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THE CATALYTIC DEHYDROGENATION OF CYCLOHEXANE AND METHYLCYCLOHEXANE OVER NICKEL LOADED Y ZEOLITES

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The dehydrogenation of cyclohexane to benzene and of methylcyclohexane to toluene was investigated over a range of nickel Y zeolites, varying the nickel content and the nature of the alkali metal co-cation (Li^+, Na^+, K^+, Rb^+ or Cs^+). The overall reaction is viewed as occuring via a series of consecutive dehydrogenation steps. Catalytic activity is correlated with the reaction time, the reaction temperature, the level of Ni^{2+} exchange and the effects of pyridine adsorption. The level of dehydrogenation is strongly dependent on the mass of supported nickel metal and the surface Bronsted acidity. Catalyst deactivation results from the deposition of coke on the catalyst surface which is promoted with increasing zeolite acidity.

1. Introduction

The importance of the catalytic dehydrogenation of naphthenes in catalytic reforming has provided much of the motivation for research in this field. Although there have been a number of studies concerning cyclohexane dehydrogenation over supported nickel metal, the role of the zeolite support has not been fully investigated. Balandin, in his multiplet theory [1], concluded that cyclohexane is converted to benzene in one step in which six hydrogen atoms are simultaneously removed. Atomic steps have been more realistically identified as taking place; the dehydrogenation of the cyclohexene intermediate has been proposed as the rate limiting step [2]. Nickel supported zeolites have been reported to exhibit a low activity for cyclohexane dehydrogenation in the temperature range 623 K–823 K [3,4]. The divalent nickel cations have been identified as the active sites [3,4]; on reduction to nickel metal, the activation energy for the reaction doubled [4]. Nevertheless, Bager et al. [5] obtained a selective dehydrogenation to benzene over nickel supported Y zeolites, the specific activity for the

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reaction increasing in the order: NiNaY < $NiNH_4Y$ < NiCeNaY < NiCaNaY. With the exception of NiNaY, which exhibited a maximum in activity at a reduction temperature of 673 K, the other catalysts attained a maximum in activity at reduction temperatures in the range 623 K–673 K [5]. A series of reports have shown that a simultaneous dehydrogenation and isomerization of cyclohexane occurs over metal catalysts [2,6,7]. Comparison of rate data indicates that isomerization is the result of catalyst acidity [6]. Rossinski et al. [8] report the formation of two kinds of hydrocarbons, i.e. (i) paraffins and C_1–C_6 olefins which are the products of ring opening or cracking reactions and (ii) cyclic hydrocarbons due to dehydrogenation/isomerization reactions.

The dehydrogenation of methylcyclohexane to toluene has been widely used for testing platinum supported catalysts [9–12]. It is generally agreed that the reaction proceeds via successive dehydrogenation steps; the first dehydrogenation step (to methylcyclohexene) has been shown by Corma [9,11] to be rate determining whereas Ponec [12] has proposed that the desorption of the product (toluene) from the metallic surface is rate controlling. Partially dehydrogenated products have been suggested to act as coke precursors [11]; the extent of catalyst deactivation was six times greater when methylcyclohexene was used as feed [9]. To date, there have been no reports on the catalytic conversion of methylcyclohexane over zeolite supported nickel. Indeed, this paper represents the only study to concern itself with the effects of varying the alkali metal co-cation on the catalytic dehydrogenation (of both cyclohexane and methylcyclohexane) of nickel metal supported on Y zeolites.

