Design of catalysts for pour-point reduction of lube oil fractions

S. Sivasanker

National Chemical laboratory, Pune - 411 008.

Abstract

The discovery of new micro-porous materials has resulted in interesting applications in petroleum refining in recent times. An example is the use of molecular sieve based catalysts for pour-point (pp) reduction of petroleum oils used for lubricating oil production. Two different catalytic processes are available for the reduction of pp of petroleum oils. These are based on shape selective cracking of the n-paraffins and wax-isomerization. The requirements of the micro-porous materials for the two catalysts are different; these are discussed. The optimization of the catalyst parameters to design good catalysts for the two processes is described.

Keywords: Dewaxing; shape-selective cracking; wax isomerization; lube oil base stocks; petroleum refining; zeolites

1. Introduction

Lubricating oil base stocks (LOBS) are manufactured from heavy petroleum (atmospheric and vacuum gas oil) fractions through a number of steps. First of all, the fraction that is suitable for producing the desired lube oil with the required viscosity is cut through fractional distillation. The various hydrocarbon components present in these fractions and their properties are presented in Table 1 [1]. The hydrocarbon components (aromatics, heterocyclics and waxes - long chain alkanes) that are not suitable for LOBS manufacture are removed from the lube cuts by 1) dearomatization to remove aromatics and most of the N and S compounds, 2) dewaxing to decrease the pour point and 3) hydrofinishing to improve stability and colour. The dearomatization is usually done by extraction with a solvent such as N-methyl 2-pyrrolidone (or sometimes by deep hydrogenation).

The oldest dewaxing process is solvent extraction, which consists of dissolving the oil in a solvent and the subsequent cooling of the solution to crystallize the wax which is separated by filtration. The oil is recovered from the solvent by distillation. The overall process is energy intensive, besides loss of LOBS can occur due to entrapment of oil by the wax.

In recent times, catalytic dewaxing developed by Mobil (and BP) in which the wax molecules are selectively cracked over shape selective zeolite catalysts has become popular. The Mobil process [2] is popular due to higher yields and wider range of feeds that can be handled. In catalytic dewaxing, the long chain alkanes (waxes possessing high melting points), which are narrow molecules (4.1Å dia), are selectivity cracked inside the pores (~5.5Å dia) of ZSM-5; the larger branched alkanes (which possess lower pour points) and the naphthenic molecules (which posses good lubricity) are not cracked. As oil loss due to entrapment in wax is not possible, the LOBS yields are larger. Also, due to the near total removal of the waxes, lower pour oils can be obtained (compared to solvent dewaxing). Other advantages of catalytic dewaxing are lower investment and operational costs. However, catalytically dewaxed oil is often slightly lower in VI than the solvent dewaxed oil.

The major limitation of the solvent and catalytic (shape-selective) dewaxing processes is the loss of yield due to the removal of the wax molecules. Chervon has commercialized a dewaxing process called 'isodewaxing' in which the wax molecules are isomerized into low pour iso-paraffins without cracking them [3]. A typical example of how the melting point of a long chain paraffin (wax) decreases dramatically on isomerization is shown in Table 2. It is also seen from the table that the VI decrease is not as marked [4]. The benefits of this process are higher LOBS yields, lower pour points than possible in solvent dewaxing and higher VI of the product. This process uses Pt/SAPO-11 as the catalyst [3] and is suitable for feeds low in S and N such as hydrocracked oils and hydrogen refined oils and waxes.

Table 1. Properties of lube base oil components [1]

Compound type	Viscosity	Viscosity Index (VI)	Pour Point	Stability	Value as lube component
n-paraffins (wax)	Low	High	High	High	Very low
Iso-paraffins	Medium	High/ Medium	Medium	Medium	High/ Medium
Alicyclics (naphthenes)	High	Low	Medium/ low	Medium/ low	Low/ medium
Aromatics	High	Low	Low	Low	Very low

Table 2. Isomerization of a long chain hydrocarbon (wax) decreases its melting point [4].

Formula	Structure	Melting point (K)	Viscosity Index
n-$C_{26}H_{54}$	Long chain, no branching	+331	~150
$C_{26}H_{54}$	C_{10}-C-C_{10} [C-C-C-C-C]	+292	125
$C_{26}H_{54}$	C_{10}-C -C_{10} [C_2-C-C_2]	-233	119

Table 3. Comparison of dewaxing processes .

