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Hydroisomerization of *n*-Pentane on Pt/La Mordenite Prepared by Competitive Cationic Exchange

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Pt/La-mordenite catalysts were prepared by competitive cationic exchange for the isomerization of *n*-paraffins. Four different La/Pt ratios (61, 81, 101 and 111) were employed. La-mordenite was first prepared from its Na-form by three exchange batches with an intermediate calcination, after which the extent of exchange reached 90%. The activity of the prepared catalysts was tested through isomerization of *n*-pentane in a pulse micro-reactor at 300°–400°C under atmospheric pressure. Results indicated the increase of isomerization with temperature up to 375°C, after which it starts to decrease. On the other hand, selectivity decreases due to the continuous increase of cracking with temperature. The catalyst La/Pt ratio showed significant effect on its performance. The best catalyst had a ratio of 101 and exhibited 98% isomerization with respect to thermodynamic equilibrium at 375°C.

INTRODUCTION

The development of dual functional catalysts for the catalytic isomerization of low molecular weight paraffins is of great importance in the petroleum refining industry. Rabo *et al*[1,2] were among the first to demonstrate the high activity of Pt and Pd zeolite catalysts in the isomerization of *n*-pentane and *n*-hexane. The catalytic properties of zeolites, especially types X, Y and mordenite containing metals of group VII, were extensively studied by Minachev *et al.*[3–5] in various reactions. The mordenite form of zeolite was known as an isomerization catalyst as such, and also when composited with a noble metal hydrogenation component[6].

For introducing a noble active component into the cavities of zeolites, imprognation [7,8] and ion exchange techniques[9] are the most suitable and widely used. However, the ion exchange competition is more advantageous over the classical impregnation and ion exchange techniques. It enables the realization of a fine dispersion and a maximum homogenous distribution of the active metal on the zeolite surface area. Besides, prepared catalysts maintain greater stability in the presence of sulphur compounds[10].

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Benesi[6] was among the first to apply the competitive cationic exchange technique for the preparation of isomerization catalysts composed of mordenite loaded with Pt or Pd. This was then further developed and applied for preparing Pt/mordenite[9], Pt/type Y and Pt/type X zeolites for the isomerization of *n*-pentane and *n*-hexane[9,11]

EXPERIMENTAL

The catalysts were prepared from Na-mordenite powder by three successive La-exchange batches, using a freshly prepared lanthanum nitrate solution. After each exchange, the slurry was filtered, washed and dried. An intermediate calcination step was carried out after the second exchange batch.

The La-exchange mordenite was then loaded with 0.5 wt % Pt, using the competitive cationic exchange technique. This work place by contacting the prepared La-mordenite with a solution composed of both, the desired Pt-ions and the competitor La-ions. The solution was prepared with different concentrations in order to provide four different ratios of La-ions to the metal cations (X/α) namely, 61, 81, 101 and 111. The source of Pt was an amine complex compound such as the Keller complex.

La and Pt were measured after each exchange batch through atomic absorption analysis (Perkin Elmer 2380).

The prepared samples were then calcined in the presence of dry air at 450°C for 2 hrs before being reduced with hydrogen at 400°C for 4 hrs.

The isomerization of *n*-pentane was selected as the model reaction for measuring the catalytic activity of the four prepared catalysts. The reaction was carried out under atomospheric pressure in a pulse micro catalytic reactor operating between 300° and 400°C. The reactor contained 500 mg catalyst and was fed with 0.2 μl pulse of *n*-pentane in the presence of hydrogen carrier gas flowing at a rate of 50 ml/min. The reaction outputs were immediatly analysed through a chromatographic column directly attached to the reactor.

RESULTS AND DISCUSSION

1. Catalyst preparation

(a) La-exchange of Na-mordenite: The Na-mordenite used in catalyst preparation had the following chemical analysis expressed in wt %, SiO_2: 69.82, Al_2O_3: 11.23, Na_2O: 6.36; MgO: 0.44; CaO: 0.24; K_2O: 0.19 and ignition loss: 11.0.

