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Development of Mono- and Bi-metallic Catalysts for Reforming of Naphtha for Production of Aromatic Concentrates and for High Octane Gasoline

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The Indian Institute of Petroleum has developed a process for the preparation of high purity alumina carrier of excellent thermal and hydrothermal stability. Using this support two types of reforming catalysts *viz.*, mono-metallic (Pt) and bi-metallic (Pt-Ir and Pt-Re) have been developed. The know-how has been firmed up at the 5 kg level of preparation and impregnation. For scale-up and production, IIP have collaborated with the Associated Cement Companies (ACC). In tests conducted with various feedstocks under conditions typical of Indian reformers, the IIP-ACC catalysts compare favourably with commercial, imported, catalysts offered for that duty.

Catalytic reforming transforms low octane naphtha into high octane gasoline and produces aromatics—concentrate rich in benzene, toluene and xylenes. Ever since the introduction of platinum catalyst supported on fluorinated or chlorinated alumina by UOP in the late forties, it has undergone remarkable progress with continuous development in catalyst and process technology[1–4]. Higher octane gasoline requirement, need for better selectivity to aromatics and higher reformate and hydrogen yields' possibility led to discoveries of platinum catalysts promoted with rhenium, iridium, germanium, tin, etc.[5–8].

Experimental procedure

Preparation of the carrier—High purity alumina support of γ or η types have been widely used for the preparation of reforming catalysts[9]. Suitable carriers of required properties were prepared by controlling the composition of alumina hydrate precursors and the conditions of activation. The main steps involved in the preparation of the alumina carrier are shown in Fig. 1. The sodium aluminate solution was neutralised with dilute nitric acid in a reaction vessel under controlled parameters of concentration, mixing rate, *p*H of the mix, agitation rate, ageing period and temperature, to get the required phases of hydrated aluminas.

Preparation of the catalyst—The activated support was suitably conditioned, impregnated with platinum or platinum and iridium or platinum and rhenium salt solutions. Drying and activation of the impregnated samples were carried out under standardized conditions. Various steps in impregnation are given in Fig. 2.

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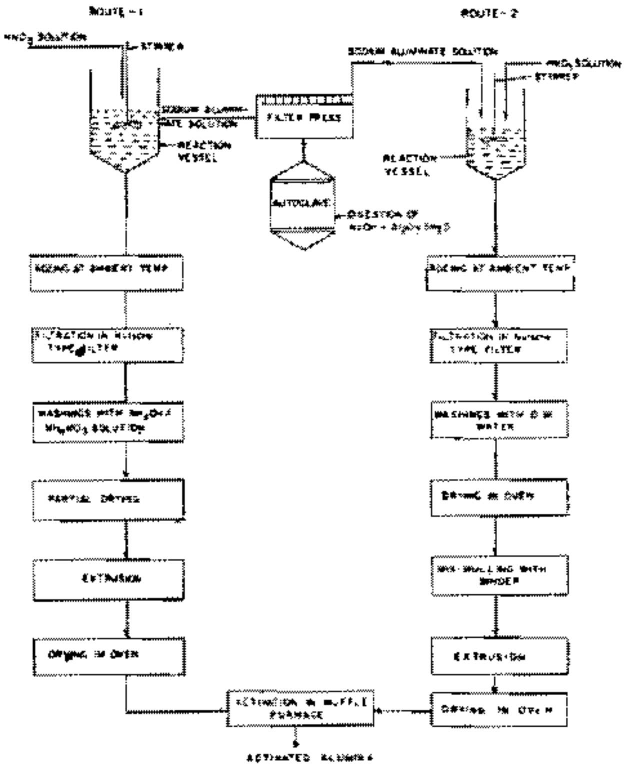