	Solvent	Catalytic dewaxing	Isodewaxing
Wax removal	Physical	Shape selective cracking of wax	Wax isomerization
Min. P.P. of DWO (^{K})	258	223	223
VI of DWO	Base	Lower than base	Higher than base
DWO yield	Base	Generally about same	Generally higher
Main byproducts	Wax	Gas, naphtha	Mostly middle distillates

Table 4. Important catalyst characteristics for the two dewaxing processes

Properties	Catalytic dewaxing	Wax-isomerization
Acidity	Strong	Moderate to weak
Pore-characteristics	Right dimensions for reactant shape selectivity – for n-paraffins	Right pore-separation at surface of crystallite
Cracking activity	Very high to crack n-paraffins	Not desired
Catalysis at surface	Not desired	Pore-mouth catalysis
Al (Si) content	Large (Al) content for high activity	Large (Si) content – uniform distribution
Crystallite size	Small for less diffusion effects	Size may not be critical

A comparison of the three processes used for pour point reduction is presented in Table 3. The two processes, shape-selective cracking and wax isomerization are based on catalysts containing molecular sieves as their active component.   However, the properties of the molecular sieves required for the two processes are different (Table 4). A brief description of the optimization of the catalyst properties to prepare good catalysts for the two processes is presented in this paper.

2. Experimental

ZSM-5 samples with different SiO_2/Al_2O_3 ratios (Al-contents) and crystallite sizes were prepared following established procedures [5]. The SAPO-11 samples were prepared both by a published method [6] and by new improved synthesis procedures [7,8].   All the synthesized samples were converted into the H-form and loaded with the metals by known procedures. The reactions were carried out in a commercial high-pressure reactor (220 ml volume) supplied by Geomécanique, France. The product samples were analyzed by a variety of techniques used in characterizing petroleum fractions including GC methods.

3.   Results and discussion

3.1 Pour point reduction by shape-selective cracking

The process is based on the selective cracking of the n-paraffin molecules present in the feed (reactant shape selectivity). The two primary considerations for the choice of the zeolite are i) reactant shape-selective properties for the conversion of the desired molecules (n-paraffins), ii) high cracking activity for n-paraffins and iii) low coke deposition rate.   An examination of the properties of all the available zeolites reveals that ZSM-5 (MFI) possesses all the required characteristics.   Besides, the material possesses a low H-transfer activity

producing soft-coke (large H/C ratio) making it easy to reactivate by flushing with H_2 at high temperatures.   Also, its high thermal stability permits repeated coke-burn off in O_2 permitting a long overall life.

In order to obtain a good catalyst, the properties of the zeolite component need to be optimized.   Two important characteristics are SiO_2/Al_2O_3 ratio (Al-content) and crystallite size. Zeolites are acid catalysts and owe their acidity to the H^+ ions present to compensate the negative charge created due to the presence of Al^{3+} ions in the silicate lattice. As a result, the number of acid sites present (and acid-catalytic activity) is a function of the Al^{3+} content of the zeolite.   The results of dewaxing a heavy neutral raffinate over Ni/H-ZSM-5 with SiO_2/Al_2O_3 ratios of 32, 84 and 347 are presented in Table 5. The shape selective cracking activities of the catalysts are reported in terms of the pour point (pp) of the product, the lower the pp, the greater the selective removal of the waxy components   (n-paraffins).   As expected, the catalyst with the highest SiO_2/Al_2O_3 ratio (lowest Al-content) is the least active (pp = 279 K).   It also deactivates faster, necessitating an increase in temperature of 75 K in 33h to maintain the same pp. The catalysts with SiO_2/Al_2O_3 ratio of 32 and 84 have higher activities and lower deactivation rates.   As the performance of both the catalysts are similar, it appears that, beyond a certain limit, higher Al-contents do not further improve dewaxing rates presumably due to diffusion limitations.

The pore dimensions of ZSM-5 (0.54 – 0.57 nm) are just adequate for the entry of the normal and slightly branched paraffins. However, in the case of heavy feedstocks (C_{20} – C_{60}), such as those used in the dewaxing of lube base stocks, the diffusion of even n-paraffins is expected to become rate limiting. Therefore, smaller crystallites with shorter diffusion paths should be more active than larger crystallites in the dewaxing reaction.   The results of the studies carried out on the influence of

