Characterization and catalytic activity of Ni-W/SiO₂-Al₂O₃ hydrocracking catalysts

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Characterization of Ni-W/SiO₂-Al₂O₃ catalysts was carried out by microcalorimetry, TPR and oxygen chemisorption. The effect of incorporation of individual metals and their sequence of addition to the support on the properties and catalytic activity for cyclohexene hydrogenation and cumene cracking was investigated. While the addition of nickel to SiO₂-Al₂O₃ has little effect on the acidity, tungsten has generated some new strong acid sites, which do not seem to have beneficial effect for cumene cracking. Low temperature TPR peak in the bimetallic catalysts falls around 760 K due to Ni-W species while the high temperature peak around 1115-1223K corresponds to W species. W/SiO₂-Al₂O₃ has a lower oxygen chemisorption than its nickel counterpart but has a higher hydrogenation rate. Tungsten is the active metal for hydrogenation. W-Ni/SiO₂-Al₂O₃ catalyst has better hydrogenation and cracking activity.

Hydroprocessing is used to upgrade fuel quality in the petroleum refining industry. The principal applications of hydroprocessing includes not only the conventional hydrotreating to remove undesirable sulphur, nitrogen and oxygen compounds from petroleum and coal-derived oils but also for more versatile processes like hydrocracking which converts high boiling refractory petroleum fractions to low boiling value-added middle distillates like kerosene, jet fuel and gas oil. Hydrocracking involves the cleavage of C-C bonds of hydrocarbons in the presence of acid sites provided by the support of the catalyst and the hydrogenation of the cracked products on the metal sites in presence of hydrogen. The major advantage of hydrocracking over catalytic cracking (FCC) is that the former produces a wide spectrum of products of high fuel quality and stability. It appears that the main components of heavy oil fraction, i.e. the polycyclic aromatics, undergo hydrogenation/ring opening in the presence of a catalyst and the hydrogenation of the cracked products on the metal sites in presence of hydrogen. The condensation and dehydrogenation reactions lead to coke formation. Cracked products give more branched paraffins than linear ones. Olefins are formed as intermediates during the conversion of saturated hydrocarbons over bifunctional catalysts in presence of H₂ as in catalytic reforming, hydrocracking and hydroisomerization.

The catalysts used in commercial applications are traditionally base metal oxides of Group VI (MoO₃, WO₃) with a promoter of non-noble Group VIII metals like Co or Ni supported on less acidic alumina for conventional hydrotreating, HDS, HDN, HDO and on a strongly acidic support like silica-alumina and zeolite for hydrocracking. Generally, amorphous silica-alumina catalysts are preferred where the aims is to maximize the middle distillates, and zeolite based catalysts are used for processes desiring gasoline production also. The main functions of a hydrocracking catalyst are hydrogenation, isomerization and cracking. The principal role of metals in a hydrocracking catalyst is to keep the acid sites active through the hydrogenation of coke precursors. With proper balance and optimization of metal/acid functions, improvement in the catalyst and process can be achieved.

Low temperature oxygen chemisorption (LTOC), temperature programmed reduction (TPR) and the acidity and acid strength distribution of Ni, W and Ni-W catalysts supported on SiO₂-Al₂O₃ has been studied and these properties have been correlated with the catalytic activity for cyclohexene hydrogenation and cumene cracking.

Experimental Procedure

Catalysts

Sample-A was a commercial SiO₂-Al₂O₃ (S_{BET} 300 m²/g). W/SiO₂-Al₂O₃-B and Ni/SiO₂-Al₂O₃-C were...
prepared by impregnation of ammonium paratungstate (APT) (NH₄)₁₀W₁₂O₄₂H₂ 5H₂O and Ni(NO₃)₂ 6H₂O respectively on SiO₂-Al₂O₃-A and contained 19 wt% W and 6 wt% Ni respectively. Hydrogen peroxide was used for the dissolution of APT. The catalysts were dried at 383K for 16 h and finally activated in air at 773K for 6 h. Ni-W/SiO₂-Al₂O₃-D and W-Ni/SiO₂-Al₂O₃-E were obtained on subsequent impregnation of 6 wt% Ni and 19 wt% W on samples B and C respectively. Sample F was a commercial Harshaw Ni-W/SiO₂-Al₂O₃ catalyst.

**Physico-chemical properties of catalyst**

TPR – The TPR technique was used to study the reduction behaviour of various catalysts. The consumption of H₂ during reduction was measured as a function of temperature. The catalyst about 0.5g was dried in argon at 50 mL min⁻¹ at 673 K for 2h prior to reduction. A 10% (v/v) H₂ in N₂ at a flow rate of 25 mL min⁻¹ was used as reducing mixture. The temperature of reduction and the consumption of H₂ was continuously monitored with a temperature programmer and a TCD cell.

Oxygen chemisorption – Low temperature oxygen chemisorption (LTOC) was studied under dynamic conditions with a pulse chemisorption unit (Pulse chemisorb 2700, Micromeritics, USA). The catalyst (~1g) was pretreated at 673K for 1h in the flow of helium and was then sulphided with 10% H₂S/H₂ at 673 K for 1h. After sulphidation, the catalyst was heated in H₂ at 723K for 3 h followed by heating in helium for 1h to remove the physically adsorbed H₂S or H₂. The sulphidation was carried out externally to avoid corrosion of H₂S to the copper plumbing of the unit. A special pyrex glass cell was designed for this purpose which could be connected to the chemisorption unit or to the external supply of gases H₂S/H₂ with a three way stopcock.

Oxygen chemisorption was studied at 273 K (ice bath). Pulses of oxygen were given to the catalyst with the flow of carrier gas helium till the areas of two consecutive peaks were the same and surface was saturated with monolayer coverage. Oxygen chemisorbed was then calculated.

