CATALYTIC OXIDATIVE DEHYDROGENATION OVER Cu^{2+} EXCHANGED NaY AND KY ZEOLITES

Brendan COUGHLAN and Mark A. KEANE *

Physical Chemistry Laboratories, University College, Galway, Eire

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The kinetics and mechanism of the oxidative dehydrogenation of cyclohexane over copper exchanged Y zeolites were studied. Benzene was identified as the primary product with cyclohexene and methylcyclopentane as secondary products. The associative adsorption of oxygen is proposed as the rate determining step. The levels of cyclohexane conversion were correlated with such diverse factors as the reaction temperature, Cu^{2+} cation loading, Cu^{2+} cation location and the extent of coke formation. The oxidative dehydrogenation of methylcyclohexane to toluene is also considered. The oxidative dehydrogenation of both cyclohexane and methylcyclohexane is shown to be strongly dependent on the nature of the alkali metal co-cation.

1. Introduction

Although the oxidative properties of ion exchanged zeolites are well known [1], the literature on oxidative dehydrogenation is scant. Among the supported ions investigated, i.e. Cu^{2+}, Pd^{2+}, Cr^{2+}, Zn^{2+} and Ag^{2+}, only CuNaY exhibited any significant catalytic activity in the oxidative dehydrogenation of cyclohexane [2]. Minachev et al. [3] suggest that the oxidation process follows two possible routes; deep oxidation to CO_2 takes place over NaY but, on the incorporation of a transition metal ion, oxidative dehyrogenation to benzene also occurs. Alumina and amorphous silica-aluminas have proved unreactive, suggesting the importance of crystallinity for this process [3,4].

Reaction kinetics for the formation of benzene show a first order rate with respect to oxygen, regardless of cyclohexane pressure [2]. The data reported by Mochida et al. [5] support a mechanism where the adsorption of oxygen is rate determining. Associative as well as dissociative oxygen may be present on CuNaY but the authors [5] assume associative oxygen to be the reactive species. From

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* To whom correspondence should be addressed. Present address: Chemistry Department, The University, Glasgow, G12 8QQ, Scotland, U.K.

kinetic data, Ben Taarit [2] has also proposed the associative adsorption of oxygen to be rate determining where cyclohexadiene dehydrogenates rapidly, the evolved hydrogen consuming adsorbed oxygen in a fast step. An alternative mechanism has been proposed [6] involving a redox Cu^{2+}/Cu^{+} equilibrium in which a dissociative activation of oxygen and the formation of cyclohexene as an intermediate is assumed. In the absence of more detailed experimental data it is not clear whether the apparent discrepancies can be accounted for by different experimental conditions. Whatever the nature of adsorbed oxygen, all the reported data point to a reaction between adsorbed oxygen and the hydrocarbon substrate. The effect of the Cu^{2+} exchange level on the oxidation activity has also been considered [5]; the parabola shaped relation was explained on the basis of cation inaccessibility.

Kharlamov and Starostina [7] observed a dehydrogenation of cyclohexane over LiY, NaY, KY, RbNaY and CsNaY using only helium as carrier gas. The dehydrogenation activity was found to increase when the univalent cations were replaced by di- and trivalent cations. In addition, Bragin et al. [8] observed a marked increase in dehydrogenation activity in going from non-acidic to acidic catalysts.

Oxidative dehyrogenation of methylcyclohexane exhibits an analogous behavior [3,4]. The route of methylcyclohexane oxidative conversion, the yield of individual products and process selectivity are also dependent on zeolite composition and structure. Sodium faujasites mainly catalyze deep oxidation and oxidative dehydrogenation to toluene. In the presence of decationized and alkaline earth zeolites, methylcyclohexane is converted to various aromatic compounds (mainly toluene and xylenes). Xylenes arise from the disproportionation of toluene, the primary oxidative product.

