

Photocatalytic degradation of n-hexadecane in water using metal-exchanged zeolites as photocatalysts

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ABSTRACT

Three transition metals of the N-middle period of the periodic table of elements, namely; Fe, Co and Ni (group VIII) were exchanged in three zeolites, namely; ZSM-5, mordenite and Y, to be used as catalysts for the photocatalytic degradation of one of the most resistive hydrocarbons (n-hexadecane) via irradiation with artificial sun-light emitted by a 200W halogen lamp for a period of 2h in water. Initial concentrations of 0.25 up to 1.0% of n-hexadecane (contaminant) were tested to examine the applicability of Langmuir-Hinshelwood heterogeneous surface kinetics, whereby the reaction rate constant, k , adsorption equilibrium coefficient, K , and number of adsorption sites, A , in the photocatalyst were calculated. The linearity of these plots which possessed positive intercepts and slopes confirmed the occurrence of the photo-reaction on the catalysts as a surface reaction. Using all zeolites as supports for the catalysts, cobalt was found to be the most active, whereas iron the least active, while using all metals as the electron-accepting component, mordenite was the most active whereas H-ZSM-5 was the least active.

The data showed that as initial concentration of the pollutant increases, the photodegradability of n-hexadecane decreases. Nevertheless, as the photodegradation rate constant increases, the adsorption equilibrium coefficient was found to decrease but the number of adsorption sites on the catalyst increased. This indicated that low hydrocarbon concentrations in water are preferred or that the hydrocarbon droplets in water were smaller. Moreover, strong adsorption of the substrate on the photocatalyst retards the reaction.

INTRODUCTION

In heterogeneous photocatalysis, a redox reaction is mediated by a photocatalyst which behaves identical to chlorophyll in the photosynthesis in green plants. The photo-excited molecules induce the reaction. The photocatalyst necessarily absorbs the photons to drive redox reactions. This distinguishes a thermal catalyst from a photocatalyst.

Water is assumed to be the source of hydrogen in the photocatalytic hydrogenation of aliphatic hydrocarbons (alkenes and alkynes) on irradiation of TiO_2 in presence of water vapour [1,2]. In addition to reduction, oxidation reactions also take place in presence of O_2 . Aromatic olefins are oxidized to benzophenone and epoxide on TiO_2 and CdS catalysts [3]. Aliphatic hydrocarbons produce alcohols at an early stage of the reaction although the detected amount is small [4]. Benzene yields phenol in aqueous media, and oxygen increases the rate 10-50 times the rate observed in O_2 -free mixtures. Hydroxyl radical species, produced by reduction of O_2 in aqueous media, are thought to attack the phenyl ring and phenol is produced. This reaction can be reproduced by the so called Fenton's reaction in which Fe^{3+} and H_2O_2 produce $\cdot\text{OH}$ radicals [5-7].

In heterogeneous catalysis the active material is often supported in a highly dispersed state on a matrix. In addition to such physical role of the support, it interferes either directly or indirectly in the reaction mechanism both in thermal and photocatalytic reactions. In the former reactions, a strong metal-support interaction may take place at higher temperatures which leads to epitaxial growth of the dispersed metal. However, in photocatalytic reactions which occur at almost ambient temperature, this epitaxy does not occur. Moreover, the electronic interaction between the dispersed metal and the support modifies the catalytic behaviour. For instance, very few Pt clusters on acidic zeolite supports are shown to be electron-deficient [8]. Another interaction between the dispersed phase and support is the spillover of hydrogen (almost extensively with hydrogen [9]), which is the migration of $\text{H}\cdot$ atoms generated by dissociation of H_2 on metal or, transition metal sulfide, from the metal to the support. Reverse spillover also occurs [10], which involves the migration of hydrogen atoms or protons from the support to the dispersed metal where it generates molecular hydrogen that desorbs to the gas phase.

In the present work, each of the three transition metals: Fe, Co or Ni have been supported on each of the zeolites ZSM-5, mordenite or Y via complete cation exchange of the original alkali metal (Na) in the as-synthesized zeolite. These materials have been used as photocatalysts to degrade one of the most resistive hydrocarbons (n-hexadecane) [11] in water.