Fig. 1—Flow sheet for preparation of alumina support

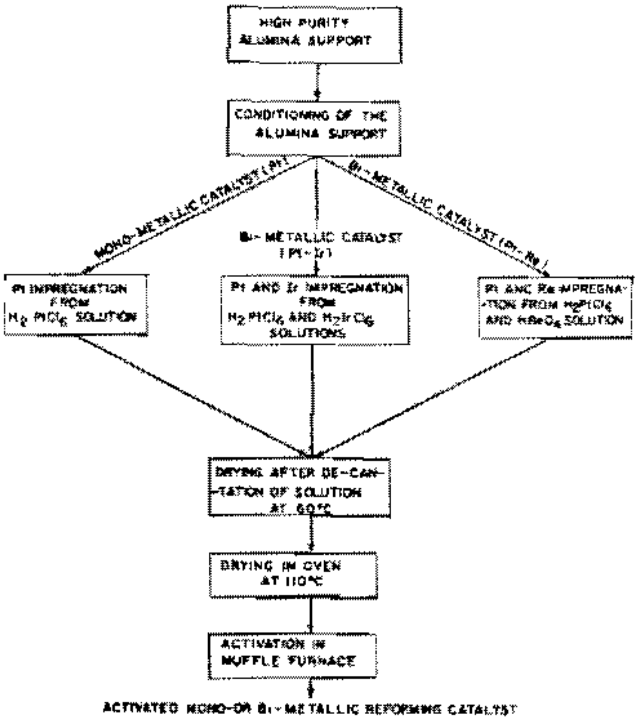

Fig. 2—Flow sheet for the preparation of mono- and bimetallic reforming catalyst

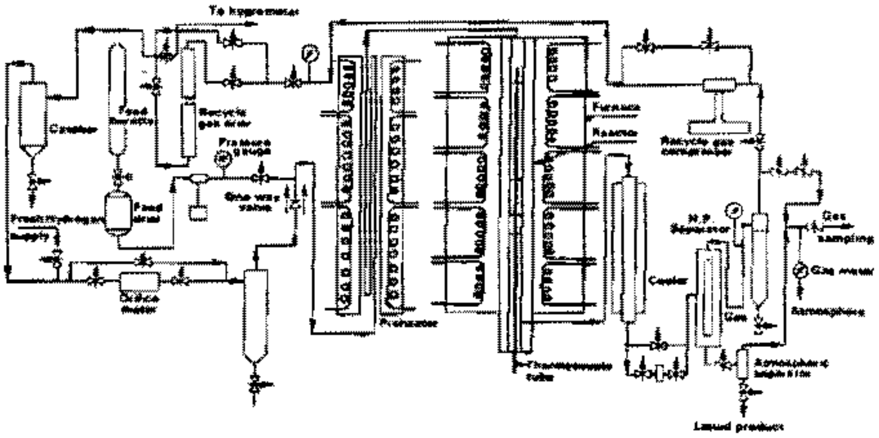

Fig. 3—Flow sheet of catalytic reforming unit

Characterization—Physico-chemical characteristics of the carrier and the finished catalysts were determined at various stages of preparation. XRD analyses for the determination of phase composition of precursor alumina hydrates and crystallinities were carried out. Impurity analyses were done by spectrophotometric methods. Pore volume and pore-size distribution were determined by high pressure mercury porosimetry. Metal dispersions were estimated by volumetric method following either hydrogen chemisorption, oxygen titration or hydrogen titration. Temperature-programmed reduction technique was used to follow the reducibility of the supported metals[10].

Performance evaluation—The performance of catalysts, both commercial and IIP-ACC's has been evaluated in a pilot plant equipped with a gas recycle compressor and a hygrometer (Fig. 3). The catalyst loading pattern in the reactor to achieve isothermal conditions is shown in Fig. 4. This pilot plant had earlier been correlated with industrial plant for yield and product quality. Space velocity, reactor temperature, pressure and hydrogen-to-hydrocarbon ratio were varied to generate correlations. The data generated in the unit could be scaled up to commercial operation. Suitably developed procedures for start-up (reduction and presulphidation), and estimation of activity, selectivity, stability, accelerated ageing and regeneration have been adopted[11]. Care was taken to control avoidable deactivation by catalytic poisons. Feedstocks of varying composition from industrial plants have been used. Ranges of operating conditions were selected to match with those of different plants in India. The feed and products were analysed for octane numbers and for hydrocarbon composition by gas chromatography, PNA analyser and mass spectrometry.