In a previous study [9], the location of Cu^{2+} ions, supported on NaY and KY, was monitored with increasing calcination temperature. This paper reports the results of a systematic investigation of the oxidative dehydrogenation of cyclohexane and its methyl derivative over a range of oxidized CuNaY and CuKY Zeolites. Kinetic and adsorptive phenomena are probed in order to elucidate the reaction mechanism and the key to catalytic activity.

2. Experimental

The starting or parent zeolite was Linde Molecular Sieve LZY-52 [formula: $Na_{58}(AlO_2)_{58}(SiO_2)_{134}(H_2O)_{260}$]. KY was prepared by refluxing 250 g of NaY with 400 cm^3 of 1 M KNO_3 for 24 hours, after which the zeolite was vacuum filtered and thoroughly washed with hot deionized water to remove the occluded salt. The zeolite was then oven dried at 373 K for a further 24 hours; this heat treatment provided the necessary energy of activation to accomplish a redistribution of the exchanged ions. The resultant KNaY samples were exchanged a further nine times and stored over saturated NH_4Cl solutions. CuNaY and CuKY samples were prepared by taking 100 g of NaY or KY and refluxing with a 400 cm^3 $Cu(NO_3)_2$ solution for 24 hours. The pH of the NaY zeolite/deionized water suspension was 9.5. It has been reported that many transition metal salt solutions are sufficiently acidic to cause structural breakdown [10]. In this study, dilute copper nitrate solutions (< 0.1 M) were employed in which the pH (as monitored by a pH meter) of the nitrate/zeolite suspension was in the range 6–7.5. Under these conditions, a single exchange cycle resulted in a maximum exchange of ca. 5 Cu^{2+}/U.C., i.e. five copper cations per unit cell. In preparing samples with loadings greater than ca. 5 Cu^{2+}/U.C., repeated exchange was necessary. Atomic absorption (Cu^{2+} concentration) and flame emission (Na^+ and K^+ concentrations) techniques, using a Perkin Elmer 360 Atomic Absorption Spectrophotometer, were employed to determine the cation content. Samples were prepared for analysis by treating 0.2 g of the hydrated zeolites with 20 cm^3 conc. HCl and stirring at room temperature for 16 hours. The resultant suspension was then filtered and made up to 250 cm^3 with deionized water. Measurements were made in the 0–5 ppm range by performing the appropriate dilutions. The standards employed were prepared from stock solutions supplied by BDH Chemicals Ltd.. From the measured ion concentrations, the precise mass of the zeolite sample and the number of unit cells per gram of parent zeolite (3.5×10^{19} for NaY and 3.3×10^{19} for KY), the number of copper cations per unit cell were determined. Thermal analyses were also conducted on all the prepared samples using a Perkin Elmer thermobalance operating in the TG mode to measure water loss as a function of temperature. Samples were labelled according to the % exchange of the indigenous alkali metal cations and the total number of Cu^{2+} ions per unit cell, eg. the CuKY-68.59 sample exhibits a 68.59% exchange of the 58 parent K^+ ions resulting in a total of 19.89 Cu^{2+}/U.C.. Diffraction patterns (using a Jeol JDX-85 Diffractometer) of each of the samples, before and after activation and catalysis, were obtained so as to ensure the maintainance of sample crystallinity. Infrared spectroscopy in the range 1200–350 cm^{-1} was also used as a check on crystallinity. The band at ca. 395 cm^{-1} has been assigned to a breathing of the pore opening in zeolites [11] and is thus the most sensitive to changes in crystallinity.