EXPERIMENTAL

1. Preparation of Photocatalysts:

Three zeolites, namely: Na-mordenite, Na-ZSM-5 and Na-Y were exhaustively exchanged for complete replacement of Na^+ with NH_4^+ using molar NH_4NO_3 solution four times each for 8h at room temperature with continuous stirring. The zeolite was washed with de-ionized water for several times to remove NO_3^- ions completely. Each of the ammonium forms of the three zeolites was completely exchanged with FeCl_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to obtain the following catalysts:

Fe-M, Fe-ZSM-5 and Fe-Y, Co-M, Co-ZSM-5 and Co-Y, Ni-M, Ni-ZSM-5 and Ni-Y. These catalysts were washed thoroughly with distilled water to remove unbound metals, then dried at 110°C overnight and calcined at 550°C for 4h.

2. Photocatalytic degradation and apparatus

The photocatalytic reaction was carried out in a cylindrical batch reactor containing 200 ml of tap water with concentration of 2.5 up to 10 g/L of n-hexadecane. Each powdered photocatalysts was added in weights ranging between 0.025 up to 0.100 g together with 0.025-0.100 g of an oxygen carrier (sodium perborate). The irradiation source was a 200W halogen lamp jacketed with a cylindrical condenser to exclude the thermal effect induced from the lamp. A flow of $25 \text{ cm}^3 \text{ min}^{-1}$ of air was continuously pumped at the bottom of the reaction mixture and distributed via a sintered glass disc. Below the disc a magnetic stirrer was placed. A fixed irradiation period of 2h was always applied.

RESULTS AND DISCUSSION

In previously published communications [11-12], the authors have found that aromatics are the most reactive, whereas paraffins are the least reactive, during their photocatalytic degradation in water using various catalysts. The rate of degradation is found to decrease

as the molecular weight of the paraffin increases [13]. Moreover, we examined n-hexadecane degradation using metal phthalocyanines loaded zeolites [14].

In the present work, n-hexadecane photocatalytic degradation is investigated using Fe-ZSM-5, Co-ZSM-5, Ni-ZSM-5, Fe-M, Co-M, Ni-M, Fe-Y, Co-Y or Ni-Y as photocatalysts in water in presence of air current and subjected to an artificial sunlight irradiation using 200W halogen lamp for two hours period.

The experimental data obtained are depicted in Fig 1 where the photocatalytic degradation of n-C₁₆ using Fe, Co and Ni on zeolite catalysts is studied as a function of the hydrocarbon initial concentration (C_{in}) in water, ranging between 0.5 and 2.0 g/200 cc. In all tests, the catalyst to hydrocarbon ratio is kept constant at 0.01% irrespective of the concentration of the hydrocarbon substrate. Evidently, the cobalt-exchanged zeolites (Co-M, Co-ZSM-5 and Co-Y) are the most active compared to the other metals (Ni and Fe) exchanged in the respective zeolites; i.e., the order of the activities of these catalysts according to the metal and zeolite components are found to be as follows:

- (a) in the mordenite containing catalysts, the order of activities is Co-M > Ni-M > Fe-M (see Fig 1a)
- (b) in the ZSM-5 containing catalysts, the activity order is Co-ZSM-5 > Ni-ZSM-5 > Fe-ZSM-5 (see Fig 1b)
- (c) in the Y (or faujasite) containing catalysts, the activity order is Co-Y > Ni-Y > Fe-Y (see Fig 1c)

The Fe loaded zeolites exhibit the lowest activities, however the difference between the activities of Fe and Ni is not large.

It has been assumed by Searcy [15] that the heats of formation of divalent oxides of the metals, under investigation, decrease in the following sequence: Fe > Ni > Co. This may reflect the decrease of ionic lability from Fe to Co and hence the increase of photocatalytic activity in this sequence. Fig 1 shows that the photodegradation of n-hexadecane is decreased as a function of increasing the C_{in} from 0.5 to 2.0 g/200 cc of water although the catalyst to hydrocarbon ratio is kept constant, which can be attributed to a better distribution of the hydrocarbon in the water and, hence, a better diffusion in the catalytic pores is encountered. This effect is obviously demonstrated by the magnitude of the values of, A, (the number of adsorption sites per g of the catalyst) derived from the kinetic data, coming next in Fig 4 in this text. Evidently, the number of these sites is much more increased via decreasing C_{in} from 1.0 to 0.5 g/200 cc than from 2.0 to 1.0 g/200 cc of water using all catalysts under investigation.