2. Materials and methods

The starting or parent zeolite was Linde Molecular Sieve LZY-52 (formula: $Na_{58}(AlO_2)_{58}(SiO_2)_{134}(H_2O)_{260}$). KY and LiY (100% exchange) and RbNaY and CsNaY (ca. 68% exchange) were prepared by exchanging out the parent Na^+ ions. 250 g of NaY were refluxed with 1 M solutions of KNO_3, $LiNO_3$, RbCl and CsCl (400 cm^3) for 24 hours after which the zeolite was filtered and thoroughly washed with hot deionized water to remove the occluded salt. The partially exchanged samples, i.e. K, Li, Rb, Cs/NaY, were exchanged a further nine times as described above. Nickel exchanged catalysts were prepared by taking 100 g of NaY, KY, LiY, RbNaY or CsNaY and refluxing with a 400 cm^3 0.1 M $Ni(NO_3)_2$ solution for 24 hours. Under these conditions, a single exchange cycle resulted in a maximum exchange of ca. 7 Ni^{2+}/U.C., i.e. seven nickel ions per unit cell. In preparing samples with loadings greater than ca. 7 Ni^{2+}/U.C., repeated exchange was necessary. All the samples were air dried at 373 K for 20 hours and stored over saturated NH_4Cl solutions in order to maintain a constant humidity. Atomic absorption and flame emission techniques were employed to determine the cation contents. Thermal analyses were conducted on all the prepared samples using a

Perkin Elmer thermobalance to measure the water contents. Samples are labelled according to the % exchange of the indigenous alkali metal co-cation and the total number of Ni^{2+} ions per unit cell, eg. the NiKY-23.52 sample exhibits a 23.52% exchange of the 58 parent K^+ ions resulting in a total of 6.82 Ni^{2+}/U.C. X-ray diffraction and infrared spectroscopy were used to monitor the crystallinity of the samples; the infrared band at 395 cm^{-1} has been shown to be very sensitive to changes in crystallinity [13].

All the catalytic reactions were carried out under atmospheric pressure in a fixed bed tubular glass reactor. The hydrated catalysts were pelletized without binder under a pressure of 4000 kg cm^{-2} and sieved in the mesh range 1.18–1.70 mm. The zeolite pellets were then activated by heating (at a fixed linear rate of 200 K hr^{-1}) to a final temperature of 423 K which was maintained for 18 hours. Mole % conversion of cyclohexane (or methylcyclohexane) after six hours on stream was used as a point of comparison between different catalysts. The W/F values quoted in this study represent the mass of hydrated catalyst in grams divided by the feed rate of cyclohexane (or methylcyclohexane) in moles per hour. Treatment of the reduced zeolite samples with pyridine to poison the surface Bronsted sites was achieved by passing a steady 2.0 cm^3 min^{-1} flow of pyridine through the activated catalyst at 473 K for 30 minutes. The catalyst was then flushed with hydrogen for an hour and the temperature raised to 573 K with a further 3 hour hydrogen (120 cm^3 min^{-1}) treatment prior to catalysis. The level of coke deposition within the zeolite pores was monitored by measuring the carbon content of spent catalysts by microanalysis. The benzene, toluene, cyclohexane and methylcyclohexane used were of AnalaR grade and were further dried by standard methods [14].

3. Results and discussion

The chemical compositions of the ion exchanged zeolites are given in table 1. Sample crystallinity, monitored by X-ray diffraction and infrared spectroscopy, was maintained before and after catalysis. The catalytic activities of these samples for the hydrogenation of benzene [15,16] and toluene [15,17] have already been studied in these laboratories. The activity of these samples in promoting the reverse reaction, i.e. the dehydrogenation of cyclohexane and methylcyclohexane, are addressed in this paper.

The dehydrogenation of cyclohexane to benzene over the range of nickel zeolites generated low conversions which steadily increased with reaction temperature in the range 473 K–598 K, fig. 1. This is in complete contrast to the hydrogenation of benzene where a reaction temperature of 473 K was established in the case of NiKY-23.52 (6.82 Ni^{2+}/U.C.) for maximum activity. The activity versus time on stream profiles for four representative catalysts are illustrated in fig. 2. All the profiles exhibit the same basic shape, that of an initial increase in

Table 1
Chemical compositions of the nickel loaded Y zeolites prepared by ion exchange

