlet to gas–solid column; D, Splitter outlet to capillary column; E, Carrier gas inlet; F, Furnace; R, Reaction vessel; S, Sampling loop; V, Sliding piston valves, showing the two sets of O-ring positions as dashed and full lines.

the zeolite (Fig. 1). The capillary was connected outside the vessel to a simple, small volume, sliding piston valve, which could isolate it from a Loenco eight-port gas sampling valve of similar general design (Loenco type L-208, Loenco Inc., CA). A further sliding piston valve allowed the sampling loop connected to the Loenco valve (volume ~1.6 cm^3) to be evacuated when desired. The tubes leading to the sampling loop from the reaction vessel, in which the gas phase could not generally be expected to have the same composition as that in the rest of the reaction vessel, were designed to be of very small volume. The total volume from the mouth of the capillary tube in the reaction vessel, through the first isolation valve, the Loenco valve to the vacuum cutoff valve was about 0.6 cm^3 (Fig. 1). Sampling was carried out in the following way. Immediately before analysis was required, the contents of the lead were removed by expansion into the evacuated space leading to the vacuum valve. This unrepresentative sample was pumped to waste for 10 sec, before the reaction vessel was reconnected to the previously evacuated sampling loop. The time of sampling was recorded when this connection was made, but it was found desirable to allow 20 sec equilibration time after this. The reaction vessel valve was then closed, and the Loenco valve used to make an injection into the chromatography apparatus. The flushing procedure, and the small volume of the lead-in capillary (~0.3 cm^3) compared with the sample loop (1.6 cm^3) insured that the sample analyzed was truly representative of the gas phase at the chosen time.

The valves were designed to operate without grease, but it was found in practice that a very light lubrication of the O-ring seals with silicon grease was desirable. Leakage past the seals was found to be negligible, and quantitative calibrations showed that the samples of hexane introduced were reproducible. After the largest doses of hexane had been contained in the sampling system, blank injections produced no hexane peak, provided that the loop was evacuated for at least 60 sec.

C. *Gas Analysis*

The gas analysis procedure was designed to allow repeated quantitative analyses of *n*-hexane and all other hydrocarbons with less than six carbon atoms at intervals of not more than 5 min. This was achieved by using a squalane coated capillary column (50 m long; 2.5×10^{-2} cm i.d., supplied by the Perkin–Elmer Corporation) and a gas–solid column (90 cm long; 0.32 cm i.d.; packed with 60–80 mesh Spheron 6 (2700) graphitized carbon black, supplied by the Cabot Corporation) in parallel. The capillary column was connected to the outlet of a gas splitter in the usual way, and the gas–solid column to the vent. The split ratio was controlled by placing a suitable throttle in series with the gas–solid column.

The Spheron column resolved all paraffins and monoolefins with four or fewer carbon atoms in the desired time, with the exception of propane and propene whose peaks overlapped. Methane could be resolved from hydrogen when the column was operated at 0°C.

When analysis for hydrogen was required, nitrogen was used as carrier, and the Spheron column was held at 0°C. A katharometer (Servomex Controls Microkatharometer, MK 158) was connected to the Spheron column, and a flame ionization detector to the capillary column.

Otherwise, helium was used as carrier, to allow greater sensitivity with the katharometer, which was then coupled to the capillary column. The flame ionization detector was used on the Spheron column, which was then kept at 50°C. The capillary column was always operated at 35°C.

Identification of products and quantitative analysis were achieved by calibration with known samples. The relative retention times observed with the capillary column agreed well with the data of Hively and Hinton (*10*). As most of the peaks observed were rather sharp, calibration using peak areas was not practicable, and peak heights were used instead. Known amounts of calibrating gas or gas mixture were injected at regular intervals during a kinetic run, and the partial pressures of all the gases in the reaction vessel worked out using these reference peak heights and relative sensitivity data obtained from previous calibration. This ensured that analysis was not significantly affected by different column conditions or detector sensitivities experienced from run to run.