Fig 1a shows that using the Co-M catalyst, n-C₁₆ photodegradation amounts to 71.0% at initial concentration (C_{in}) of 0.5g/200 cc and 48.0% at C_{in} of 2.0g/200 cc. Comparatively, using the Ni-M and Fe-M photocatalysts, n-C₁₆ photodegradation is evidently insignificantly different. So, using these catalysts, the degradation levels are 36.0-21.0% and 35.0-19.0%, respectively.

Correlation of the photodegradation activities of the catalysts according to the zeolite components incorporating the same metal is depicted in Fig 2. Fig 2a describes the role of mordenite, ZSM-5 and Y zeolites when Co is the transition metal incorporated, whereas Figs. 2b and 2c show the role of these zeolites when Ni and Fe, respectively, are the transition metals incorporated. Fig 2a shows that, only Co in mordenite exhibits the highest photoactivity, whereas Ni (Fig 2b) and Fe (Fig 2c) incorporated in the three zeolites do not show significant activity variation. Ultimately, the Co loaded mordenite zeolite can be considered the photocatalyst of choice in this investigation.

In the catalysts under investigation, the transition metal is principally located inside the zeolite channels since an exhaustive cation – exchange procedure has been performed. This procedure has almost excluded all the protonic acid sites in these zeolites. The photocatalytic degradation of the hydrocarbon substrate has been affected by the combined activities of the metal and zeolitic sites. The most significant sites in the zeolites are the acid sites; of these sites, the Brønsted type has been almost totally removed via cation exchange. Only Lewis type acid sites may be present in the catalysts under investigation. The Lewis and metal sites in these catalysts should mutually interact electronically in presence of the irradiated photons. However, the obviously higher activity of mordenite may be closely related to the topology of the porous space in the mordenite zeolite structure and its relationship to the molecular traffic control, characteristic for this zeolite [16]. Mordenite possesses only unidirectional structure among the three zeolites investigated; ZSM-5 and Y zeolites being of tridirectional structures. In these tridirectional channels structures, reverse-diffusion of n-hexadecane can occur and the photodegradation activity decreases using these zeolites. The dimensions of the channels may not be significantly effective, since ZSM-5 possesses the smallest (~5.5Å⁰) whereas Y possesses the largest (13Å⁰); mordenite is of intermediate dimension (~7Å⁰).

Kinetic treatment

The data obtained through experimental photocatalytic degradation of n-hexadecane in water using the metal – exchanged zeolitic catalysts have been kinetically treated according to the heterogeneous, kinetic model of Langmuir-Hinshelwood applying the rate equation, (1)

$$\text{Rate} = r = \frac{k K C_{in}}{1 + K C_{in}} \quad (1)$$

where r is the rate per g catalyst, k is the photocatalytic degradation rate constant; K is the adsorption equilibrium coefficients and C_{in} is the initial concentration of the pollutant in water. The values of k and K have been calculated according to plots of $1/r$ vs. $1/C_{in}$ using the Fe, Ni, Co metals supported on MOR, ZSM-5 or Y (Fig 3). These plots show good linearity indicating that the photoreaction under study behaves as a surface reaction (heterogeneously catalyzed reaction) that realizes the role for hole and electron recombination.

Equation (2) can be derived from equation (1) to fit the requirements of a batch reaction.

$$V (dc/dt) = (m A k K C_{in}) / (1 + K C_{in}) \quad (2)$$

$$-(m A t) / V = 1/k K \ln(C/C_{in}) + (C - C_{in}) / k \quad (3)$$

where V is the volume of liquid in the reactor, A the moles of adsorption sites per g of catalyst and m is the mass of catalyst.

The data obtained in Table 1 show that using the Co-M catalyst, the reaction rate constant, k , is highest ($20 \times 10^{-3} \text{min}^{-1} \text{g}^{-1}$) whereas the adsorption coefficient, K , is lowest (0.357kPa^{-1}).

On the other hand, the lowest k value ($4.167 \times 10^{-3} \text{min}^{-1} \text{g}^{-1}$) in this study is obtained using the Fe-ZSM-5 catalyst, whereas the highest adsorption coefficient, K , lies between Ni and Fe exchanged ZSM-5 ($0.857, 0.887 \text{kPa}^{-1}$ respectively). Generally, the higher the k value, the lower the K value. This indicates that the adsorption of the paraffinic substrate involved, is so strong as it retards the reaction rate. The number of adsorption sites (Fig 4) decreases as a function of increasing the initial concentration of the pollutant. Catalysts containing Ni and Fe incorporated in mordenite show comparable numbers of adsorption sites, whereas Co-M exhibits higher values at all initial concentrations. However, the metals Co, Ni or Fe on the

medium – pore zeolite (ZSM-5) don't show significant differences in their A values, indicating that the lower diffusion rate in the sinusoidal channels in this zeolite [17] may have contributed to exclude differences in the number of adsorption sites. Nevertheless, Y zeolite (large pore) shows some similarity to

mordenite (large pore) in that Ni and Fe have almost equal numbers of adsorption sites. In general, the k values correlate directly with the corresponding A values but contrawise with the K values, i.e., a larger number of mildly adsorbing sites are necessary for more active photocatalysts.