Ignition loss is considerably high due to the presence of zeolitic water which is expelled on heating the mordenite above 300°C as experimetally confirmed by both DTA and TGA. Chemical analysis of the Na-mordenite sample also indicates its high SiO_2/Al_2O_3 molar ratio which reached 10.54.

The exchange of Na with La in the original mordenite sample was realized at three different levels, which were determined with respect to the $3Na^+ \rightarrow La^{3+}$ thermodynamic equilibrium exchange isotherm. Results are illustrated in Fig. 1, which describes the effect of number of exchange batches on the extent of exchange. The first exchange level approached 21%, while the second reached 36%. On the other hand, the third exchange level, which followed an intermediate calcination at 450°C, reached 90% exchange which is significantly high. This increase upon intermediate calcination could be attributed to two main reasons: (i) the migration of Na^+ cations from the network of the small cages to other positions accessible to further cation exchange, and (ii) the dehydration of hydrated La^{3+}cations in order to strip off the water molecules which enlarge the radius of the introduced La^{3+} cation from 1.15 Å to 3.96 Å and thus prevent it from penetrating into the network of small cages.

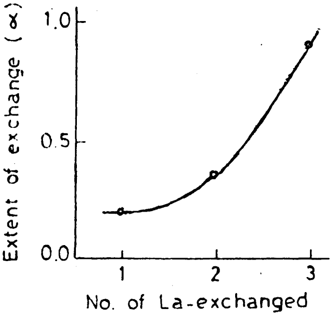

Fig. 1. Effect of number of La-exchange batches on the extent of exchange.

Finally, it is worth noting that the third exchange level has exceeded that of the thermodynamic equilibrium. However, the latter is only carried out at room temperature and is not violated by technique similar to those of intermediate calcination or repeated contact with hot salt solution.

(b) Introduction of platinum: Pt was introduced to the third level La-exchanged mordenite by single competitive cation exchange, in which La^{3+} was the only competitor. The amount of Pt cations introduced were calculated by measuring the concentration of Pt in the mother liquor left after the reaction using atomic absorption spectrophotometer.

Figure (2) represents the competition curve which demonstrate the relation between the fraction of Pt remaining in solution at equilibrium with the zeolite (Y/α) and the ratio of the total number of competitor cation to that of Pt cation in the medium (X/α).

The optimum zone of competition, where the metal is supposed to be finally dispersed and homogeneously distributed over the mordenite support, appears at $X/\alpha \simeq 100$. At this point, the mother liquor is practically exhausted (*i.e.*, the

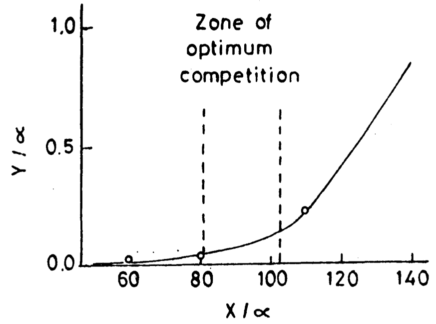

Fig. 2. Competition curve.

residual Pt remaining in solution is very low) and the slope of the curve starts increasing suddenly and rapidly.

2. Catalytic activity of prepared catalysts

The catalytic activities of the four prepared Pt/La-mordenite catalysts were measured through the isomerization of *n*-pentane in a pulse reactor operating between 300° and 400°C, under atmospheric pressure.

The isomeization of *n*-pentane practically leads to 2-methyl butane only, since neopentane is not formed. The activity of catalysts prepared became almost constant after less than 10 pulses at about 15 minutes intervals. Accordingly, the average of conversion after 10 injections was taken as the catalyst activity at the corresponding temperature.