All the catalytic reactions were carried out under atmospheric pressure in a fixed bed tubular glass reactor. The details of the catalytic apparatus and test procedure are given elsewhere [12]. Cyclohexane (or methylcyclohexane) was fed into the reactor from a precision motor driven syringe (Braun Perfusor Model 871 102). The syringe was carefully calibrated before use by monitoring the volume of cyclohexane delivered in a given time interval for different gear settings of the motor. The catalyst sample was pelletized without binder under a pressure of 4000 kg cm^{-2} and sieved in the mesh range 1.18–1.70 mm. The hydrated copper zeolite was then activated by heating in an oxygen/nitrogen stream (120 cm^3 min^{-1}, $O_2 : N_2 = 11 : 100$) to a final temperature of 723 K which was maintained for 18 hours. X-ray diffraction analyses of the calcined samples did not reveal the presence of CuO; rather atomic absorption analyses confirmed that the supported copper species was in the form of Cu^{2+} cations. Product analysis was carried out on the liquid samples, collected in a liquid nitrogen trap, using a Pye Unicam GCV Chromatograph with a flame ionization detector; the chromatograph was used in conjunction with a Shimadzu Chromatopac C-R3A data processor. The products of the reaction were identified by comparison of the retention times with those of known standards. Using these known standards, solution mixtures with compositions close to those of the reaction products were prepared and subsequently used to convert the integration output from area % to mole % by multiplying by the appropriate conversion factor. Analysis of the reaction products was made using a 5% Bentone/5% di-iso-decylphthalate on Chromosorb W chromatography column with a carrier gas (N_2) flow rate of 20 cm^3 min^{-1} and column temperature at 338 K. The integration conditions used were as prescribed in the Shimadzu model for optimum operation.

Adsorption phenomena were probed by means of a chromatographic technique. A pyrex glass column, of internal diameter 3 mm and overall length 30 cm, was packed with 2 g of the copper exchanged Y zeolite which had been pelletized in the mesh range 0.6–1.18 mm. The column was placed in the oven of the chromatograph and heated at 10 K min^{-1} in a 120 cm^3 min^{-1} nitrogen/oxygen ($N_2 : O_2 = 11 : 100$) to a final temperature of 723 K which was maintained for 18 hours. The temperature was then lowered to the desired sorption temperature and 2μl of benzene was injected onto the zeolite at various temperatures in the range 373 K–573 K using the same nitrogen/oxygen mixture (97 cm^3 min^{-1}) as carrier gas. The corresponding retention times, measured by the flame ionization detector, were recorded on the integrator as described above. The hydrocarbons (purchased from BDH Chemicals Ltd.) used in these studies were of AnalaR grade and were further dried by standard methods [13].

3. Results and discussion

The chemical compositions of the ion exchanged samples are given in tables 1 and 2. By and large, the exchange process was stoichiometric. The extent of hydrolysis, as evidenced by the number of protons present in the structure, was slight and occurred only for the lower exchanged samples. Sample crystallinity, monitored by X-ray diffraction and IR spectroscopy, was maintained in each case before and after zeolite activation and catalysis.

The anhydrous NaY and KY zeolites exhibited very low oxidative dehydrogenation activities. Neither silica nor alumina catalysts showed any oxidative activity whatever which suggests that the crystallinity of the support plays some role in promoting cyclohexane conversion, in agreement with previous contentions [3,4]. Catalysis over Ni^{2+} exchanged Y zeolites only resulted in the forma-

Table 1
Chemical composition of CuNaY samples prepared by ion exchange

Zeolite sample	Na^+/U.C.	Cu^{2+}/U.C.	H^+/U.C.	Water content (wt. %)
NaY	58.00	–	–	24.86
CuNaY-8.00	50.90	2.32	2.46	25.49
CuNaY-22.62	42.74	6.56	2.14	25.88
CuNaY-34.03	38.33	9.29	1.10	26.32
CuNaY-44.69	31.14	12.96	0.94	26.69
CuNaY-55.55	25.20	16.11	0.68	27.05
CuNaY-64.00	20.34	18.56	0.54	27.24
CuNaY-74.14	14.50	21.50	0.50	27.86
CuNaY-86.69	7.41	25.14	0.31	28.41
CuY	–	29.00	–	28.73

tion of trace amounts of benzene whereas CuNaY and CuKY promoted the dehydrogenation reaction with the level of benzene formation increasing with reaction temperature, fig. 1. The nature of the supported transition metal ion therefore determines the extent of oxidative dehydrogenation to a greater extent than any effect of support crystallinity. The catalytic parameter represented by W/F is defined as the mass of hydrated catalyst in grams divided by the feed rate of reactants in moles per hour; basically it is a measure of the number of active sites available for the conversion of each molecule of reactant.