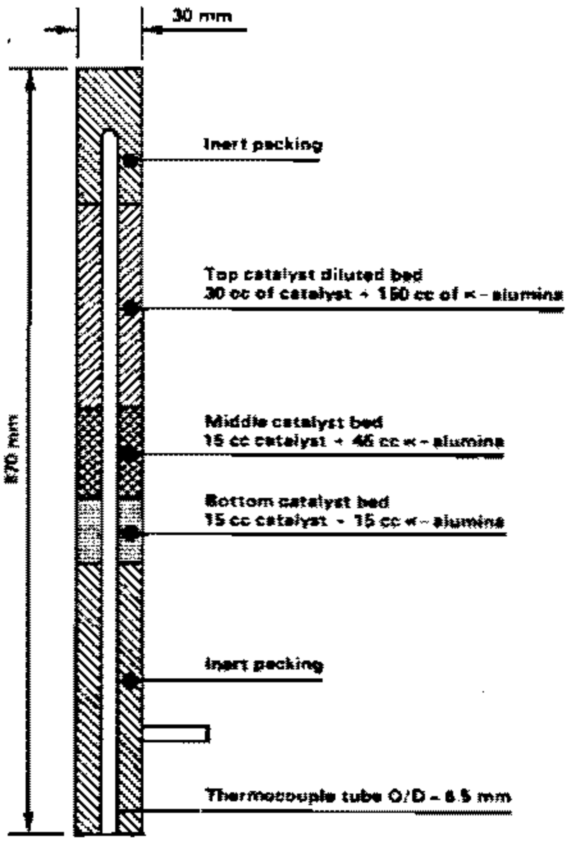

Fig. 4—Loading of catalyst in the reactor

Results and discussion

Carrier and catalysts—The demand for improved catalyst formulations to get higher C_5^+ yield and product quality through high severity reforming operation has resulted in the introduction of promoters to platinum on the one hand and to have alumina carriers of higher thermal and hydrothermal stability on the other. The present trend, as far as the alumina carrier is concerned, is towards the use of γ aluminas of high purity and crystallinity obtained from precursor hydrates largely consisting of pseudoboehmites and bayertie. Thermal and hydrothermal stability studies on various catalysts, *vis-a-vis* Pt metal sintering, have shown the superiority of pseudoboehmite and bayerite based carrier[12]. Such carrier reduces coke formation and improves selectivity.

Typical properties of various mono- and bimetallic reforming catalysts are presented in Table 1. IIP-ACC catalysts have properties equivalent to those of imported commercial catalysts. Of the total pore volume of 0.5 to 0.6 ml/g, the distribution of 80 to 90% pore volume lies in 30-50 Å region of pore radius for most of the catalysts. Fig. 5 shows typically the pore structure of IIP-ACC catalyst (sample A5) which compares well with that of a commercial catalyst (A1). The most efficient utilisation and accessibility to metal surface, a factor of prime importance can be managed in catalyst manufacture and is measured as metal dispersion. The type of support and method of impregnation are important for good metal dispersion. The values of metal dispersions for different catalysts are also given in Table 1. A metal dispersion of the order of 70 to 96% estimated in all IIP-ACC samples points to the efficacy of the impregnation technique followed and also to good metallic activity.

Table 1—Physico-chemical Characteristics of Catalysts

Catalyst/ Type	Sample Designation	Composition, weight							XRD Data		S_{BET} (m^2/g)	Pore vol (ml/g)	Metal dispn (%)	Bulk density (g/ml)
		Na_2O (ppm)	Fe_2O_3 (ppm)	SiO_2 (ppm)	Pt (%)	Ir (%)	Re (%)	Cl (%)	% Crystallinity	Cryst. size(Å)				
Monometallic														
Commercial	A1	34	—	—	0.35	nil	nil	1.15	66	70	199	0.58	74	0.7
Commercial	A2	—	—	—	0.375	"	"	0.9	69	70	—	0.85	—	—
Commercial	A3	—	—	—	0.6	"	"	0.7	62	70	269	0.34	—	—
IIP	A4	21	196	—	0.35	"	"	1.05	60	65	200	0.52	90	0.72
IIP-ACC	A5	23	225	451	0.35	"	"	1.1	65	65	230	0.61	96	0.61
IIP	A6	45	—	—	0.35	"	"	1.0	70	68	170	0.54	70	—
IIP-ACC	A7	38	224	574	0.55	"	"	0.92	60	50	239	0.58	83	0.69
IIP	A8	26	280	—	0.37	"	"	1.02	70	68	212	0.53	84	—
Bimetallic														
Commercial	B1	47	—	—	0.35	0.04	nil	0.87	—	—	182	0.55	65	0.7
Commercial	B2	—	—	—	0.3	nil	0.3	1.03	—	—	210	0.58	79	0.66
Commercial	B3	27	287	—	0.3	nil	0.3	1.0	61	59	180	0.5	84	0.62
IIP	B4	43	320	—	0.35	0.04	nil	1.02	65	62	190	0.55	70	—
IIP	B5	35	290	—	0.3	nil	0.3	—	58	55	165	0.4	86	0.74

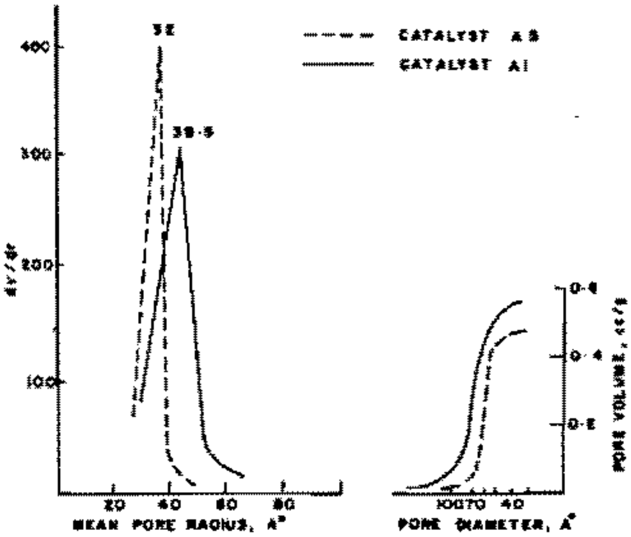

Fig. 5—Pore structure of catalysts by mercury porosimetry

The temperature-programmed reduction technique shows the manner of supported metal reduction. Metal-support and metal-metal interactions are indicated in the TPR profiles of the catalysts and thus dependent on the method of preparation of the catalysts. Typical profiles of a few catalysts are shown in Fig. 6. Supported Pt and Pt-Ir samples, understandably, give similar profiles, indicating at least two metal-support interaction sites. While supported Re reduces at higher temperatures with TPR peak around 880 K, the TPR profiles of Pt-Re catalysts indicate the ease of reduction of Re(oxide) in presence of Pt. The single peak around 500 K is attributed to the formation of Pt-Re bimetallic phase[13].