The effect of reaction temperature on *n*-pentane isomerization over the four different prepared catalysts is illustrated in Fig. (3) from which it is quite obvious

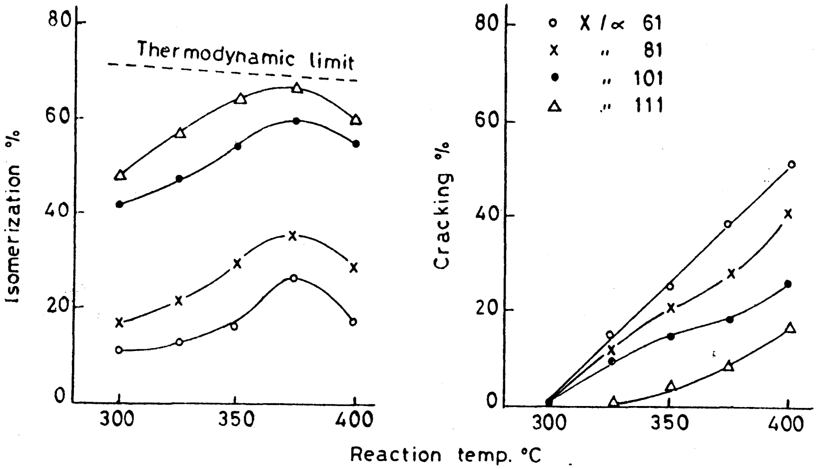

Fig. 3. Isomerization of *n*-pentane over typical prepared catalysts.

that the total conversion, which includes both isomerization and cracking, increases with the increase of reaction temperature from 300° to 400°C. As for the isomerization activity, it does not behave similarly, it increases with temperature until a maximum is reached at 375°C, after which it starts to decrease. On the other hand, cracking continuously increase with the increase of temperature.

Although the increase of isomerization with reaction temperature contradicts the thermodynamic feasibility of *n*-pentane isomerization (marked by a non continuous line on Fig.), yet this could be interpreted by the fact that the metal loaded mordenite catalysts act as bifunctional catalysts. The mechanism of those catalyst involves in its first step the dehydrogenation of *n*-paraffin to *n*-olefin on the metallic sites of the catalyst, and this dehydrogenation reaction is thermodynamically favoured with the increase of reaction temperature.

Comparing the actual results obtained with those of the thermodynamic equilibrium at the corresponding temperatures, (Fig. 3), it could be observed that catalyst No. 3 characterized by X/α = 101 approached the thermodynamic limit by about 98% when the reaction temperature was 375°C.

Table 1 gives the percentages approach from the thermodynamic equilibrium, of the four prepared catalysts, at two different temperature, namely 300°C, where all catalysts are 100% selective for isomerization and 375°C, where they exhibit their maximum isomerization activity.

TABLE 1
ISOMERIZATION OF *n*-PENTANE, PERCENTAGE APPROACH FROM EQUILIBRIUM

Catalyst No.	X/α	% Approach from equilibrium	
		300°C	375°C
1	61	15.7	38.5
2	81	23.6	52.4
3	101	68.6	97.8
4	111	59.3	87.8

For further illustration of the effect of competitor ion (La^{3+}) concentration (expressed in terms of X/α during the competitive exchange step) on the prepared catalysts behaviour, Figs. 4 and 5 were plotted.

From Fig. 4, expressing the catalyst behaviour at 375°C, it is obvious that by increasing the concentration of La^{3+}, the isomerization increases to a maximum of 66.5% (98% of the thermodynamic equilibrium) while cracking is reduced to its minimum level (8.3%). However, further increase of La^{3+} concentration expressed in terms of X/α does not improve the catalyst behaviour; as isomerization starts to drop and cracking to increase significantly. Similar trends of behaviour could also be observed at the other reaction temperature.