D. *Experimental Procedure*

The zeolite samples were outgassed for at least 4 hr at room temperature, before slowly heating to the final reaction temperature over a period of 8 hr. Outgassing was then continued for a further 12 hr. Temperatures were measured with a calibrated chromel–alumel thermocouple, placed in a well in an aluminum block which was a close fit to the reaction vessel. The furnace used allowed a temperature jump of 30–40°C to be made, and a new isothermal condition attained within about 10 min, so that a single catalyst reactant mixture could be studied at two temperatures.

To avoid any possibility of sorbed molecules appreciably blocking the zeolite channels, the dose of hexane used was limited to one molecule per supercage. After each gas phase sample was removed, the measured partial pressures of all the components were corrected by a factor calculated as the ratio of the number of molecules removed to the total number present. The reaction was then treated as if it were occurring in a closed system. This procedure is only correct for a first-order reaction, but as only about 1% of the gas phase was removed at each sampling, any errors introduced are negligible.

In situ krypton adsorption measurements at 77°K were used to show that outgassing was not causing the zeolite framework to collapse. Surprisingly, all the samples studied—NaX, NiX–0.55, NiX–2.1, NiX–14.7, NiX–20.3, NiX–47.0 and NiX–60.8 gave the same krypton BET specific surface area within an experimental error of ±2%. This contrasts with measurements of the argon adsorption capacity (*11*), and the water content of the fully hydrated zeolites, made on samples from the same batches of ion-exchanged material, both of which depend, as expected, on the degree of ion exchange (*11*, *12*). Nevertheless, we take these results to indicate a satisfactory outgassing procedure.

Routine powder X-ray diffraction measurements using nickel filtered copper K_α radiation were made from time to time. When accurate diffraction angles were required an internal standard of dried Analar sodium chloride was mixed with the zeolite.

RESULTS

NaX did not produce a significant cracking reaction below 500°C. At this temperature, about 2% of the reactant *n*-hexane was consumed per hour. The initial products were methane (35 mole %), ethene (25 mole %), propane (22 mole %), ethane (10 mole %) and *n*-butane (7 mole %). There was no other detectable product. This distribution is similar to that found by Frilette, Weisz and Golden (*1*) on cracking *n*-dodecane over NaX, and is typical of thermal cracking by a free radical mechanism. A blank reaction in the empty Pyrex reaction vessel at 500°C was only slightly slower. It produced similar proportions of C_1 to C_3 hydrocarbons, but with 1-butene as the only other product. The BET area of the NaX catalyst was about 80 m^2, whereas the geometric area of the Pyrex vessel was only about 0.02 m^2. Our NaX is thus a very poor cracking catalyst, and less effective per unit area than Pyrex glass. In fact, it seems probable that both solids take part in both initiation and termination steps of an essentially gas phase chain reaction, and have rather little net effect. Chrysochoos and Bryce (*13*) suggested that their quartz reaction vessel behaved in a similar way at this temperature.

The results obtained with NiX catalysts were quite different and showed the following general pattern. Reaction proceeded at a convenient rate to study (half-life in most cases 1–2 hr) at about 400°C. With a freshly outgassed, new sample of catalyst, the only initial reaction observed was a decrease in hexane pressure and the slow formation of hydrogen. After a long induction period, which was not very reproducible but was usually 1.5–2 hr at 400°C, methane began to form over NiX–20.5 and NiX–47.0, and the rate of this process at first increased with time. When all the hexane had just disappeared, the hydrogen pressure reached a maximum value, and thereafter slowly declined. Methane concentration reached a steady maximum value after a slightly longer period (Fig. 2). Gas phase reactants and products did not show a mass balance in either carbon or hydrogen. The initial values for the ratio of hydrogen molecules formed per hexane molecule consumed were about 0.5, 1.3 and 2.8 for NiX–0.55, NiX–20.5 and NiX–47.0, respectively. With NiX–47.0 it was very noticeable that any attempt to fit the kinetic curve with a simple first-order rate law expression resulted in rate constants which increased with time.