Performance evaluation of catalysts—The most efficient utilisation of reforming catalyst calls for selective start-up operation and conditioning of the catalyst[11]. In order to reduce the initial fast coke lay down on the catalyst and to control the hydrogenolysis activity, sulphidation of fresh as well as the regenerated catalysts was carried out by hydrogen sulphide

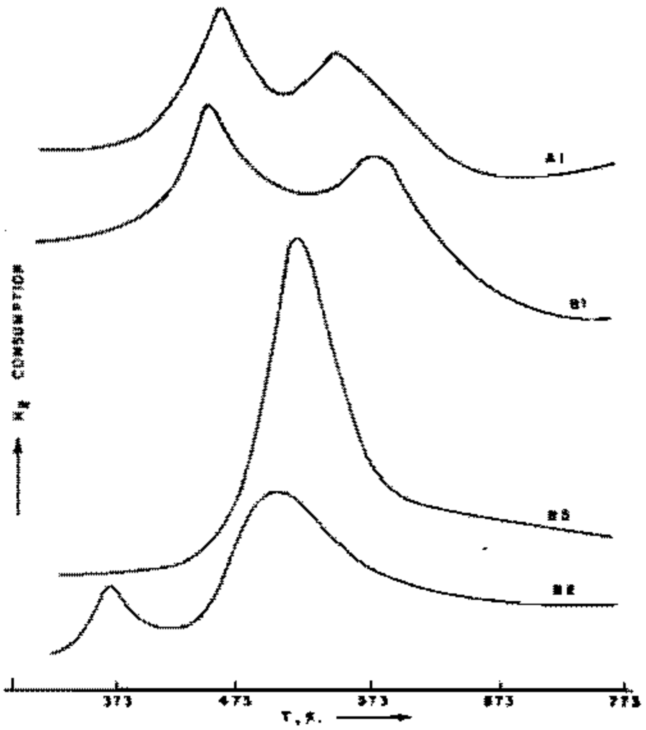

Fig. 6—Temperature-programmed reduction profiles of mono- and bi-metallic catalysts

or suitable organic sulphur compounds under specific conditions. Thereafter, the activity tests for various catalysts were carried out for 100 to 700 hours.

The data generated in IIP pilot plant for aromatics production under typical conditions are compared in Table 2 with those of industrial plant using a commercial multimetallic catalyst. Similar C_5^+ and aromatic yields indicate that the performance in IIP pilot plant could well be correlated with industrial unit operations.

Mono-metallic catalysts—The performance of IIP's mono-metallic catalyst (A4) is compared with that of a commercial catalyst (A2) in Table 3. The tests were performed using a paraffinic feedstock. The data indicate the equivalence of IIP catalyst to the commercial catalyst. Also included in Table 3 is the temperature-octane-yield sensitivity of IIP's catalyst (A4), which is well in accordance with plant realizations with commercial catalysts.

Table 4 gives a comparison of the performance of two different batches of IIP's mono-metallic catalysts (A4 and A8) under identical conditions. The similar yields and product quality clearly demonstrate the reproducibility of the catalyst preparation technique.

At high octane severity, IIP's mono-metallic catalyst (A6) compares well with a commercial catalyst (A3), with respect to both product yields and octane, as seen in Table 5 and Fig. 7. Another batch of mono-metallic IIP-ACC catalyst (A7) having 0.55 wt% Pt was evaluated for C_8 aromatics production. The data are presented in Fig. 8. The weight per cent yields of total aromatics and C_8 aromatics vary in the range of 61-63.6% and 42-43.6% respectively. The average yield of aromatics at different

Table 2—Comparison of IIP's Pilot Plant and Industrial Plant Data

Feed Boiling Range	110-140°C	
Catalyst	IIP Pilot Plant Commercial	Industrial Multi-metallic..
Reactor pressure (bar)	20	20
Wt % yield		
C_5^+ Reformate	91.97	91.34
Total aromatics	77.6	77.0

Table 3—Pilot Plant Data on IIP and Commercial Mono-metallic Catalysts

Feed boiling range (ASTM)		85 - 156°C	
Composition (vol %)			
Paraffins		77	
Naphthenes		15	
Aromatics		8	
Catalyst	A2 (commercial)	A4 (IIP)	
Reactor temperature (°C)	482	482	490
Reactor pressure (bar)	24	24	24
WHSV	2	2.1	2.1
Reformate (RONC)	83	83	86.3
Wt % yield,			
C_5^+ Reformate	84.5	85	81.5
Hydrogen	0.8	0.8	0.9