Zeolite sample	AM^+/U.C. [a]	Ni^{2+}/U.C.	Water content (wt.%)
NaY	58.00	–	25.08
NiNaY-3.59	55.74	1.04	25.50
NiNaY-6.82	53.69	1.98	25.34
NiNaY-12.48	50.66	3.62	26.29
NiNaY-15.82	48.82	4.53	26.53
NiNaY-19.31	46.14	5.60	26.46
NiNaY-22.76	44.00	6.60	26.61
NiNaY-26.38	41.67	7.65	26.75
NiNaY-27.79	40.92	8.06	26.84
NiNaY-29.90	41.04	8.67	26.82
NiNaY-32.59	38.32	9.45	27.17
NiNaY-35.73	36.02	10.42	27.63
NiNaY-48.76	30.03	14.14	28.59
NiNaY-63.10	22.32	18.30	29.13
NiNaY-78.62	14.64	22.80	29.48
NiNaY-90.10	6.90	26.15	29.96
NiY	–	29.00	30.44
KY	58.00	–	22.41
NiKY-5.17	54.74	1.50	22.63
NiKY-8.04	53.34	2.33	22.31
NiKY-10.69	51.50	3.10	22.69
NiKY-17.90	47.52	5.19	23.61
NiKY-23.52	44.18	6.82	23.54
NiKY-26.86	42.42	7.79	24.17
NiKY-30.52	39.70	8.85	24.36
NiKY-35.62	36.87	10.33	24.81
NiKY-44.72	31.85	12.97	25.52
NiKY-46.97	30.80	13.62	25.96
NiKY-49.07	29.77	14.23	26.37
NiKY-54.48	26.22	15.80	26.91
NiKY-57.45	24.80	16.66	27.34
NiKY-62.52	22.30	18.13	27.60
NiKY-73.79	16.30	21.40	28.04
NiKY-81.97	13.13	23.77	28.43
NiKY-86.62	8.36	25.12	29.34
NiY	–	29.00	30.16
LiY	58.00	–	27.79
NiLiY-8.83	52.34	2.56	27.90
NiLiY-21.21	44.58	6.15	28.16
NiLiY-43.10	32.02	12.40	28.84
NiLiY-63.72	20.66	18.48	29.33
NiLiY-80.55	14.18	23.36	29.87
RbNaY	40.23	17.77	20.43
NiRbNaY-7.31	35.79	17.75	20.82
NiRbNaY-18.62	29.40	17.68	21.89

Table 1 (continued)

Zeolite sample	AM^+/U.C. [a]	Ni^{2+}/U.C.	Water content (wt.%)
NiRbNaY-27.31	24.30	17.70	23.02
NiRbNaY-35.13	19.83	17.62	24.15
NiRbNaY-47.41	15.24	15.74	25.94
NiRbNaY-59.10	10.32	15.10	27.36
CsNaY	39.76	19.24	7.84
NiCsNaY-3.55	36.64	19.20	10.13
NiCsNaY-16.41	29.22	19.14	12.31
NiCsNaY-22.03	26.00	19.06	13.14
NiCsNaY-31.07	20.72	18.74	14.86
NiCsNaY-44.28	13.60	18.74	16.63
NiCsNaY-54.83	11.24	17.00	19.37

[a] $AM^+ = Na^+, K^+, Li^+, Rb^+$ or Cs^+.

activity followed by either the attainment of a steady state conversion or by a slow continuous fall off in activity. From a previous study [18] concerned with probing the surface acidity of reduced nickel zeolites, it was shown that the higher nickel loaded sodium or lithium based zeolites exhibited the highest levels of Bronsted acidity. The slow continuous deactivation with time on stream was a characteristic of the more acidic samples and is exemplified by the profile for NiNaY-48.76 (14.14 Ni^{2+}/U.C.) shown in fig. 2. In common with benzene hydrogenation [15,16], the rate of deactivation for cyclohexane dehydrogenation is proportional to the zeolite acidity. The initial increase in benzene formation over the 0.5–1.0 hour interval suggests an initial induction period over the first half hour which is probably due to a saturation of the catalyst surface with