When a sample of catalyst was reused in a second reaction, after re-outgassing, the results were considerably changed. With NiX–20.5 and NiX–47.0 the initial rate of *n*-hexane removal increased about three- and fivefold, respectively, and the initial rate of hydrogen formation about tenfold. The hydrogen concentration still passed through a maximum at about the same time as the last of the hexane disappeared. Methane formation again followed a sigmoid curve, but the induction period was reduced (typically to 40–50 min at 400°C). The relative amounts of hydrogen and methane finally produced were about the same as before. This ratio was about ten with NiX–20.5 and about three with NiX–47.0. Slightly more of the hydrogen in the *n*-hexane found its way into gas phase products over the used catalyst (70% compared with 60% on NiX–20.5; 85% compared with 80% on NiX–47.0). Figure 3 shows typical kinetic results obtained with a used catalyst.

Continued use of a catalyst led to gradually increasing activity, but the product distribution and general form of the kinetic curve remained very much the same. A catalyst prepared by impregnating NiX with nickel nitrate solution, followed by drying and reduction in hydrogen at 400°C again gave only methane and hydrogen as products of hexane cracking. The mass balance on gas phase products accounted for 25% of the carbon and 85% of the hydrogen in the hexane dose. Allowing for the increased nickel content of this catalyst (about 50% of the nickel present after impregnation was due to ion exchange, the

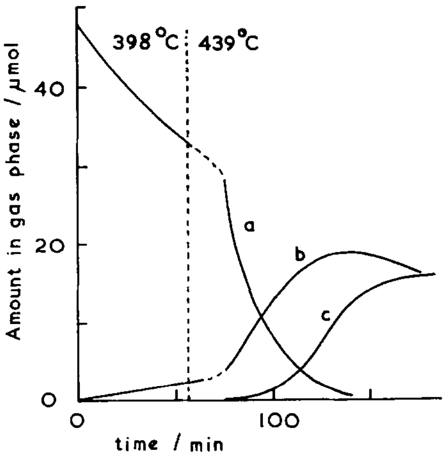

FIG. 2. Reaction over a fresh sample of NiX–20.5: (a) *n*-Hexane; (b) Amount of hydrogen, divided by 10; (c) Methane; The temperature was increased at the position of the dotted line, and was stabilized within 10 min to the higher value. Ordinate: Amount in gas phase (µmole). Abscissa: Time (min).

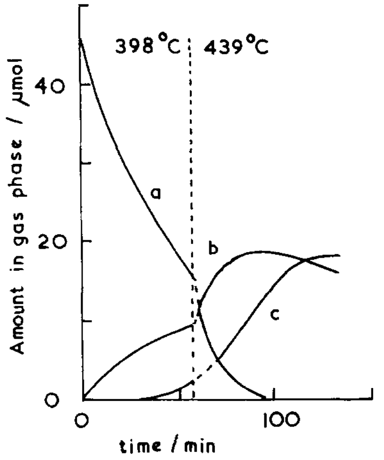

FIG. 3. Reaction over a previously used sample of NiX–20.5: (a) *n*-Hexane; (b) Amount of hydrogen, divided by 10; (c) Methane; The temperature was increased at the position of the dotted line, and was stabilized within 10 min to the higher value. Ordinate: Amount in gas phase (µmole). Abscissa: Time (min).

remainder to occluded salt), it behaved in all ways like a used sample of NiX–47.0. Reproducibility of reaction rates using fresh samples of catalyst was about ±20%.

After repeated use, the outgassed catalyst gradually changed color from pale brown through deep brown to black. X-Ray diffraction measurements indicated the presence of nickel crystallites, but no other new solid phase. Although an interstitial nickel carbide, Ni_xC with $x > 4$, has been reported to give a diffraction pattern very similar to nickel metal (*14*), this assignment did not provide as good a fit for either the diffraction angles or the relative intensities of our observed lines. Gouy balance measurements revealed ferromagnetism. Microanalysis showed the presence of carbon, one much-used sample containing as much as 14% by weight.