This study is only concerned with the oxidative reaction which can be represented by:

$$O_2 + 2/3C_6H_{12} \rightarrow 2/3C_6H_6 + 2H_2O.$$

However, catalysis over the lower copper loaded zeolites (< ca. 7 Cu^{2+}/U.C.) yielded minor amounts of cyclohexene in the product mixture which suggests a consecutive reaction in which cyclohexene is further converted to benzene.

Table 2
Chemical composition of CuKY samples prepared by ion exchange

Zeolite sample	K^+/U.C.	Cu^{2+}/U.C.	H^+/U.C.	Water content (wt. %)
KY	58.00	–	–	22.14
CuKY-9.97	51.00	2.89	1.22	22.35
CuKY-24.55	42.36	7.12	1.40	23.13
CuKY-37.45	35.34	10.86	0.94	23.38
CuKY-52.90	26.94	15.34	0.38	25.15
CuKY-68.59	18.00	19.89	0.22	26.09
CuKY-77.38	12.42	22.42	0.70	26.94
CuKY-92.03	4.42	26.69	0.20	27.06
CuY	–	29.00	–	28.53

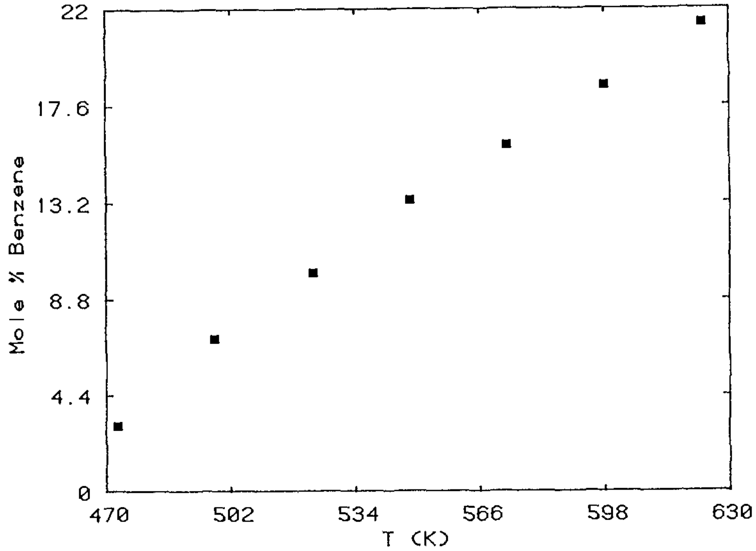

Fig. 1. Mole % conversion to benzene (after 6 hours on stream) over CuKY-9.97 as a function of reaction temperature: W/F = 223.5 g mol^{-1} hr; $N_2:O_2 = 1.00:0.11$.

Considering the distribution of activities over the range of samples in fig. 2, it can be observed that the rate of benzene formation increases with copper loading, for both CuNaY and CuKY systems, up to ca. 20 Cu^{2+}/U.C. above which the reaction rate decreases rather abruptly in the case of the CuNaY system and less so for CuKY. It has been shown [9] that the first 15 Cu^{2+} ions locate in the small cages of the anhydrous unit cell where they are inaccessible to the reactant

