

NICKEL ZEOLITE Y CATALYSTS. CATALYTIC ACTIVITY FOR THE METHANATION OF CARBON MONOXIDE USING NICKEL ZEOLITE Y CATALYSTS

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Nickel zeolite Y catalysts have been prepared by ion exchange. The catalysts were characterized for BET surface area and carbon monoxide adsorption. The metal areas were found to increase with degree of nickel exchange. Catalytic activities of these catalysts were measured for the hydrogenation of carbon monoxide in the range of 523–673 K. All the catalysts retain their crystalline structure after reduction with hydrogen at 723 K. Turnover number for methane formation increases with increase in degree of nickel exchange and nickel metal area. The degree of dispersion of the nickel was found to be independent of nickel loading.

Introduction

Hydrogenation of carbon monoxide has been extensively studied using nickel supported catalysts [1–4]. Conventional nickel catalysts are widely used in industry but are highly sensitive to poisoning by sulfur-compounds. On the other hand, zeolites have been used in various petroleum refining processes because of their higher activity and better tolerance to sulfur and nitrogen poisoning than the conventional amorphous support [5–8]. Hydrogenation catalysts based on zeolites usually contain platinum or transition metals impregnated, or in a dispersed atomic form. The latter, with active metals being introduced by means of ion exchange, are known to be more catalytically active and resistant to impurities [9, 10]. Virtually nothing has been published on the catalytic activity of nickel-zeolite catalysts for the methanation of carbon monoxide although nickel supported on alumina and nickel supported on silica have been used extensively for this reaction [11].

An attempt has been made to develop and characterize a nickel-zeolite catalyst which would be effective in the methanation of carbon monoxide.

Experimental

Catalyst preparation and materials

The catalyst samples were prepared from Union Carbide molecular sieve SK—40 (1.5 mm extrudates) which is the sodium form of a Y-type zeolite. The catalyst was prepared in two stages. First, the Na-Y zeolite was converted to the Ca-Y form and then to the Ni-Y form by ion exchange [12]. Four different concentrations of Ni-Y catalysts were prepared by repeated ion exchange namely 4.21, 5.69, 6.78 and 6.82 wt. % nickel. All the samples were dried at 373 K for 24 h and subsequently were calcined at 673 K for 16 h before reduction. These catalysts were crushed and screened to $-80+100$ mesh and then stored in a dessicator. All the catalysts were reduced in the reactor in flowing hydrogen (\approx at 100 ml/min) at 723 K for 16 h before the start of a test run. High purity hydrogen and CO (both Matheson 99.95% purity) were further purified before entering the reactor. Argon (99.95% purity) was used as a carrier gas in the chromatographic analyses.

Catalytic activity measurement

Methanation activities were measured in a flow reactor set up described elsewhere [4]. Catalytic activity measurements were carried out with \approx 500 mg of the catalyst in the reactor. Blank runs with Na-Y and Ca-Y zeolites were also carried out in the temperature range 523—673 K under the same flow conditions in order to check their activity. Under these conditions, both zeolites were found to be inactive.

Catalyst characterization

BET surface area, nickel content, degree of nickel exchange, nickel metal area and acidity were determined in order to characterize the catalysts. Average nickel metal crystallite size was calculated from the active metal areas. These values are shown in Table I.

Results and Discussions

It is seen from Table I that there was little difference in nickel concentration (\approx 0.29%) between catalysts SB3-Ni (third nickel exchange) and SB4-Ni (fourth nickel exchange). However, there was a big difference in the degree of nickel exchange between the two catalysts. This behavior can be explained on the basis of different sites such as S_I , S_{II} , S'_I and S'_{II} in the zeolite matrix [14]. During the ion exchange process, nickel (Ni^{2+}) ions are distributed in these sites. Ni^{2+} ions prefer S_I sites and are filled first. Degree of exchange gives an indication of Ni^{2+} ions distributed among these sites. In catalyst SB3-Ni it is likely that Ni^{2+} ions cannot occupy all the available positions and a part of Ni^{2+} ions are sitting outside the matrix, whereas in SB4-Ni most of the sites are occupied although the nickel concentration is nearly same. It has been reported in the literature that the maximum loading limit of the Ni^{2+} ions in zeolite Y is approximately $71 \pm 2\%$ at 318 K [15]. In other words, one might not be able to exceed the nickel concentration by more than 6.82% by ion exchange of zeolite Y, as an exchange of 72.2% was achieved for the catalyst SB4-Ni.