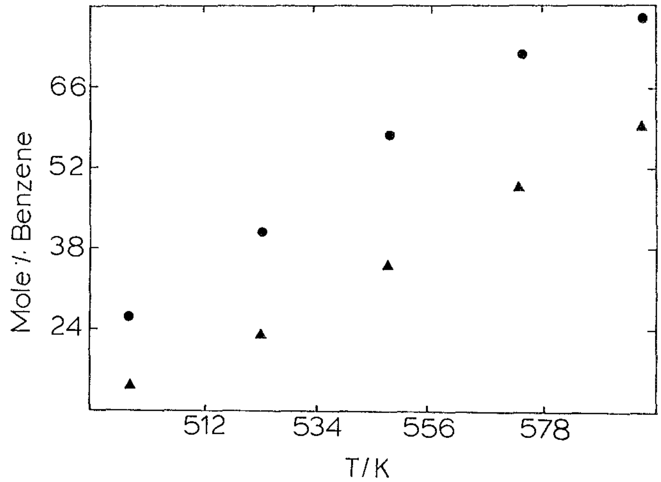

Fig. 1. Variation of cyclohexane dehydrogenation over NiKY-23.52 (6.82 Ni^{2+}/U.C.) (●) and NiNaY-22.76 (6.60 Ni^{2+}/U.C.) (▲) with reaction temperature: $W/F = 161.8$ g mol^{-1} hr.

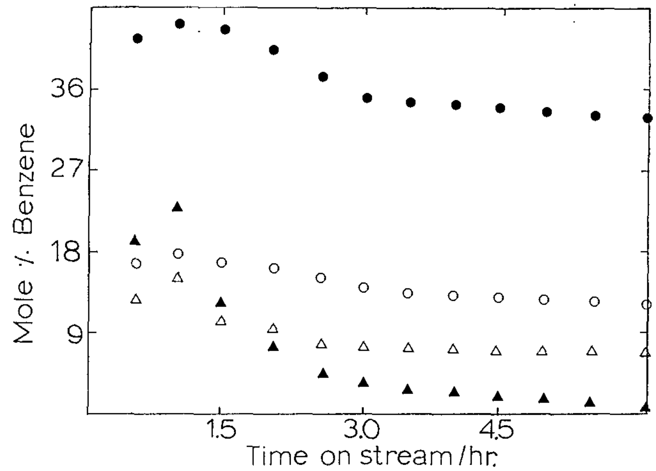

Fig. 2. Variation of cyclohexane dehydrogenation over NiKY-49.07 (14.23 Ni^{2+}/U.C.) (●), NiKY-23.52 (6.82 Ni^{2+}/U.C.) (○), NiNaY-22.76 (6.60 Ni^{2+}/U.C.) (△) and NiNaY-48.76 (14.14 Ni^{2+}/U.C.) (▲) with reaction time: $T = 373K$; $W/F = 161.8$ g mol^{-1} hr.

benzene. Indeed, from infrared and chromatographic studies conducted in these laboratories [15], it has been shown that under catalytic conditions benzene interacts much more strongly than cyclohexane with reduced nickel zeolites. Therefore, during the initial period of catalysis the zeolite surface selectively adsorbs benzene in preference to the reactant cyclohexane which results in a relative enrichment of cyclohexane in the product mixture. It is instructive to note in fig. 2 that the initial increase in activity is more marked for the sodium based samples; this is consistent with a stronger adsorption of benzene on NiNaY compared to NiKY [15]. The observed induction period suggests that the desorption of benzene from the active surface is rate determining.