crystallite size on the reaction are presented in Table 6. To obtain a dewaxed product of nearly the same pour point (263 ± 2 K), the smaller crystallites (0.1 µm) are able to operate at 28 K lower temperature than the larger crystallites (5 µm). Another disadvantage of larger crystallites is that, due to the higher temperatures of operation and longer residence of the cracked products inside the pores, the yield of light gases arising by secondary cracking reactions tend to be higher. For example, the temperatures required to dewax an inter neutral feed (pp = 321 K) to a pp of 263 K were 619 and 602 K when the crystallites were 5 and 0.5 µm in size, respectively and the $C_1 – C_4$ gas yield over the two catalysts were 14.2 and 10.1 wt %, respectively. Small crystallites, however, expose a larger external surface area and are less shape-selective than large crystallites. They also

catalyze the cracking unwanted cracking (of branched paraffins and cyclic alkanes) causing lower yield of the dewaxed oil (DWO) and also lowering the viscosity index of the product.   Therefore the external surface needs to be passivated with silicious materials to increase DWO yield and VI.

It is possible to synthesize ZSM-5 with either Al^{3+} or Fe^{3+} in the lattice, the Al-ions produce a more acidic catalyst than the Fe-ions.   The effect of isomorphous substitution of ZSM-5 on acid strength of the zeolite and dewaxing activity are presented in Table 7.   The Fe-isomorph desorbs NH_3 earlier (628 K) than the Al-analogue (698 K) and is less acidic. It is seen from Table 7 that the more acidic Al-isomorph is more active; it dewaxes the gas oil to the same pp at a lower temperature (623 K) than the Fe-isomorph (641 K).

Table 5. Influence of SiO_2/Al_2O_3 ratio

SiO_2/Al_2O_3 ratio	Crystallite size (μm)	Time On Stream (h)	ReactionTemp. (K)	pp (K)
32	~ 0.5µm	76	563	265
32	~ 0.5µm	208	573	271
84	~ 0.5µm	76	562	266
84	~ 0.5µm	208	569	271
347	~ 0.5µm	13	596	279
347	~ 0.5µm	46	671	279

Feed: Heavy neutral; catalyst: Ni-ZSM-5; press: 3.0 MPa; WHSV (h^{-1}): 0.8; H_2/Oil (v/v): 400.

Table 6. Influence of zeolite crystallite size on catalytic activity

Crystallite size (μm)	Reaction Temp. (K)	Product yield(wt %)		Wt % DWO	DWO pp (K)
		C_1-C_4	$C_5 – IBP$		
5.0	619	14.2	13.8	72.0	263
1.0	602	10.1	15.9	74.0	264
0.1	593	9.7	15.8	74.5	261

Feed: Inter neutral; conditions same as Table 5.

Table 7. Influence of acid strength on dewaxing activity of MFI

Zeolite	TPD of NH_3; peak max. (K)	Reaction Temp. (K)	pp of DWO (K)	C_5+ (wt%)
ZSM-5 (Al)	698	623	263	70.6
ZSM-5 (Fe)	628	641	264	77.5

Feed: Atm. GO; catalyst: Pt-H-ZSM-5; press: 50 MPa; WHSV (h^{-1}): 2; H_2/Oil (v/v): 300

Table 8. Influence of metal component on hydrodewaxing

Catalyst / metal	Dewaxing Temp. (K)	Catalyst / metal	Dewaxing Temp. (K)
H-ZSM-5	295	H-ZSM-5 / Pd	310
H-ZSM-5 / Ni	298	H-ZSM-5 / Pd-Zn	315

Feed: Heavy neutral; press: 3 MPa; WHSV (h^{-1}): 0.65; H_2/Oil: (v/v): 400; DWO pp: 273 K

Table 9. Influence of feed paraffin content on DWO yield.

Feed	n-paraffin content (wt %)	DWO pp (K)	Δpp (K)	DWO yield (wt %)
Spindle (SP)	16	263	27	72.5
Light neutral (LN)	12	263	46	75.0
Inter neutral (IN)	8	267	54	79.0
Heavy neutral (HN)	4	273	58	83.3
Bright stock (BS)	-	273	60	86.9

The addition of a metallic component to a cracking catalyst often enhances its activity, reduces deactivation and improves its regenerability. The influence of three different metallic components on the performance of ZSM-5 in the dewaxing of a heavy neutral feed are presented in Table 8. It is noticed that for the highly S-rich (1.1 wt %) feed used, Pd based catalysts are less active than the Ni-catalyst. Even though the Ni-catalyst possesses nearly the same activity as metal free ZSM-5, the presence of Ni enhances catalyst life and improves the regenerability of the catalyst in H_2 and O_2.