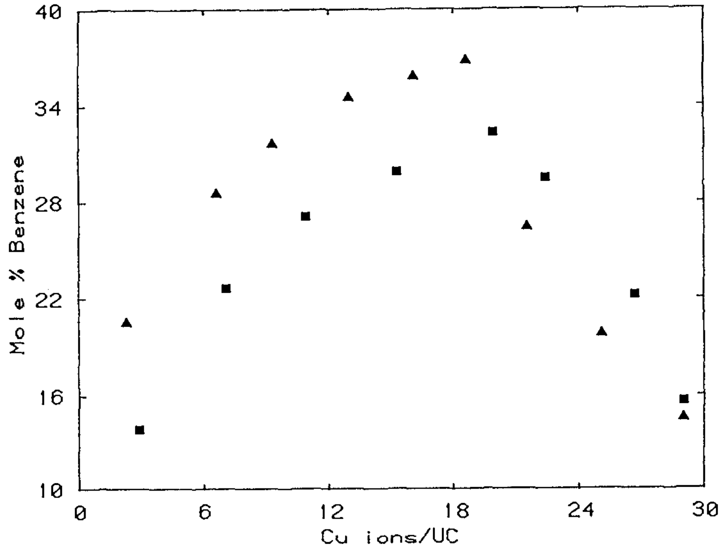

Fig. 2. Mole % conversion to benzene (after 6 hours on stream) over CuNaY (▲) and CuKY (■) as a function of copper loading: W/F = 223.5 g mol^{-1} hr; $N_2:O_2 = 1.00:0.11$; $T = 573$ K.

cyclohexane molecules. Some of the Cu^{2+} ions must therefore be displaced into the accessible supercages in order to promote catalysis. As already reported [9,12], in the case of the the hydrated ion exchanged samples and more importantly the activated zeolites, the Cu^{2+} ions are less rigidly fixed to the aluminosilicate framework of the NaY support compared with KY and are thus freer to migrate to the open sites. This would account for the observed higher levels of cyclohexane conversion exhibited by the copper-dilute CuNaY samples. Catalytic activity is therefore dependent not only on the level of copper exchange but also on the basicity of the alkali metal co-cation; as the small cage Cu^{2+} ions are more strongly coordinated to the more basic KY framework [9] the catalytically active metal ions are less free to enter the supercages where cyclohexane conversion takes place. The cusp-like shape of the activity profiles has previously been reported for the CuNaY system [5]. However the proposed explanation, that of Cu^{2+} inaccessability [5], is not acceptable in the light of the observed mobility of the Cu^{2+} ions [9]. The drop in activity, which is more pronounced for CuNaY at higher copper contents, i.e. the more acidic samples [12], must be related to a deactivation process. In acidic catalysts the usual mode of deactivation occurs by coking, a process involving the generation of large molecules within the pore structure too large to diffuse out. To test whether coke deposition occured in this study, the residual carbon content of a number of spent samples was measured and the results are presented in fig. 3. It can be observed that the spent samples contain considerable residual carbon and therefore the most likely explanation for catalyst deactivation is the gradual accumulation of involatile coke on the

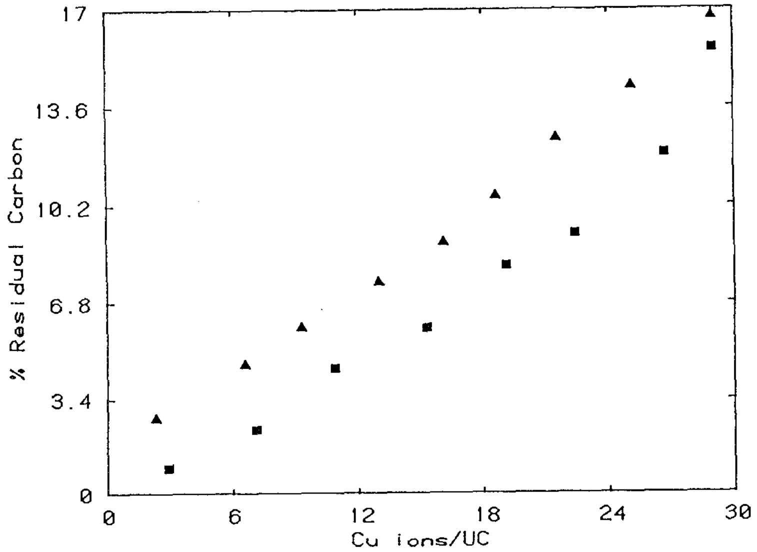

Fig. 3. Level of coke formation during catalysis (after 6 hours of stream) over CuNaY (▲) and CuKY (■) as a function of copper loading: W/F = 223.5 g mol^{-1} hr; $N_2:O_2 = 1.00:0.11$; $T = 573$ K.