Table I

Analytical Data and Chemisorption Measurements of Ni-Y Zeolite Catalysts

Serial No.	Catalyst	Total Nickel Content (kg Ni/kg Catalyst)	Degree of Nickel Exchange %	BET Surface Area (km ² /kg)10 ³	Nickel ^a Metal Area (km ² /kg)10 ³	Average Crystallite size, nm	% Dispersion ^b	Acidity [*] >H ₂ SO ₄ , 3·10 ⁻⁴ % (moles butylamine / kg)
Supports								
1.	Na-Y	—	—	538 ± 25	—	—	—	0.30
2.	Ca-Y	—	—	530 ± 30	—	—	—	1.13
Catalysts								
3.	SB1-Ni	0.0421	21.2	538 ± 10	20.2	0.90	36.1	1.63
4.	SB2-Ni	0.0569	46.0	560 ± 22	27.9	0.87	36.7	1.70
5.	SB3-Ni	0.0678	61.4	597 ± 10	34.9	0.80	38.5	1.57
6.	SB4-Ni	0.0682	72.2	552 ± 14	35.6	0.78	39.1	1.75
Data from Brooks et. al; [13]								
7.	Ni Zeolon	0.0324	—	—	30	0.50	69.4	—
8.	Ni Dav Z14	0.0592	—	—	22	0.60	33.2	—

a corrected for CO adsorption on the support at same temperature and CO vapor pressure.

b Linear form of CO bonding.

It is important that the zeolite catalysts should not lose their crystallinity during experimentation after ion exchange at 353 K and calcination at 673 K for 16 hr. All the catalysts used in the present study were tested for crystallinity and were found to have retained their crystallinity.

Chemisorption Measurements

The chemisorption data for Ni-Y catalysts are listed in Table I. It is seen that the amount of carbon monoxide chemisorbed increases with increase in nickel concentration. Also, it is interesting to note that the average crystallite size and the nickel dispersion does not vary much with nickel concentration.

It is observed that the zeolite support Ca-Y retains little CO whereas the unreduced nickel zeolite (Ni²⁺-Y) retains a substantial amount of CO implying that the CO chemisorption can occur on nickel cations Ni²⁺. This observation is confirmed by the work of ANGEL and SCHAFFER [16] who reported that CO forms adsorptive bonds with Ni²⁺ and Ni⁺, using infrared spectra of zeolite Y. BROOKS AND CHRISTOPHER [13] also observed similar behaviour of CO on nickel zeolon and nickel Dav. Z14 catalysts. As the CO chemisorption occurs both on nickel cations as well as on metallic nickel (Ni⁰), suitable corrections must be applied to calculate the actual nickel metal area. It has also been established that only Ni⁰-Y is responsible for the hydrogenation activity in ethane hydrogenolysis whereas Ni²⁺-Y is inactive [17]. Therefore, a suitable correction was applied in order to measure nickel metal area (*i. e.* Ni⁰-Y area).

Catalytic Behaviour

The catalytic behaviour of all the Ni-Y catalysts is shown in Table II. All the activities are compared at 573 K. The activation energies varied from 71.5 to 79.0 MJ/kmol which are comparable with the reported [11] values between 73 to 130 MJ/kmol. The catalytic activity is expressed as turnover numbers and increases with

Table II
Catalytic behaviour of Ni—Y catalysts in the synthesis reaction

Serial No.	Catalysts	Turnover Number N_{CH_4} ($s^{-1} \cdot 10^3$) 573 K	Pre-exponential factor A ($s^{-1} \cdot 10^{-3}$)	Activation Energy E_{CH_4} (MJ/kmol)
1.	SB1-Ni	1.35	21.7 ± 6.9	79.0 ± 9.6
2.	SB2-Ni	1.30	10.5 ± 8.6	75.7 ± 18.5
3.	SB3-Ni	5.36	23.1 ± 1.6	71.8 ± 2.4
4.	SB4-Ni	7.68	25.2 ± 3.4	71.5 ± 5.6

increase in nickel concentration and degree of nickel exchange. Calculations show that the metal area expressed per kg of nickel metal increases with increase in the degree of exchange showing that, as the degree of nickel exchange increases, more nickel is uniformly distributed inside the zeolite matrix leading to better dispersion and higher activity.