Five different feeds were dewaxed with a Ni-ZSM-5 catalyst. The results of the studies are presented in Table 9. The temperature and space velocity were varied to obtain the desired pp for the different LOBS. It is noticed that the pour point reduction (Δpp) and product yield depend on the n-paraffin content of the parent feed.

3.2. Pour point reduction by isomerization

The desired characteristics of the molecular sieve to be used in the isomerization catalysts are: 1) high isomerization activity with low cracking activity, 2) large amount of acid sites with uniform distribution of acidity and 3) pore-mouth activity. Among the various zeolites and molecular sieves available, SAPO-11 has been found to possess the above characteristics to a good measure.

Acid centres are created in silicoaluminophosphate (SAPO) molecular sieves when a Si^{4+} ion replaces a P^{5+} ion in the framework of the parent aluminophosphate (AlPO$_4$) generating a negative charge, and the negative charge is balanced by a H^+ ion. It is also possible that a number of Si^{4+} ions replace many Al^{3+} and P^{5+} ions in a group forming a SiO_2 island. Such SiO_2 islands are expected to result in less number of acid centres (per Si^{4+}) than the isolated Si^{4+} ions [9]. Besides SiO_2 islands, SiO_2-Al_2O_3 patches with very strong acidity may also result. Thus, when Si incorporation is not uniform, a material with lower number of acid sites and containing a broad distribution of both weak and strong acid sites might result. Our studies on different SAPOs confirmed these ideas and novel synthetic methods were developed that could produce a better distribution of Si^{4+} in SAPO frameworks resulting in more uniform acidity distribution and greater activity and selectivity in isomerization reactions [7,8].

Two SAPO-11 samples (a) and (na) were prepared using, respectively, the conventional published procedure [6] and by an improved method [7]. The XRD patterns of the two samples were similar. The ^{27}Al MAS NMR spectra of the samples were also similar consisting of a single line

around δ = ~ 38 ppm due to Al^{3+} ions in T_d sites in the framework. There were, however, marked differences in the ^{29}Si MAS NMR spectra of the two samples. The NMR chemical shift of the isolated Si ions [Si(4Al)] is around δ = -90 to –95 ppm, while it is around –105 to –110 ppm for the Si ions in SiO_2 islands. In general, due to the large number of Si species possible in the SAPOs, in most cases, two broad features corresponding to the isolated and island type Si species are noticed. The ^{29}Si MAS NMR spectra of the two SAPO-11 samples are presented in Figure 1. It is noticed that the signal due to isolated Si species is more prominent than the one due to Si islands in the case of SAPO-11 (na) and is vice versa for SAPO-11 (a).

The compositions of the two samples [$(Al_{0.59}P_{0.32}Si_{0.07})O_2$ for SAPO-11(na) and $(Al_{0.57}P_{0.38}Si_{0.5})O_2$ for SAPO-11(a)] reveal that there is a greater substitution of P^{5+} by Si^{4+} in SAPO-11 (na) than in SAPO-11(a). This provides additional evidence for the presence of more isolated Si species in SAPO-11(na). The TPD of pyridine adsorbed over these samples revealed that SAPO-11(na) possesses a larger number of acid centres than SAPO-11(a) [7]. Not only does it possess more weak acid sites (pyridine desorbing < 300^oC), it also possesses more moderate acid sites (pyridine desorbing > 300^oC). This confirms that the Si ions are better dispersed in the framework in SAPO-11(na).

Table 10. Studies on pour point reduction of a hydrocracker bottoms feed for LOBS production[a]: Characteristics of feed and product fractions[b].

	Feed	Product fractions	
		643 – 673 K	673 – 713 K
Density @ 288 K (g/cc)	0.8321	0.8298	0.8312
Viscosity @ 373 K (cst)	3.53	2.45	3.31
Viscosity Index	-	107	112
Pour point (K)	300	249	261
S (ppm)	<50	-	-
N (ppm)	<20	-	-
Sim. Dist. (D-2887)			
IBP ((K)	483	515	587
50% (K)	685	650	680
95% (K)	760	695	722

Catalyst: Pt-SAPO-11; Press: 100Mpa; Temp (K): 613; WHSV (h^{-1}): 1.0; H_2/Oil (v/v): 400; [a]: experiments done by CPCL R & D; [b]: Feed provided by CPCL, analysis done by CPCL.