Table 3
Retention times for cyclohexane and methylcyclohexane injected onto columns of activated and spent CuNaY and CuKY Zeolites: N_2 flow rate = 97 cm^3 min^{-1}; $T = 573$ K

Zeolite sample	Feed	Retention time/min.	
		Activated	Spent
CuNaY-8.00	CH	14.6	12.0
	MCH	16.8	12.5
CuNaY-34.03	CH	14.9	9.8
	MCH	17.0	10.1
CuNaY-64.00	CH	17.2	7.8
	MCH	20.1	8.0
CuKY-9.97	CH	12.1	11.4
	MCH	13.3	12.2
CuKY-37.45	CH	12.9	10.5
	MCH	13.6	10.9
CuKY-68.59	CH	15.8	12.0
	MCH	17.0	12.4

CH: Cyclohexane; MCH: Methylcyclohexane.

catalyst surface. The retention times of cyclohexane injected onto a column of activated reduced copper zeolites were measured before and after catalysis and are given in table 3. It may be observed that the retention times (and hence the levels of surface interaction) are markedly lower for the spent samples, particularly for the higher copper loaded NaY catalysts. The deposition of coke during catalysis serves to, in effect, "plug" the zeolite pores, restricting access of the reactant cyclohexane molecules to the intracrystalline Cu^{2+} cations with a lower associated contact time with the active surface. The higher levels of acidity associated with the sodium based zeolites [14] must serve to promote coke formation and hence an increased rate of deactivation. In addition, catalysis over the more acidic CuNaY (> 20 Cu^{2+}/U.C.) samples generated a considerable volume of methylcyclopentane in the product mixture. Ko et al. [15] have visualized methylcyclopentane formation as being initiated by the transfer of a hydride ion from cyclohexane to a zeolitic Lewis acid site with the formation of a cycohexyl carbonium ion which subsequently isomerizes to the methylcyclopentyl cation which then generates methylcyclopentane on addition of a hydride ion.

The oxidative dehydrogenation of cyclohexane to benzene over CuKY-24.55 (at steady state conversions) was measured as a function of reaction temperature and the partial pressures of cyclohexane and oxygen. Sets of measurements were made of the reaction rate by increasing or decreasing the reaction temperatures at constant reactant pressures; reaction rates were reproducible within ±10%. From the exponential rate expression,

$$R = k\left(P_{\text{oxygen}}\right)^{n}\left(P_{\text{cyclohexane}}\right)^{m},$$

Table 4
Reaction kinetics for the oxidative dehydrogenation of cyclohexane over CuKY-24.55

Temperature/K	n [a]	m [b]
473	0.68	0.00
523	0.81	0.00
573	1.05	0.12
623	1.13	0.20
673	1.20	0.33

[a] order with respect to O_2.
[b] order with respect to C_6H_{12}.

the formal reaction orders, n in oxygen and m in cyclohexane, were derived by means of logarithmic plots. The partial pressure with respect to oxygen was varied by changing the oxygen flow rate while maintaining the overall flow rate constant by dilution with nitrogen. The calculated reaction orders in cyclohexane and oxygen are listed in table 4. Both orders increase with reaction temperature but the values for oxygen are much higher than for cyclohexane suggesting the stronger adsorption of the hydrocarbon. The reactivity of the adsorbed species was probed by the chromatographic technique described earlier. Three distinct cases were studied:

(a) oxygen (in a nitrogen stream: $O_2 : N_2 = 11 : 100$) was preadsorbed on the zeolite and cyclohexane was injected in a stream of nitrogen;

(b) cyclohexane was preadsorbed on the zeolite and a stream of oxygen/nitrogen ($O_2 : N_2 = 11 : 100$) was passed over the catalyst bed.

(c) cyclohexane and oxygen/nitrogen ($O_2 : N_2 = 11 : 100$) were passed through the zeolite bed which had earlier been thoroughly purged with nitrogen.