NiX–0.55 behaved quite differently. This material lost its catalytic activity after about half the first dose of *n*-hexane had reacted, and a small amount of hydrogen been formed. No methane was observed. Outgassing this material did not restore its activity, and the used catalyst showed very low activity and was not ferromagnetic, although its apparent susceptibility was increased.

As water, either as water molecules or surface hydroxyl groups, was almost certainly a product of reaction, a few experiments were performed with water pretreated catalysts. A normally outgassed unused sample of NiX–20.5 was dosed with about 0.03 water molecules per nickel ion. No effect on the rates or product distribution was observed. A dose concentration ten times as great as this on a previously used sample of NiX–47.0 also failed to produce any significant change in reactivity.

These results show that adsorption of product water molecules has little or no effect on the kinetics, and that production of hydrogen and methane is not due to the reaction of an intermediate nickel carbide with water, as would appear possible from the results of Freel and Galwey (*15*).

Some experiments were also performed in which hydrogen was mixed with the reactant hexane. When the hydrogen to *n*-hexane molecular ratio was three, and the catalyst a used sample of NiX–20.5, the major effects were an increase in the rate of removal of *n*-hexane (by a factor of about three) and a considerable slowing in the rate of formation of hydrogen (about tenfold). The rate of methane formation was not significantly altered. A hydrogen: hexane ratio of 16 with a used NiX–47.0 catalyst again led to an increased initial rate of hexane removal, but in this case the initial rate of methane formation was increased about tenfold, and hydrogen was slowly consumed and not liberated as in other runs. The rate of all reactions rapidly decreased with time, and reaction stopped when about 35% of the hexane had been consumed. Raising the reaction temperature from 400 to 439°C did not produce any effect, and the catalyst activity was not restored after outgassing for 12 hr at 475°C. Because this result was so surprising the experiment was repeated, and exactly the same behavior occurred. A catalyst of the same composition, which had been prereduced with hydrogen before dosing with the hydrogen–hexane mixture did not show this rate deceleration or loss of activity, and was unique in that all the carbon in the hexane was quantitatively converted to methane.

The involatile residue normally left on the catalyst after an experiment could not be removed by treatment with hydrogen, even at 510°C. Treatment with air at this temperature was also without effect.

The influence of the degree of ion exchange on the reactivity of the catalyst at 400°C is shown in Fig. 4. The behavior of the unused catalysts shows a striking resemblance to the results reported by Pope and Kemball (*6*). Little change in activity with ion exchange is observed over the range of catalysts examined, although the original NaX was about ten times less active at a temperature 120°C higher.

DISCUSSION

Our results with NiX are similar to those of Galich *et al.* (*16*) for the temperature at which reaction took place and the large

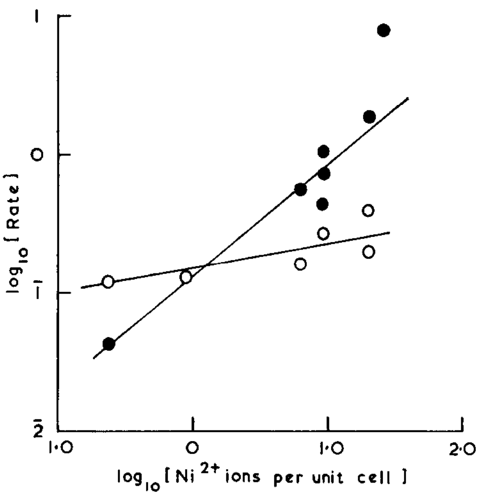

FIG. 4. Rate of n-hexane removal from the gas phase at 400°C and 0.8 kN m^{-2} (6 Torr) by used and unused catalysts. Rates are expressed as μmoles of n-hexane per g of catalyst per min: ○ Unused; ● Used. Ordinate: log$_{10}$ (Rate). Abscissa: log$_{10}$ (Ni^{2+} ions per unit cell).

amount of hydrogen in the gas phase products, but we did not observe any production of olefins or aromatics. The fact that we obtained only one gas phase hydrocarbon product, methane, prompted an examination of the equilibrium situation. Tabulated data (*17*) show that for reactions in which n-hexane produces carbon and one other hydrocarbon stoichiometrically at the temperatures we have used, the production of methane is strongly favored on thermodynamic grounds. However, on this basis, hydrogen should not be a product so that a chemical equilibrium does not appear to explain the simple product distribution.