Cyclohexane conversion at 573 K after six hours on stream as a function of nickel loading for a range of nickel exchanged alkali metal Y zeolites is presented in figs. 3 and 4. The shape of the profiles are identical to those observed for benzene hydrogenation over the same samples [15,16]. This suggests that the source of the catalytic activity is the same for both the forward and reverse reactions. In the case of the NiNaY samples (fig. 3), the level of benzene formation increases with nickel content up to a loading of ca. 7 Ni^{2+}/U.C. above which the activity decreases with increasing nickel loading; the higher loaded samples (12 Ni^{2+}/U.C.) exhibit negligible conversions after 8 hours. The NiKY samples show the same increase in activity (which is greater than that for the NiNaY system) up to ca. 7 Ni^{2+}/U.C. but also exhibit a marked increase in benzene formation at ca. 13 Ni^{2+}/U.C. which again begins to drop with further nickel exchange. In the case of the nickel-rich samples, i.e. 18 Ni^{2+}/U.C., dehydrogenation activity is negligible activity after 14 hours on stream. From the previous degree of Ni^{2+} reduction studies [19] the mass of nickel metal generated

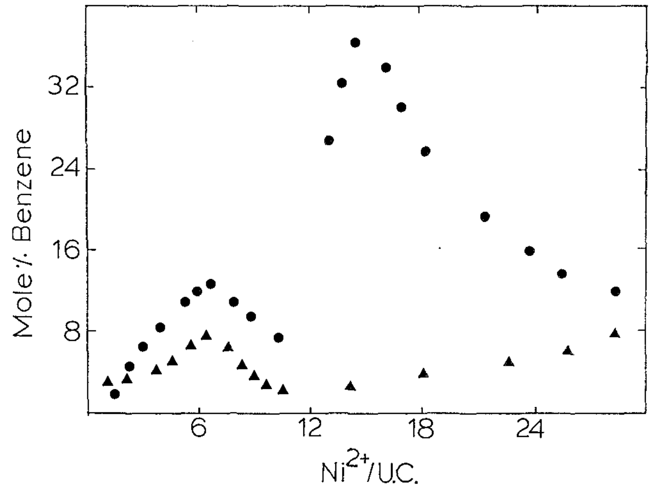

Fig. 3. Variation of cyclohexane dehydrogenation over NiKY (●) and NiNaY (▲) with nickel loading: $T = 373$ K; $W/F = 161.8$ g mol^{-1} hr.

was calculated. The correlation between the mass of nickel metal formed during the reduction process and the catalytic activity of the reduced nickel zeolites is presented in table 2. It can be seen that in the absence of a high level of Bronsted acidity (assumed for the pyridine treated samples), the extent of dehydrogenation is proportional to the mass of supported nickel metal present during catalysis. From the present study, it appears that the nickel metal is the catalytically active component and not the unreduced nickel cations as has previously been suggested [3,4]. The level of Bronsted acidity [18] and the extent of Ni^{2+} reduction [19] are dependent on the nature of the charge balancing co-cations. Hence, the overall

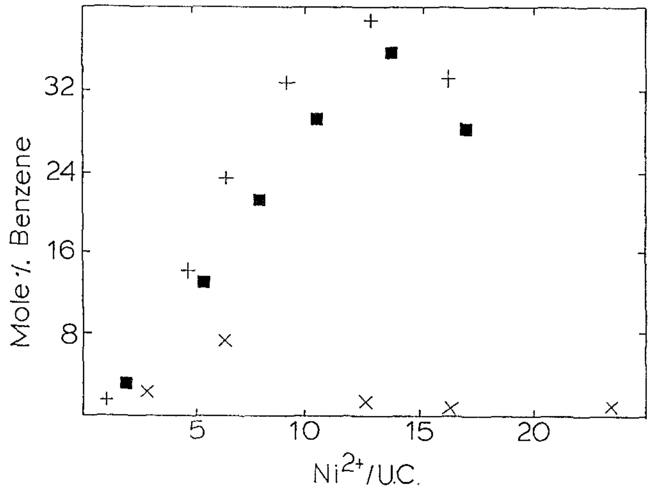

Fig. 4. Variation of cyclohexane dehydrogenation over NiCsNaY (+), NiRbNaY (■) and NiLiY (×) with nickel loading: $T = 373$ K; $W/F = 161.8$ g mol^{-1} hr.