Table 4—Comparison of Performance of Two Batches of IIP Mono-metallic Catalysts

Feed boiling range (ASTM)	90 - 136°C	
Composition (Vol %)		
Paraffins	44.7	
Naphthenes	48.9	
Aromatics	6.9	
Catalyst	A4	A8
Reactor temperature (°C)	480	483
Reactor pressure (bar)	24	24
WHSV	3.0	3.1
Reformate (RONC)	90	91
Wt % yield		
C_5^+ Reformate	91.3	91.6
Hydrogen	2.4	2.5

Table 5—Pilot Plant Data on IIP and Commercial Mono-metallic Catalysts (at high octane)

Feed boiling range	110-140°C	
Composition (Vol %)		
Paraffins	53.9	
Naphthenes	31.7	
Aromatics	14.4	
Catalyst	A6 (IIP)	A3 (Commerical)
Reactor temperature (°C)	491	490
Reactor pressure (bar)	18	18
WHSV	2.0	2.0
Reformate (RONC)	99.5	98.6
Wt % yield		
C_5^+ Reformate	86.4	86.2
Hydrogen	2.3	2.5

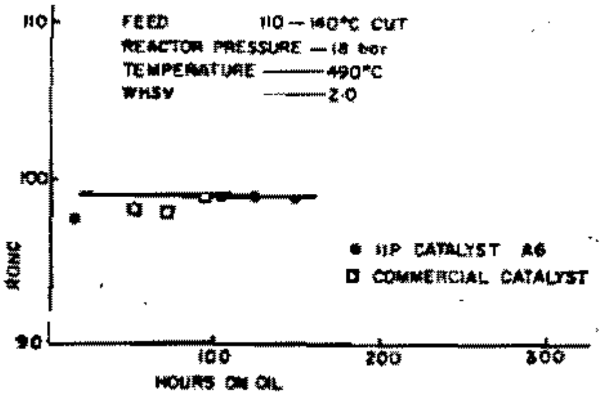

Fig. 7—Comparison of IIP (A6) and commercial (A3) mono-metallic catalyst

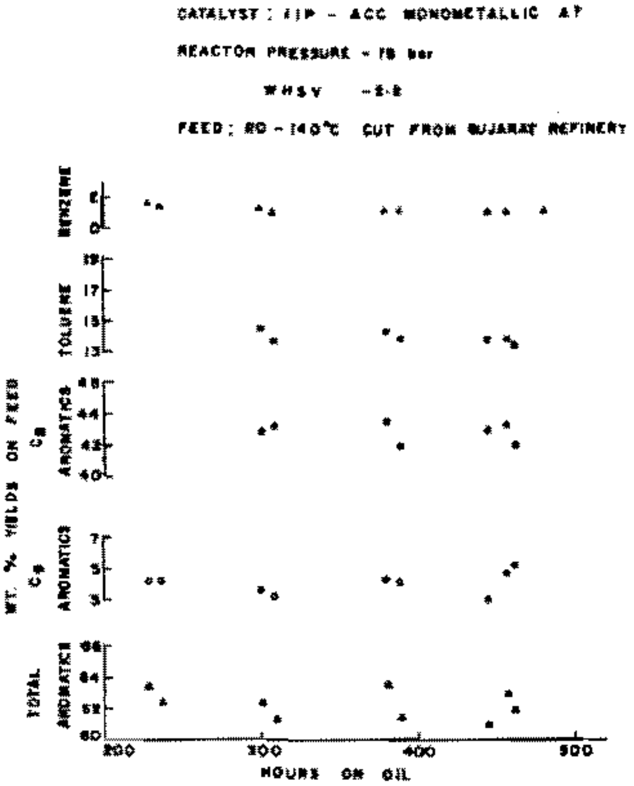

Fig. 8—Performance stability of IIP-ACC mono-metallic (A7) catalyst

temperatures are also given in Fig. 9. These yields compare well with yields to be expected from the use of commercial catalysts.

The stability and regenerability of IIP's mono-metallic catalysts have been found to be very good. The yield-data on IIP's catalyst, A4, for instance, for three cycles, each lasting about 250 hr on stream are presented in Fig. 10. All the data are normalised to 90 RONC. The data indicate the excellent stability of the catalyst in three cycles. At the end of each cycle, the catalyst was subjected to accelerated ageing during which 6-10 wt% coke was deposited on the catalyst. The RONC of the reformate vs hours on oil are plotted in Fig. 11 for the three cycles. It is a testimony to the special regeneration and reactivation procedure developed by IIP which more than restores the fresh catalyst activity in the third cycle. Fig. 12 shows the stability of another IIP-ACC catalyst (A5) under ultra-high severity tests.