CONCLUSION

Cobalt incorporated in any of the three zeolites H-ZSM-5, mordenite or Y gives highest photodegradation activity compared to Ni or Fe on the same zeolite. Activity variation between Ni and Fe is insignificant although Fe is of somewhat lower activity. Mordenite gives highest performance whereas H-ZSM-5 gives lowest performance. Increased initial concentration of $n\text{-C}_{16}$ decreases its photodegradability.

Langmuir-Hinshelwood kinetics is applied successfully. Accordingly, the photoreaction rate constant, k , the adsorption coefficient, K , and number of adsorption sites, A , have been calculated. Generally, higher k and A values are obtained at lower K values.

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Table 1

Langmuir- Hinshelwood kinetic parameters estimated for the photocatalytic degradation of n-hexadecane using the different catalysts under investigation

Catalysts	$k \times 10^{-3}$, $\text{min}^{-1} \cdot \text{g}^{-1}$	K , k Pa^{-1}	A (*), Site g^{-1}
Co-M	20.0	0.3571	62978
Ni-M	6.45	0.6264	46677
Fe-M	5.26	0.7529	47987
Co-ZSM-5	5.0	1.33	48696
Ni-ZSM-5	4.65	0.8866	46214
Fe-ZSM-5	4.167	0.8571	45289
Co-Y	8.33	0.7059	51991
Ni-Y	5.55	0.80	47555
Fe-Y	5.0	0.80	45959

(*) at $C_{in} = 0.5 \text{ g/200 cc}$.