Table 2

Effect of pyridine adsorption on the extent of cyclohexane dehydrogenation to benzene ($W/F=161.8$ g mol^{-1} hr) over a range of reduced nickel zeolites

Zeolite	Untreated		Treated with pyridine	
	gNi^0 [a]	Mole % C_6H_6 [b]	gNi^0	Mole % C_6H_6
NiNaY-6.82	0.3	3.6	0.3	4.2
NiNaY-17.28	1.4	6.1	1.4	8.4
NiNaY-35.73	2.2	2.8	2.6	13.1
NiNaY-63.10	3.4	2.0	4.9	17.6
NiNaY-90.10	4.3	6.6	6.7	30.1
NiKY-5.17	0.2	2.9	0.2	3.5
NiKY-17.90	1.3	10.1	1.4	10.6
NiKY-35.62	2.0	7.5	2.7	18.9
NiKY-62.52	3.7	20.6	5.3	27.4
NiKY-81.97	4.2	10.7	6.3	28.3
NiLiY-21.21	1.5	5.8	1.7	8.5
NiLiY-63.72	2.6	0.8	4.1	15.4
NiLiY-80.55	3.0	0.5	5.9	18.8
NiRbNaY-18.62	1.4	12.1	1.4	14.0
NiRbNaY-35.13	2.3	19.9	2.4	23.3
NiRbNaY-59.10	3.2	16.6	4.0	29.9
NiCsNaY-16.41	1.4	13.2	1.4	15.2
NiCsNaY-31.07	2.0	23.4	2.3	26.6
NiCsNaY-54.83	3.4	25.9	3.9	31.3

[a] 10^{-3} gNi^0 (gzeolite)$^{-1}$.

[b] 6 hours on stream.

dehydrogenation activity is strongly influenced by the basicity of the alkali metal cation. The activity versus nickel loading plots for catalysis over NiLiY, NiRbNaY and NiCsNaY are illustrated in fig. 4. The NiLiY samples exhibit a similar behavior to the NiNaY systems albeit with lower % conversions. The NiRbNaY and NiCsNaY samples show an increased activity with increased nickel loading up to ca. 14 Ni^{2+}/U.C.; the highest exchanged samples also exhibited the slow continuous deactivation, remarked upon previously, which rendered the catalysts completely inactive after ca. 32 hours on stream.

Although benzene was the principal product, methylcyclopentane (MCPa) was also isolated in the product mixture. The level of MCPa formation is plotted against nickel loading for a range of catalysts in fig. 5; MCPa fomation was negligible over the range of NiRbNaY and NiCsNaY samples investigated. It can be observed that % MCPa formation increases with nickel loading and hence with increasing zeolite acidity. Indeed, the overall order of increasing MCPa production, NiCsNaY < NiRbNaY < NiKY < NiNaY < NiLiY, mirrors that of increasing Bronsted acidity as inferred from infrared studies [18]. Catalytic deactivation in zeolites normally results from coke formation or the deposition of polynuclear

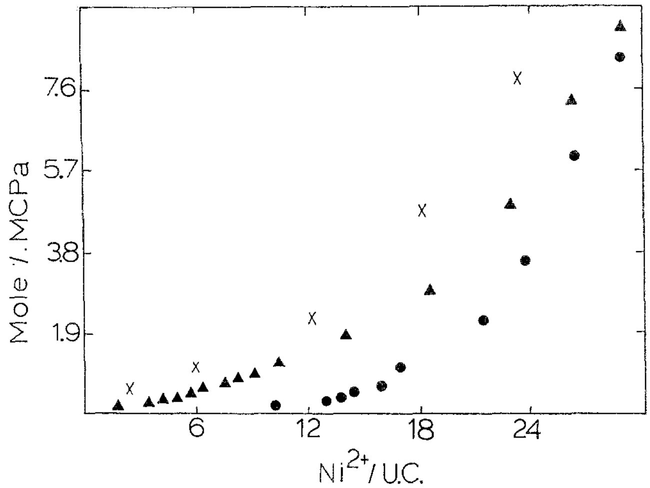

Fig. 5. Variation of MCPa formation over NiLiY (×), NiNaY (▲) and NiKY (●) with nickel loading: $T = 373$ K; $W/F = 161.8$ g mol^{-1} hr.