The data generated revealed that of the three above situations only the former yielded benzene; the latter two cases showed no evidence of reaction. These results indicate the negligible contribution of the strongly adsorbed cyclohexane in benzene formation and are consistent with an associative adsorption of oxygen as the rate determining step. The following steps therefore describe the oxidative dehydrogenation of cyclohexane over CuNaY and CuKY:

$O_2(g) + Cu^{2+} \rightleftharpoons O_2(ads)$ slow, rate determining step
$C_6H_{12} + O_2(ads) \rightarrow C_6H_8(ads) + H_2O$ rate is determined by the level of Cu^{2+} exchange
$C_6H_8(ads) \rightarrow C_6H_6 + H_2$ fast
$2H_2 + O_2(ads) \rightarrow 2H_2O$ fast.

The observed activities yielded no evidence to suggest that cyclohexadiene acts as a reactive intermediate. The experimental data therefore support the earlier

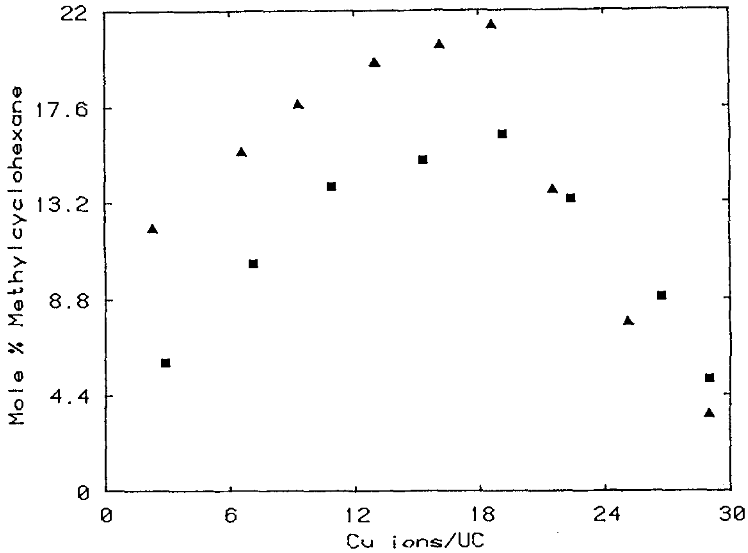

Fig. 4. Mole % conversion to toluene (after 6 hours on stream) over CuNaY (▲) and CuKY (■) as a function of copper loading: W/F = 392.8 g mol^{-1} hr; $N_2:O_2 = 1.00:0.11$; $T = 573$ K.

proposals of Ben Taarit [2] and Mochida et al. [5] and confirm that the associative adsorption of oxygen is rate determining.

In the presence of oxygen, methylcyclohexane was converted mainly to toluene with trace amounts of benzene and ethylbenzene isolated in the product mixture. The reaction followed the same trends exhibited by the cyclohexane conversion, i.e. improved yields on exchange of divalent Cu^{2+} cations and higher levels of toluene formation over the copper dilute CuNaY samples, fig. 4. However, the actual levels of conversion were lower than for the cyclohexane feed. This may be explained on the basis of a stronger adsorption of methylcyclohexane due to the additional interaction of the CH_3-group with the zeolite surface, table 4. In addition a higher level of coke was generated during the conversion of methylcyclohexane, eg. after 6 hours on stream the spent CuNaY-74.14 (21.50 Cu^{2+}/U.C.) exhibited 12.7% and 17.5% residual carbon for the oxidative dehydrogenation of cyclohexane and methylcyclohexane respectively. The latter two factors serve to explain the lower overall rate of methylcyclohexane dehydrogenation.

4. Conclusions

Copper exchanged NaY and KY zeolites prove very active in the oxidative dehydrogenation of cyclohexane and methylcyclohexane. The observed differences in the activities of CuNaY and CuKY can be explained by the combined action of Cu^{2+} ion migration and coke deposition. The reaction is viewed as occuring in sequential steps with the associative adsorption of oxygen being rate determining

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