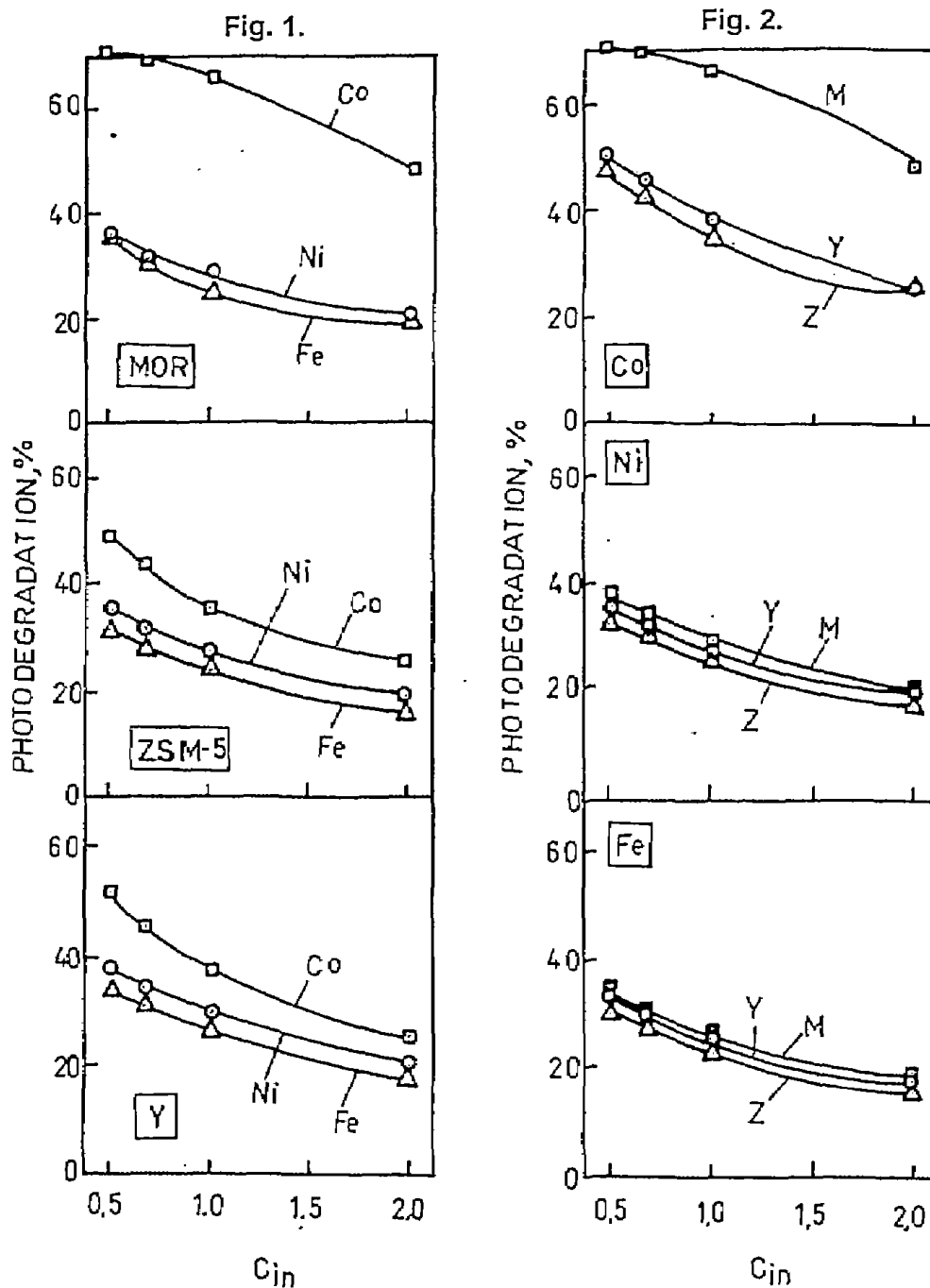


Fig. 1. Photodegradation Reactivity of n-hexadecane using photocatalysts composed of each zeolite incorporating the different metals.

Fig. 2. Photodegradation Reactivity of n-hexadecane using photocatalysts composed of each metal in the different zeolites.