aromatic molecules within the pore structure thereby restricting access to the active sites. In this study the % carbon content (and hence the level of coking) of a range of spent samples was measured and the results are recorded in table 3. It

Table 3
Extent of coke formation during the dehydrogenation of cyclohexane ($W/F = 161.8$ g mol^{-1} hr) and methylcyclohexane ($W/F = 196.4$ g mol^{-1} hr) over a range of reduced nickel zeolites at 573 K

Zeolite sample	Ni^{2+}/U.C.	% residual carbon	
		C_6H_{12} feed	$C_6H_{11}CH_3$ feed
NiLiY-21.21	6.15	9.33	10.22
NiLiY-43.10	12.40	15.13	17.42
NiLiY-63.72	18.48	16.56	18.88
NiLiY-80.55	23.36	19.23	22.42
NiNaY-22.76	6.60	7.61	8.44
NiNaY-48.76	14.14	14.24	17.13
NiNaY-63.10	18.30	15.56	17.80
NiNaY-78.62	22.80	16.80	19.00
NiKY-23.52	6.82	5.44	6.25
NiKY-49.07	14.23	11.20	12.88
NiKY-62.52	18.13	12.23	14.28
NiKY-81.97	23.77	14.88	16.66
NiRbNaY-35.13	10.19	4.88	7.73
NiRbNaY-47.41	13.70	7.83	9.78
NiRbNaY-59.10	17.14	9.88	12.14
NiCsNaY-31.07	9.01	2.12	4.33
NiCsNaY-44.28	12.84	4.76	6.93
NiCsNaY-54.83	15.90	7.11	9.23

can be seen that the spent samples contain considerable residual carbon levels and therefore the most likely explanation for catalyst deactivation is the gradual accumulation of involatile coke in the zeolite channels. The extent of coke formation (at any particular level of nickel exchange) increases according to NiCsNaY < NiRbNaY < NiKY < NiNaY < NiLiY and therefore mirrors the order of increasing MCPa formation and that of increasing surface acidity. In the case of benzene hydrogenation [15,16], the desorption of cyclohexene from the metal sites is viewed as being the precursor for MCPa and, ultimately, coke formation. In order to determine whether the desorption of the strongly adsorbed benzene acts as a possible precusor for coke formation during the dehydrogenation of cyclohexane, one set of experiments were carried out where various cyclohexane/benzene feeds were passed over a range of reduced nickel zeolites. Varying the benzene/cyclohexane ratio had absolutely no influence on catalyst deactivation beyond a simple dilution of the reactants. The desorption of cyclohexene (which is formed by the abstraction of the first two hydrogens) to react at the acid sites may also be the initiation step for coke formation in a manner previously described for the hydrogenation of benzene [15,16]. Indeed, pyridine adsorption which enhanced benzene formation (table 2) was also accompanied by a decrease in MCPa formation and suppressed coking.

The activity versus time on stream profiles for the formation of toluene from a methylcyclohexane feed over a NiNaY and NiKY sample of similar nickel loading are shown in fig. 6. The increase in % conversion in the 0.5–1.0 hour period, which was observed for cyclohexane conversion, is also a characteristic of toluene formation. From a consideration of figs. 2 and 6, it may be observed that the initial increase in % conversion is more marked for methylcyclohexane dehydrogenation. This is consistent with an increased relative interaction of