A comparison of the performance of the catalyst prepared by the improved (optimized) method is presented in Fig. 2. It is noticed that the improved SAPO-11 has a higher conversion besides a larger I/C ratio even at high conversions. Studies over model hydrocarbons such as n-hexane and n-hexadecane were carried out to optimize the Pt loading of the catalyst. The results revealed that a Pt loading of about 0.5% is most suited for maximum isomerization selectivity.

The pour point reduction of a LOBS feedstock (hydrocracker bottoms) through isomerization of the waxy component was investigated over Pt(0.5%)-SAPO-11, with good distribution of Si^{4+} ions, prepared by the improved method. The pp of the feed was 300 K. The characteristics of the feed and two product fractions are presented in Table 10. It is seen that a significant decrease in product pp is achieved over the SAPO-11 catalyst. The yield of the dewaxed oil was >90% and the VI of the fractions was ~110.
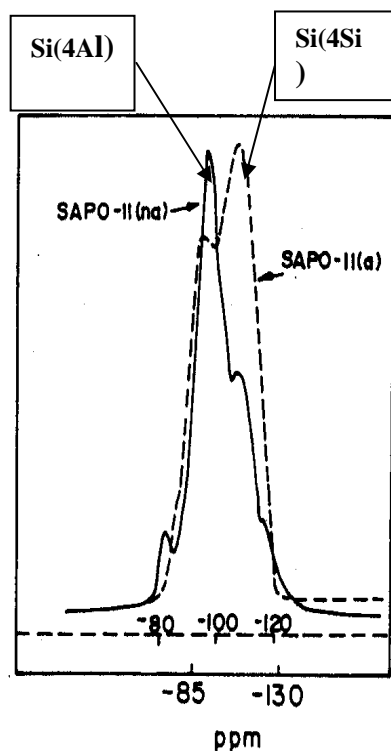
Fig.1. ^{29}Si – MAS NMR spectra of SAPO-11 samples synthesized by different methods; SAPO-11 (a), conventional method; SAPO-11 (na), improved method.
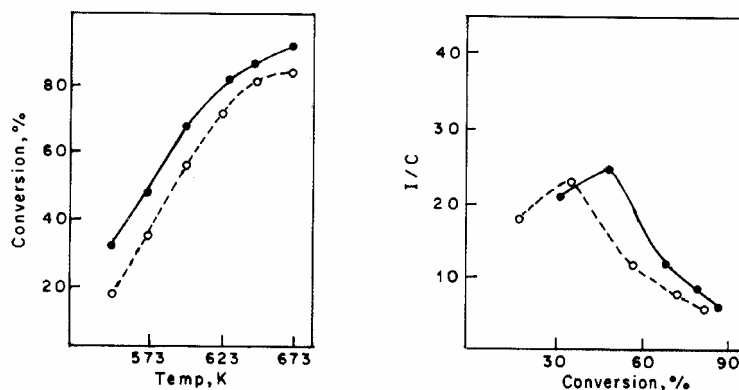
Fig.2. Influence of preparation method on the performance of SAPO-11 in the transformation of n-hexane (-------, Conventional preparation procedure; ——, improved preparation procedure)

4. Conclusions

Pour point reduction of lube oil base stocks can be typically carried out by two catalytic processes, one based on shape-selective cracking and another based on wax isomerization. The design of the catalysts for the two processes are different based on the nature of the reaction considerations.

References

1. Sequeira, A. Jr., "Lubricating Base Oil and Wax Processing", Marcel Dekker Inc., New York (1994).
2. Smith, K.W., Starr, W.C., Chen, N.Y., Oil and Gas Journal, May 26, p.75 (1980).
3. Miller, S.J., Microporous Materials, 2, 439 (1994).
4. Le Page, J-F, "Applied Heterogeneous Catalysis", Editions Technip, Paris (1987).
5. Kulkarni, S.B., Shiralkar, V.P., Kotasthane, A.N., Borade, R.B., Ratnasamy, P., Zeolites, 2, 313 (1982).
6. Lok, B.M., Messina, C.A., Patton, R.L., Gajek, R.T., Cannon, T.R., Flanigen, E.M., U.S. Patent 4,40,871 (1984).
7. Sinha, A.K., Sivasanker, S., Ratnasamy, P., Ind. Eng. Chem. Res., 37, 2208 (1998).
8. Sinha, A.K., Sainkar, S.S., Sivasanker, S., Micropor. Mesopor. Mater. 31, 321 (1999).
9. Barthomeuf, D, Zeolites, 14, 394 (1994).