It seems clear that in our work nickel ions in the zeolite are reduced to nickel atoms, which then migrate to form nickel metal crystallites on the external surfaces of the zeolite particles. X-Ray and magnetic measurements support this view, and this type of behavior by reduced nickel ions is well established (*18*, *19*). Measurements of the rate of disappearance of n-hexane on both used and unused catalysts show that the nickel ions and nickel metal chemisorb hexane at rather similar net rates at 400°C, with the activity of the metal being slightly greater. This helps to explain why the removal of n-hexane does not follow a simple rate law. It is also quite probable that hydrogen produced during reaction could inhibit hydrogenolysis (*20*), which may further complicate the curves. The autocatalytic production of methane suggests that cracking only occurs over the nickel metal under the conditions of our experiments. The results are very similar to those observed with catalysts of nickel supported on silica–alumina (*20*).

Comparison of the initial rate of hydrogen production with the rate of disappearance of hexane does not give a very reliable estimate of the average number of carbon hydrogen bonds broken on chemisorption, as it is known that hydrogen will react with NiX under the conditions used in the work (*11*). The fact that the hydrogen concentration observed reaches a maximum, and then declines slowly suggests that this reaction was taking place during our experiments. It is clear, however, that chemisorption is dissociative on both used and unused catalysts, and that the degree of dissociation is far greater over the used material. The results are consistent with the rupture of one or two C–H bonds for chemisorption on an ion, and with very extensive bond breaking, producing a highly carbonaceous residue over the nickel metal.

Infrared studies of alkene adsorption on silica-supported nickel help to confirm these views (*21*). Ethene adsorption at −78°C was largely associative, but as the temperature was raised a dissociative mechanism soon became more important, and the degree of dissociation continued to increase to the highest temperature studied (150°C). 1-Butene behaved in a similar way. The adsorbed species underwent self hydrogenation–dehydrogenation reactions, and could also be hydrogenated with hydrogen gas, so that these results can presumably be taken to indicate the fate of adsorbed alkanes as well. Ethene showed a marked tendency to dimerise above 20°C. Results at 150°C showed very low intensities for C–H absorption, indicating little hydrogen content in the adsorbed residues. A trace of methane was observed in the gas phase at 150°C.

Although we could not detect any carbon residue by X-ray diffraction, krypton adsorption measurements on an extensively used catalyst (containing 14% by weight of carbon, according to microanalysis) revealed an increased adsorption capacity which was too great to be accounted for purely by adsorption on the nickel crystallites produced. Surprisingly, even this large amount of carbon had not reduced the activity of the catalyst. This must mean that the chemisorbed residues are readily mobile, and form aggregates on the external surface of the zeolite.

We think that the behavior of the used, or essentially supported nickel catalyst, may be explained by the ability of the product from dissociative chemisorption of hexane to undergo two competing reactions, viz., polymerization or carbon–carbon bond scission. There is much evidence to show that the α carbon–carbon bond is very selectively broken on hydrogenolysis over nickel (*22*). This readily explains the production of methane, but not why other products (e.g., pentanes) are absent. We suggest that residues containing more than one carbon atom are multiply bonded to the surface, so that they are not readily desorbed and polymerization to larger residues almost invariably follows. After α carbon–carbon bond breaking, the desorption of methane is competitive with the reformation of this bond, or addition of the single carbon fragment to another adsorbed residue. Only when there is a large surface concentration of adsorbed hydrogen as with a hydrogen reduced catalyst used in the presence of excess hydrogen, does all the reactant carbon finish up as methane by a succession of α bond breakages followed by hydrogenation and desorption of the single carbon fragment. In none of our other experiments did significantly more than one methane molecule appear as a product for each hexane molecule consumed, and the usual figure was nearer one-half.