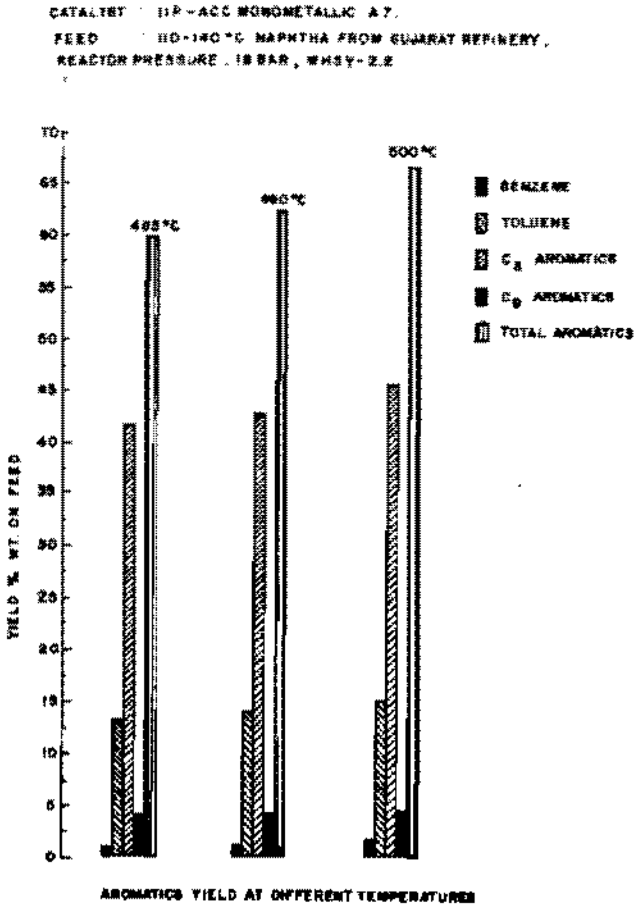

Fig. 9—Yields obtained at different temperatures with mono-metallic catalyst A7

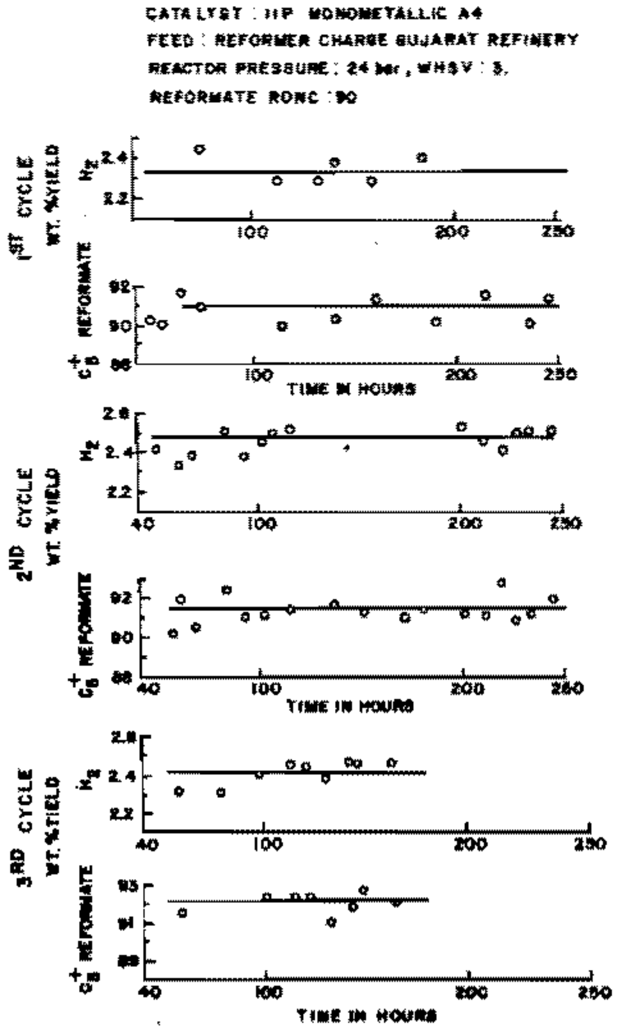

Fig. 10—Yield stability of IIP mono-metallic (A4) catalyst in three cycles

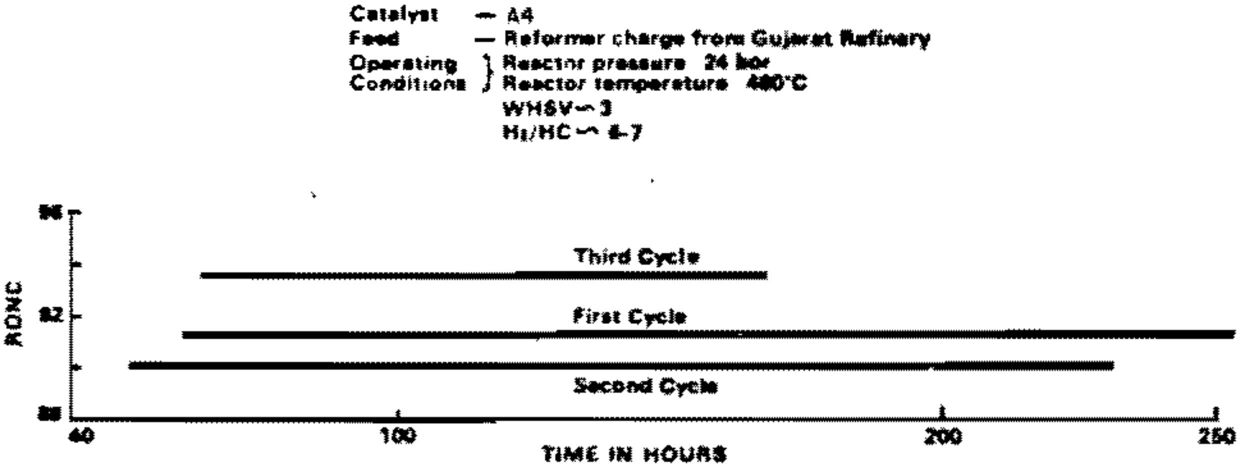

