

CREATION OF ACID SITES BY La-IONS IN L ZEOLITE

S. Sivasanker, S.G. Hegde, S.V. Awate, S.R. Padalkar and
S.B. Kulkarni

National Chemical Laboratory, Pune 411 008, India

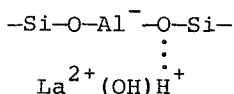
Received December 8, 1986

Accepted February 19, 1987

The creation of strong acid sites in alkaline K-L-zeolites on ion-exchanging with La-ions is reported. Acidity measurements have been carried out by temperature programmed desorption of adsorbed ammonia. Reaction data which confirm the creation of acid sites are also reported.

Сообщают об образовании сильноокислых центров на щелочных цеолитах К-Л с помощью ионного обмена ионами La. Измерение кислотности производили с помощью ТПД адсорбированного аммиака. Приводятся экспериментальные данные, подтверждающие образование кислых центров.

The acidities and cracking activities of faujasites are known to increase on ion-exchanging with rare-earth ions [1]. The reason for the increased acidity of REY zeolites is the hydrolysis of the water associated with the rare-earth ion [2] to give species of the type shown below:



The H^+ ion in the structure (shown above) is believed to be responsible for the acidity. However, because the parent zeo-

lites are themselves very acidic, and the strengths of the acid sites formed fall within the range of acidities possessed by the parent zeolites, it is difficult to see the creation of these acid sites by physical methods like adsorption of bases. Therefore, in order to identify these acid centers, one should generate them in a system whose acidity spectrum falls outside the range of acidity of these acid sites. We have incorporated La^{3+} ions in a non-acidic K-L-zeolite and examined the creation of acid centers by the TPD of NH_3 .

EXPERIMENTAL

Zeolite K-L was prepared by the method of Breck and Acara [3]; ion-exchanging with Ba and La chloride salts was carried out by known procedures [4]. The exchanged samples were washed till no chloride ions were detected in the filtrate, dried at 383 K and calcined at 823 K for 6 h. The compositions of the samples are reported in Table 1. The samples were then ion-exchanged with $\text{Pt(II)(NH}_3)_4(\text{NO}_3)_2$ solution to give 0.8 % Pt by weight in the catalysts. The Pt-containing catalysts were calcined at 533 K. The TPD studies of adsorbed NH_3 were carried out on the samples by procedures reported earlier [5]. The reforming of n-hexane was carried out at atmospheric pressure using 2 g of compacted and granulated Pt loaded catalysts.

Table 1
Composition of the Samples

S a m p l e	Composition (wt.%)					
	SiO_2	Al_2O_3	K_2O	Na_2O	BaO	La_2O_3
K-L	59.39	21.78	18.48	0.35	-	-
Ba, K-L	61.13	18.85	10.21	0.12	9.69	-
La, K-L	58.89	21.59	12.02	-	-	7.5

RESULTS AND DISCUSSION

The TPD spectra of the K-L zeolite and its ion-exchanged forms (Ba, K-L and La, K-L) are presented in Fig. 1.

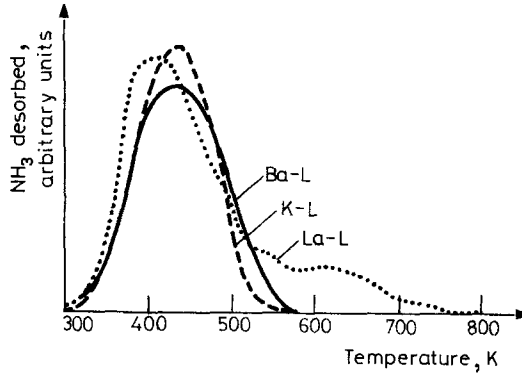


Fig. 1. TPD of NH_3 on L-zeolites

The TPD spectra of the Ba-exchanged sample has also been presented in the same figure. This sample has a spectra which is nearly identical to that of the parent K-L-zeolite, showing that Ba incorporation does not introduce acid centers. Recently Hughes et al. [6] have reported that Ba incorporation does not create acidity in K-L-zeolites if the sample is calcined at elevated temperatures as has been done in our case. As both Ba and La forms were prepared in a similar manner, it is obvious that the acidity in the La, K-L-sample is due to La-ions.

The DHC of n-hexane on the Pt-loaded samples is reported in Table 2.

Table 2

Reforming of n-hexane on Pt-zeolites

(Temp.: 733 K, Press: 1 atm, WHSV : 2 h^{-1} , H_2/HC (mol): 6)

Catalyst	Yield (wt.%)			
	After 10 min on stream		After 3 h on stream	
	Benzene	Iso-hexanes	Benzene	Iso-hexanes
Pt, K-L	30.00	4.90	24.20	4.41
Pt, La, K-L	27.90	8.92	5.92	7.25

It is observed that both Pt, K-L and La, Pt, K-L produce nearly the same amount of benzene (30 and 27.9 wt.%, respectively) initially but after 3 h on stream, the La-containing catalyst deactivates much more than the K-L-catalyst. At 3 h on stream, the La-sample produces only 5.19 % benzene while the K-L-sample is still yielding 24.2 % benzene. The rapid deactivation of the La-sample is attributed to the presence of strong acid centers which produce coke and coke precursors which poison the metallic sites responsible for the DHC reaction. In fact, earlier workers [7] have also reported that acidity in these zeolites is detrimental to their DHC activities.

The presence of acid centers in the Pt, La, K-L-catalyst is also confirmed by the more extensive formation of iso-hexanes on this sample (Table 2).

REFERENCE

1. J.N. Miale, N.Y. Chen, P.B. Weisz: *J. Catal.*, 6, 278 (1966).
2. P.A. Jacobs: *Carboniogenic Activity of Zeolites*, p. 46. Elsevier, Amsterdam 1977.
3. D.W. Breck, N.A. Acara: *U.S. Pat.*, 711,565 (1958).
4. V.P. Shiralkar: *Ph.D. Thesis, Univ. of Pune, India, July 1980.*
5. S.G. Hegde: *Ph.D. Thesis, Univ. of Pune, India, January 1983.*
6. T.R. Hughes, W.C. Buss, P.W. Tamm, R.L. Jacobson: *Proc. 7th Intern. Conf. Zeol., Tokyo, August 17-22, 1986*, p. 725.
7. J.R. Bernard: *Proc. 5th Intern. Conf. Zeol., Napoli, Ed. L.V.C. Rees, Heyden, London, 1980*, p. 686.