We now consider the initial stages of reaction on an unused catalyst. The cation sites in molecular sieve X which are accessible to *n*-hexane are well separated, so that it appears that each adsorbed hexane molecule could be bonded to only one nickel ion. This is consistent with the relatively slow initial formation of hydrogen by a dissociative adsorption mechanism which breaks one or perhaps two C–H bonds. We cannot be sure that the experimental value for the number of bonds broken is not too high, due to some contribution from a more extensive dissociation process on some nickel metal which has been formed even in the early stages of reaction. The hydrogen produced from the initial dissociation is then thought to be responsible for the reduction of nickel ions to nickel atoms, which migrate to form metal crystallites as discussed earlier. These processes are fast under our experimental conditions (*11*). It is hard to see, however, why the nickel metal first formed, which is apparently quite capable of dissociatively adsorbing hexane, does not act as a hydrogenolysis catalyst until after an induction period. This may be a result of the relative concentrations of "hexane" and hydrogen at the catalyst surface at various stages of the reaction. Initially, in the absence of added hydrogen, hexane residues greatly predominate over hydrogen, so that stoichiometric considerations make the production of methane very improbable. The fact that the induction periods were shorter on a used catalyst, and even further decreased on hydrogen reduced NiX, are consistent with this.

We have already described how the variation of activity of previously unused catalysts as measured by the rate of irreversible removal of *n*-hexane from the gas phase, as a function of ion exchange level, bears a striking resemblance to the result of Pope and Kemball. The used catalysts, however, behaved quite differently and showed an approximately linear increase in activity with ion exchange (Fig. 4). The results with NiX–0.55 are particularly interesting. At this level of exchange, there is only about 1 nickel ion per 40 supercages, and yet dissociative adsorption of at least 2 hexane molecules per 3 supercages can occur on the previously unused catalyst. The amount of hydrogen produced is far less than would be formed over nickel metal, so that the same nickel ions must successively chemisorb several hexane molecules. On reuse of the catalyst, dissociation is much more complete on adsorption, but the rate of adsorption is decreased and eventually ceases before all the hexane is used up. The extent of dissociation points to some adsorption by nickel metal but it seems that the metal produced, atom for atom, does not adsorb hexane as readily as the unreduced ions. The quick decay in adsorption rate, and failure to produce methane, may indicate that the metal activity at these low concentrations is destroyed by poisons present in the system. The special nickel ions, which are active for the chemisorption of hexane and are preferentially ion exchanged into the zeolite, are presumably gradually reduced to nickel metal, but their activity in this reaction cannot be very exceptional or the characteristic reaction of unused catalyst would stop even sooner. The failure of the special group of ions to to show very facile reduction with hydrogen is consistent with other work carried out in this laboratory (*11*). The linear increase in metal activity on the used catalysts with ion exchange is also in agreement with that work. It was found that about one-third of the nickel ions in NiX were relatively easily reduced and that this fraction was not very dependent on the ion exchange level. This suggested that there is not any marked preference by nickel ions for any of the various crystallographic sites during exchange, and is consistent with the views of other workers (*23–25*). The reactivity results show that the special ions behave towards reduction with hydrogen as fairly typical members of this much larger group of relatively easily reduced ions.

We have no explanation for the fact that the use of hydrogen–hexane mixtures could cause the activity to decrease with time, whereas no similar effect was observed in the absence of added hydrogen, or when a mixture was used, but the catalyst had been pretreated with hydrogen. It may be significant that when mass balances were performed after runs which had shown strong deceleration, the involatile residue formed had a net composition of more than two hydrogens per carbon. The highest ratio obtained in the more usual experiments was 1.2 (on used NiX–20.5, treated with a hydrogen–hexane mixture), and was generally less than one. The lowest value, 0.5, was obtained with the zeolite-supported nickel catalyst, but a rather similar result was found with a used sample of NiX–47.0.

It may therefore be that polymeric residues containing relatively large amounts of hydrogen are poisons for the nickel catalyst, whereas the more highly carbonaceous residues are not. If this is so, the reasons for it seem obscure.

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