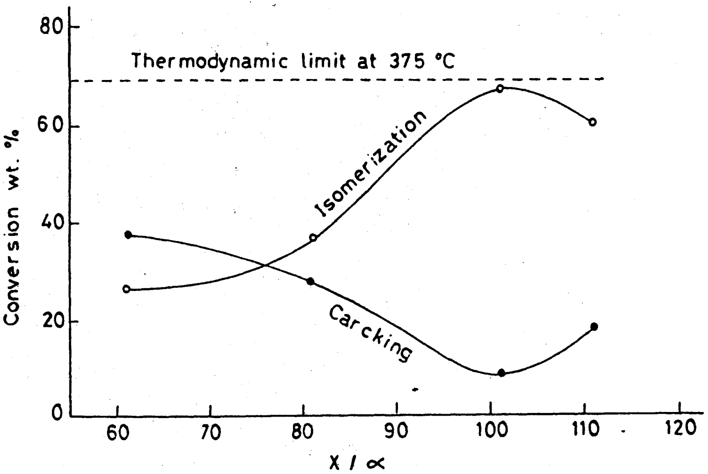

Fig. 4. Effect of competitor concentration on isomerization activity at 375°C.

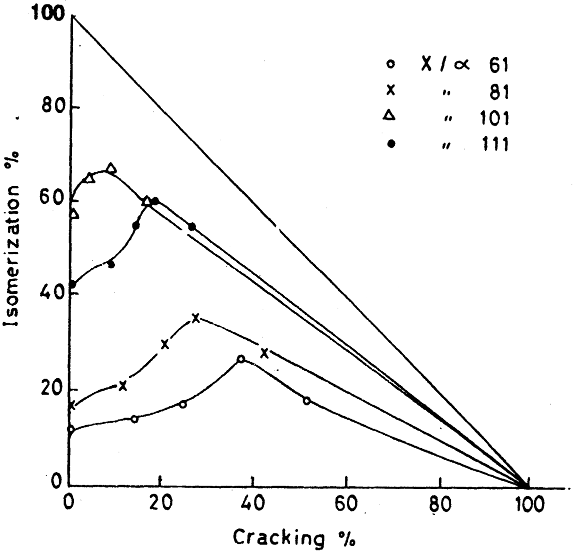

Fig. 5. Waterman representation: Effect of competitor concentration on catalyst selectivity.

Fig. 5 illustrates the isomerization selectivity of the four prepared catalysts through the Waterman representation[12], which describes the percentage isomerization as function of percentage cracking.

Accordingly from results demonstrated in Table-1, as well as Figs. 4 and 5, it could be noted that, at X/α of 101, the prepared catalyst exhibits maximum isomerization and highest selectivity. This could be attributed to the fact that X/α of 101 corresponds to the optimum zone of competition which acquires the prepared catalyst the finest dispersion (quasi-atomic) of the active Pt metal as well as its maximum possible homogenous distribution over the mordenite support. Actually, the realization of the previsously mentioned finest dispersion and best homogenous distribution is of great significane in Pt-loaded zeolite catalysts due to that: (i) the amount of Pt used is very poor with respect to the exchangeable sites and (ii) the Pt ion has a great affinity towards the zeolite and leads to its heterogenous distribution on the zeolite support.

Conclusions

1. La-exchange after an intermediate calcination step increased the $3Na^+ \rightarrow La^{3+}$ extent of exchange from 36% to 90%.
2. Introducing Pt into the mordenite support by competitive cationic exchange, with the competition ion concentration corresponding to the optimum competition zone, leads to the preparation of a highly active and selective catalyst for *n*-paraffin isomerization.
3. The realization of 66.5% isomerization at 375°C (98% approach from thermodynamic limit) was achieved by a 0.5% Pt-0.9 La-Na-mordentie catalyst prepared by three Na-La exchange batches, including intermediate calcination at 450°C, followed by a competitive cationic exchange at a La/Pt ionic ratio of 101. The catalyst was calcined at 450°C in the presence of very dry air before being reduced in a stream of pure hydrogen at 400°C for 4 hrs.

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