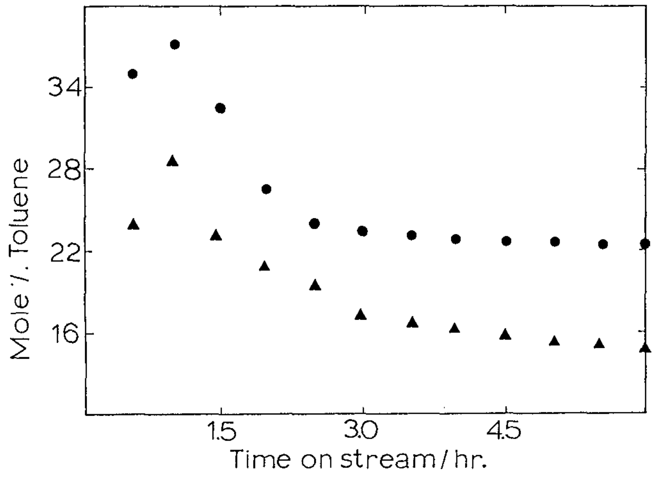

Fig. 6. Variation of methylcyclohexane dehydrogenation over NiKY-23.52 (6.82 Ni^{2+}/U.C.) (●) and NiNaY-22.76 (6.60 Ni^{2+}/U.C.) (▲) with reaction time: $T = 373$ K; $W/F = 196.4$ g mol^{-1} hr.

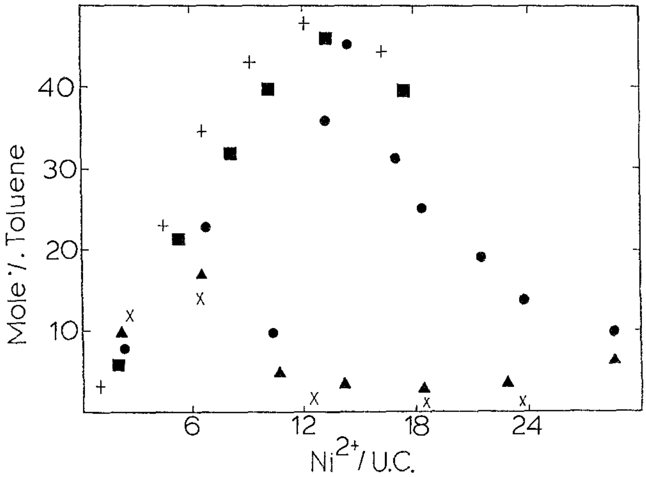

Fig. 7. Variation of methylcyclohexane dehydrogenation overNiCsNaY (+), NiRbNaY (■), NiKY (●), NiNaY (▲) and NiLiY (×) with nickel loading: $T = 373$ K; $W/F = 196.4$ g mol^{-1} hr.

toluene (compared to benzene) with the zeolite surface under catalytic conditions as measured in these laboratories [15]. The overall activity profiles for the range of nickel exchanged zeolites, plotted in fig. 7, exhibit the same basic shapes observed for cyclohexane dehydrogenation (figs. 3 and 4) which suggests a common reaction mechanism. A higher conversion of methylcyclohexane, compared to cyclohexane (as feed), was observed for catalysis over the lower nickel loaded (< 14 Ni^{2+}), less acidic samples. Methylcyclohexane conversion over the higher loaded samples is accompanied by increased deactivation with lower conversions relative to the dehydrogenation of cyclohexane. This must be related to the higher levels of coking observed for the methylcyclohexane conversion, table 3. As methylcyclohexene was isolated in minor amounts in the product mixture the dehydrogenation process must proceed via consecutive dehydrogenation steps as was suggested in previous reports [9,11].

4. Conclusions

The dehydrogenation of cyclohexane and methylcyclohexane over nickel exchanged Y zeolites is postulated to proceed via a series of consecutive dehydrogenation steps. As in the case of benzene hydrogenation [15,16], the desorption of cyclohexene from the active sites initiates MCPa and coke formation during cyclohexane dehydrogenation. Although the nickel zeolites serve as fertile media in promoting dehydrogenation reactions, the overall catalytic activity of the metal component is dependent on the acidity of the support. The effect of the nature of the charge balancing alkali metal co-cation is explained on the basis of the associated levels of Ni^{2+} reduction (or mass of nickel metal generated) and zeolite Bronsted acidity.

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