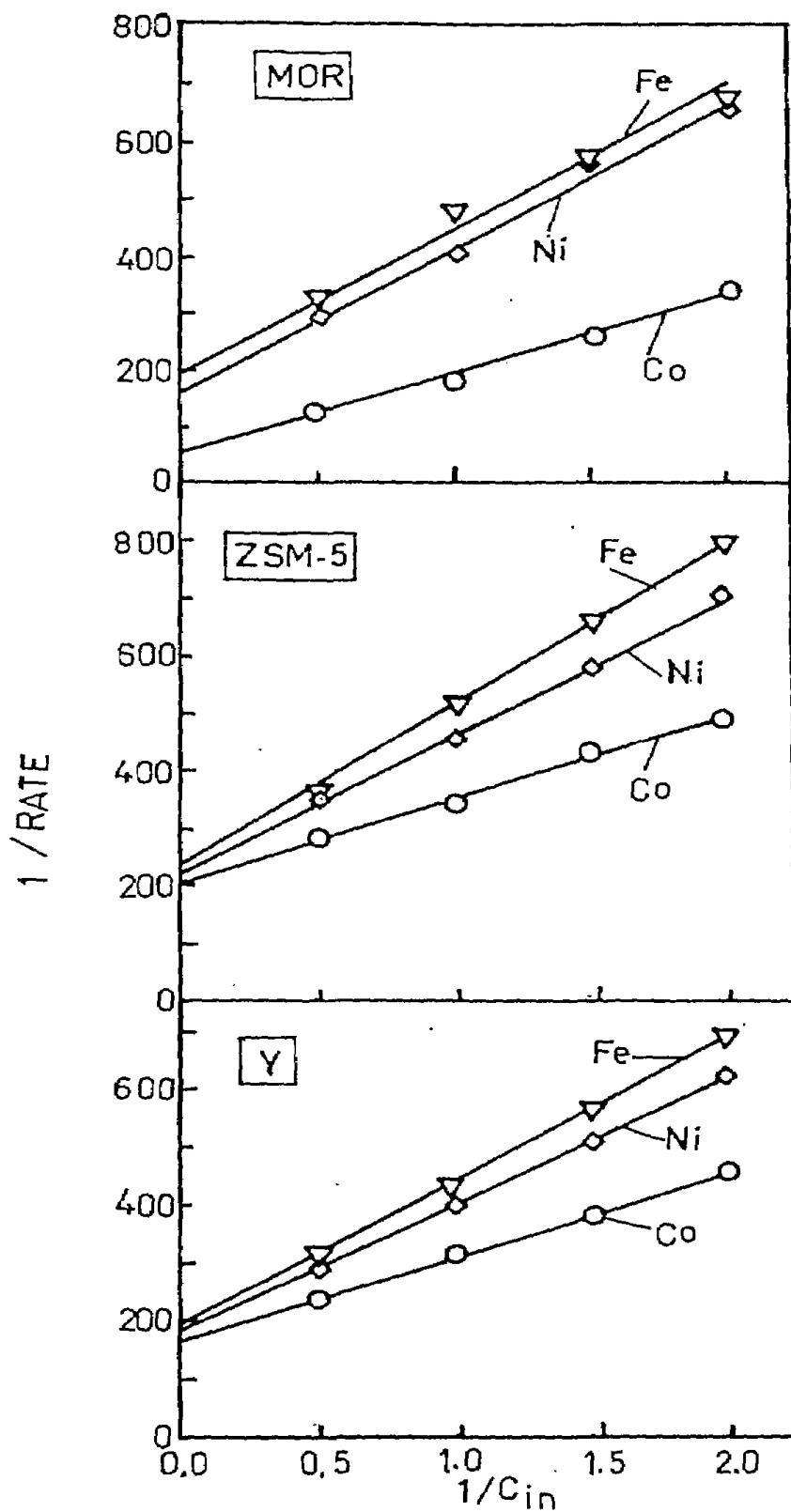


Fig. 3. Langmuir-Hinshelwood kinetic plot for n-hexadecane photodegradation using the different photocatalysts.

$10^3 \times$ NUMBER OF ADSORPTION SITES

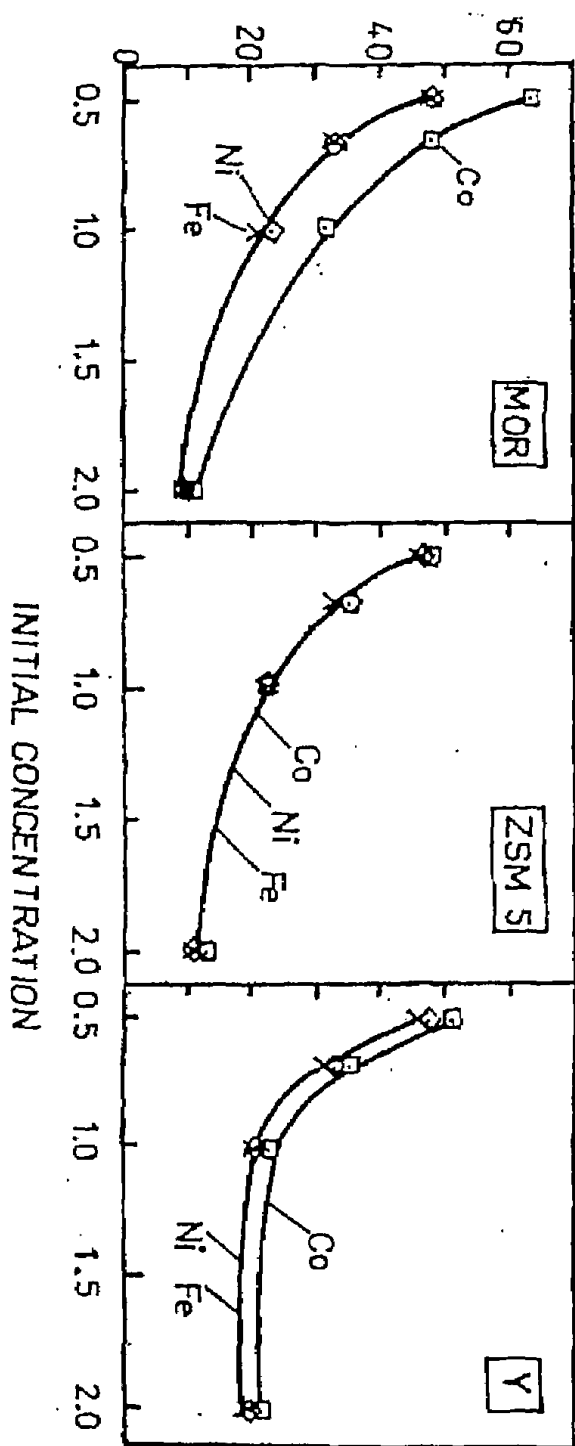


Fig. 4. Number of adsorption sites calculated for n-hexadecane photodegradation using the different catalysts.