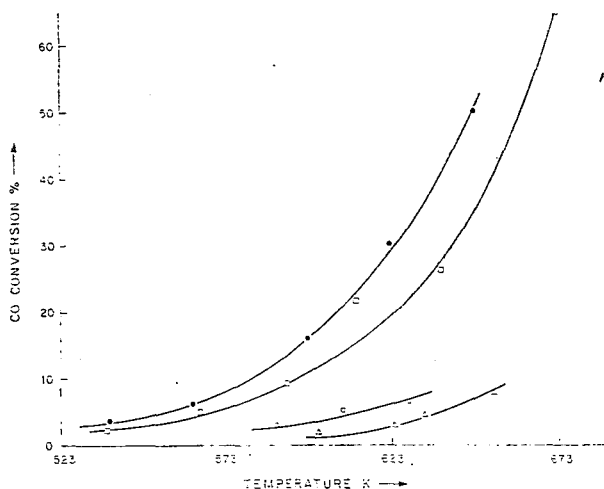


Fig. 1. Effect of degree of nickel exchange on the CO conversion: Δ SB1-Ni; \circ SB2-Ni; \square SB3-Ni; \bullet SB4-Ni. Weight of the catalyst: 500 mg.

Fig. 1 shows the effect of degree of nickel exchange on carbon monoxide conversion in the temperature range 523—673 K. The conversion increases as the degree of nickel exchange increases. It is known that nickel ions (Ni^{2+}) located in S_I positions (interior, sixfold co-ordination with oxygen ions) are harder to reduce than those in the S_{II} positions (surface of the super cage, threefold co-ordination with oxygen ions). Furthermore, since nickel prefers the S_I to the S_{II} position, it is possible that all the locations of S_I are filled with nickel ions in catalysts SB1-Ni and SB2-Ni which results in lower turnover numbers. Fig. 1 shows that the conversion of CO increases sharply after 573 K. This might be due to the internal diffusional resistance which is experienced by the reactant molecules as they are transported through the narrow pores to the catalytic sites within the zeolite matrix crystal. One of the most striking characteristics of zeolite diffusion is its strong dependence on temperature which generally increases exponentially with the temperature [18]. Therefore, it would be expected that the conversion would increase exponentially with temperature under steady state conditions above 573 K as Fig. 1 indicates.

The introduction of a nickel atom in the zeolite matrix is associated with the introduction of a proton and thus, it is expected that the highly loaded catalysts are also catalysts of high acidity. Table I shows that acidity of Ni-Y catalyst is higher than Ca-Y support. Also, the maximum exchanged catalyst (SB4-Ni) shows the maximum acidity. It has been reported in case of Ca-Y zeolite that with cations in S_{II} and S_{III} positions a strong enhancement of the acidity results due to the lower electrostatic shielding in these positions and to the asymmetric charge distribution caused by higher charged cations [19]. During the nickel exchange, as the degree of exchange increased, the nickel ions occupied S_{II} and S_{III} positions beside S_I positions by replacing Ca^{2+} ions and thereby resulted in higher acidity. Furthermore, more Ni^0 atoms are available for the reaction (as Ni^{2+} ions in S_{II} and S_{III} positions are easy to reduce to Ni^0 atoms). It can be concluded therefore that the observed increase in methanation activity is due to increase in the acidity and availability of more Ni^0 atoms for the reaction.

Conclusions

Ni-Y zeolite containing Ni^0 is an active catalyst for the methanation of CO. Chemisorption of CO revealed that a substantial amount of CO is retained by unreduced Ni-Y catalyst indicating that CO chemisorption occurs at Ni^{2+} ions too. The amount of CO chemisorbed increases as the nickel concentration increases. CO conversion and turnover numbers for methane formation increase with increase in the degree of nickel exchanged. The degree of nickel dispersion is independent of nickel loading.

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