Fig. 11—RONC vs hours on oil for IIP mono-metallic (A4) catalyst

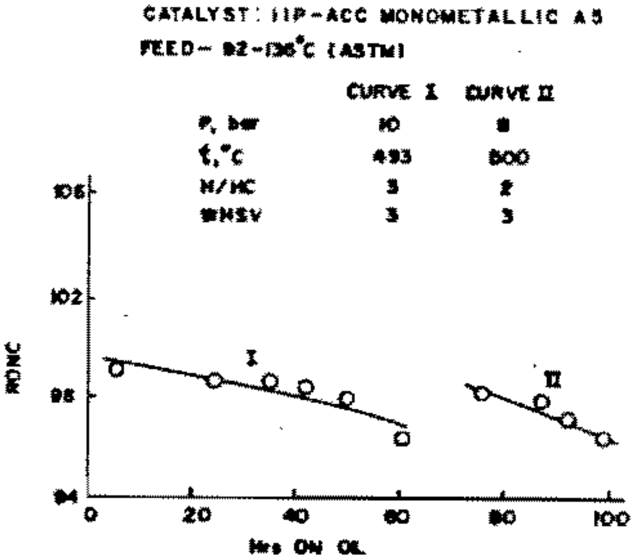

Fig. 12—Ultra severe conditions tests of IIP-ACC mono-metallic (A5) catalyst

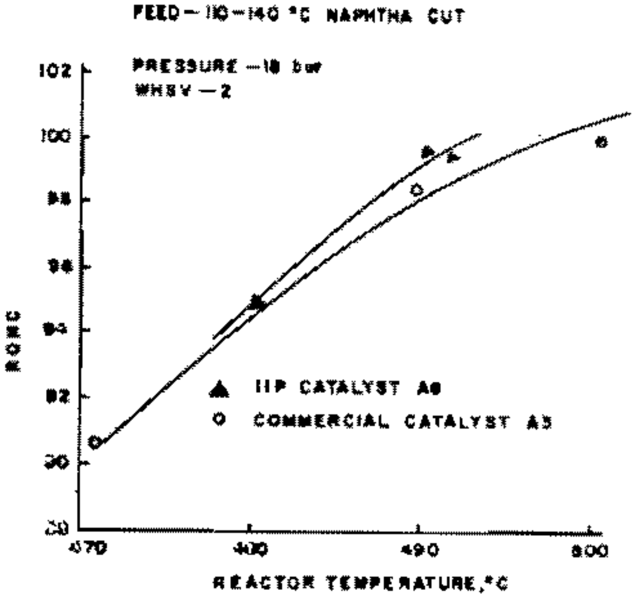

Fig. 14—Temperature response of IIP (A8) and commercial (A3) mono-metallic catalysts

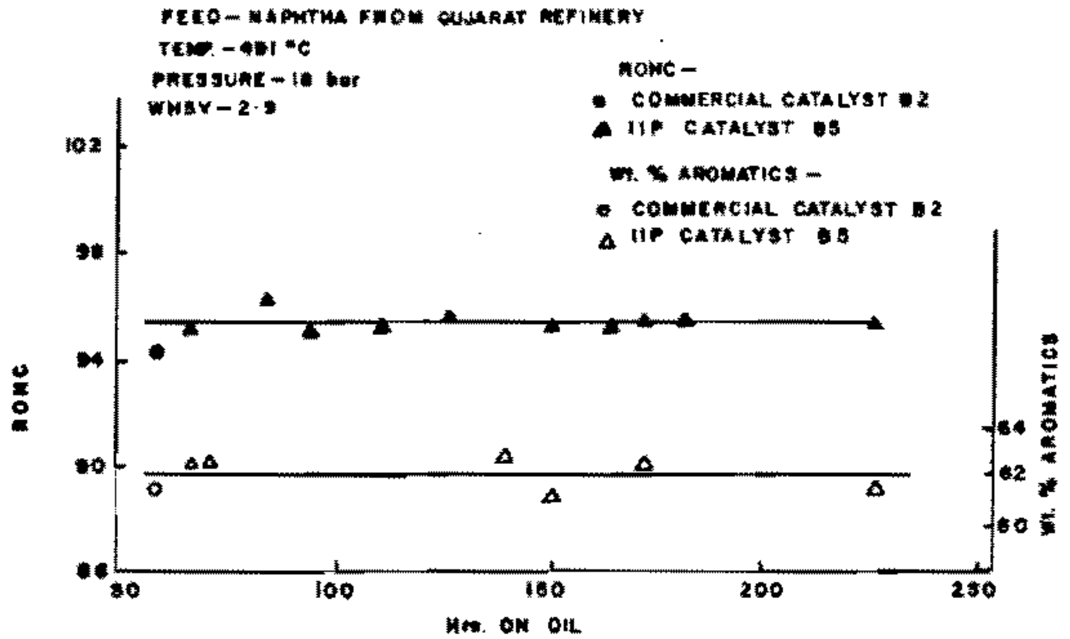

Fig. 13—Performance stability of Pt-Re catalysts

Bi-metallic catalysts—Concomitant with the announcement of Rheniforming catalyst by Chevron fot low pressure reforming, IIP extended its development work to cover a range of bi-metallics for possible, specific applications in India. The data obtained with one such formulation (B5) are compared with those of a present-generation Pt-Re catalyst (B2) in Fig. 13. The data demonstrate the excellent activity, selectivity to aromatics and

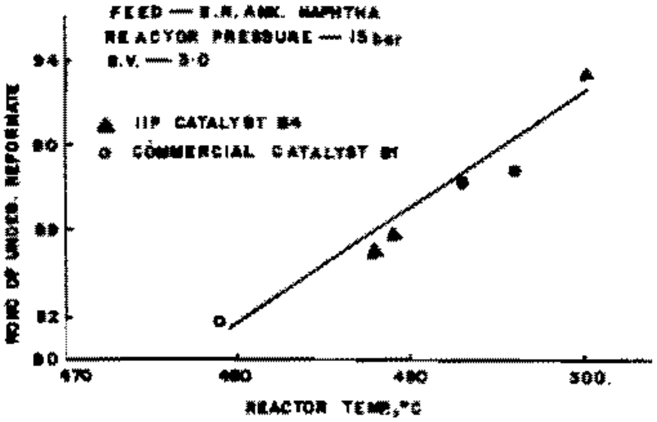

Fig. 15—Temperature response of IIP (B4) and commercial (B1) Pt-Ir catalyst

stability of IIP's bi-metallic catalyst. Similar results were obtained with our Pt-Ir formulations also.

Temperature response—The temperature response of IIP formulations *viz.*, the monometallic, Pt-Ir bi-metallic and Pt-Re bi-metallic, are compared with commercial catalysts in Figs. 14, 15 and 16 respectively. This clearly establishes the competitiveness of IIP's reforming catalysts.

Conclusion

Indigenous development of a whole range of reforming catalysts has been realized by IIP-ACC. As a result, IIP, along with ACC are now in a position to offer mono- and bi-metallic reforming catalysts for commercial trials in existing reformers in India. If these trials are successful, then Indian catalysis will gain a real fillip.

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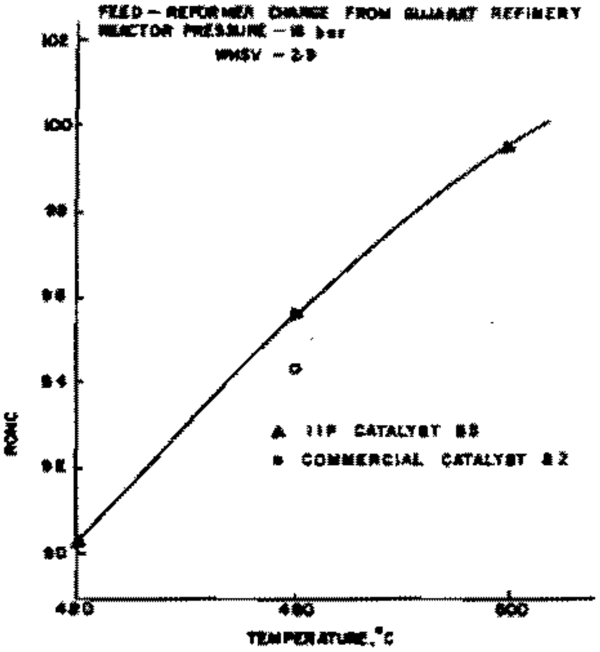

Fig. 16—Temperature response of IIP (B5) and commercial (B2) Pt-Re catalyst

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