Surface acidity and acid strength distribution – Surface acidity and acid strength distribution were measured through heats of adsorption of ammonia using a Tian-Calvet heat flux microcalorimeter (C-80, Setaram, France) connected to a glass vacuum volumetric adsorption unit for catalyst pretreatment and probe gas delivery. A Validyne low pressure transducer (USA) has been attached to the vacuum system for precision pressure measurements below 1 torr. The catalyst sample (0.1-0.2 g) was outgassed under high vacuum (10⁻⁵ torr) at 723 K for 4 h and adsorption of ammonia was conducted at 448 K to exclude physisorption.

Differential heats of ammonia adsorption versus adsorbate coverage were obtained by measuring the heats evolved from sequential doses of small quantities of ammonia (µmol) on to the catalyst until the surface is saturated. The heat of adsorption generated for each dose was calculated from the resulting thermograms and the amount of ammonia adsorbed from the initial and final pressures. The differential heat curves i.e. the differential heats of NH₃ adsorption as a function of surface coverage provide information about the concentration and strength of acid sites on the catalyst surface.

Catalytic activity – Cumene cracking and cyclohexene hydrogenation were studied as test reactions for catalytic activity. The catalyst testing was carried out in a continuous plug flow bench top glass micro-reactor operating at 673K and atmospheric pressure and interfaced to a gas chromatograph. The catalyst sample (~0.2 g) placed between quartz wool in the glass reactor was sulphided at 673 K for 2h using CS₂ and H₂ saturated vapours at 298 K. After sulphidation the feed cumene or cyclohexene vapours were introduced to the catalyst bed from a pre-saturator held at 298 K in the stream of H₂ gas. The flow rate of the feed and the particle size of the catalyst (0.4-0.5 mm) were so chosen that there were no external or internal diffusion effects. The rate was calculated from the equation \( r = \frac{x}{F} \) where \( r \) is rate, mol h⁻¹ g⁻¹ catalyst; \( x \) is the fractional conversion, \( w \) is the weight of the catalyst in g and \( F \) is the flow rate of gas, mol h⁻¹. The products of cumene cracking and cyclohexene hydrogenation were analyzed by gas chromatography with a 2 m stainless steel column packed with 10% OV-17.

**Results and Discussion**

**Reducibility**

Reduction of pure WO₃ (prepared from APT) has been investigated by Ogata et al.⁹ to study the effect of various oxidation states of W on hydrocracking of n-heptane. Massoth and Bidlack¹⁰ have found that sulphidation of WO₃ is thermodynamically more favourable (Δ\( F^* \)-30.5 kcal) than reduction (Δ\( F^* \)+6.5 kcal).
The reduction of supported WO$_3$ is more difficult than unsupported WO$_3$. The extent of reduction was found to increase with metal loadings. TPR and Raman spectroscopic studies revealed two species, surface tungstate and crystalline WO$_3$ on WO$_3$/SiO$_2$. It is the surface tungstate which is active for catalytic reaction. Relative proportions of two phases depend upon the metal loadings, at about 20% W loading, 50% crystalline and 50% surface tungstate species exist.

The TPR profiles of catalysts are shown in Fig. 1. W/SiO$_2$-Al$_2$O$_3$-B has shown a shoulder at 848K due to the reduction of a small amount of WO$_3$ to WO$_2$ and a sharp peak at 1214K indicating complete reduction of oxide to W species. In Ni/SiO$_2$-Al$_2$O$_3$-C, the reduction starts around 623K with maximum reduction rate around 760K and the reduction seems to be completed around 973K. In Ni-W/SiO$_2$-Al$_2$O$_3$-D, the catalyst in which first W and then Ni was impregnated has shown sharp peak at 760K due to the presence of easily reducible predominantly NiO species together with tungsten, reduction of which has been facilitated by nickel moieties. Another peak at 860 K is due to the reduction of Ni-W bimetallic species. The broad peak at 1115-1223K region indicate reduction of tungsten oxide species to tungsten metal. On the other hand, W-Ni/SiO$_2$-Al$_2$O$_3$-E, the catalyst in which W is on the top has shown a shoulder at 735K due to W dominant Ni species and a peak at 865 K due to bimetallic Ni-W species. A broad peak around 1197K indicate reduction of WO$_2$ to W. The commercial Ni-W/SiO$_2$-Al$_2$O$_3$-F has shown a low temperature peak at 773K due to Ni-WO$_2$ species and a peak at 1215K corresponding to complete reduction of tungsten dioxide to W metal.

Although the TPR profiles presented here give only a semi quantitative information of the reducibility of metal oxides, yet these indicate clearly the formation of active species during reduction. In bimetallic systems consumption of H$_2$ by individual metals cannot be accurately assessed because of the strong interactions between the metallic species in the catalyst. The catalyst-B which contains W only has a total H$_2$ consumption of 9.72 a.u., the major portion of which correspond to the reduction of oxide to W at 1214K. The shoulder at 848K indicate the reduction of a little portion of WO$_3$ to WO$_2$ which is quite likely as in the absence of nickel, the reduction of WO$_3$ is difficult.
Table 1 - Physico-chemical properties and catalytic activities of Ni-W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Total acidity (mmol NH\textsubscript{3}/g cat.)</th>
<th>Acid strength distribution* (mmol NH\textsubscript{3}/g cat.)</th>
<th>Oxygen chemisorption at 273K mL STP/g cat.</th>
<th>Cyclohexene hydrogenation rate x 10\textsuperscript{2} mol h\textsuperscript{-1} g\textsuperscript{-1}</th>
<th>Cumene cracking rate x 10\textsuperscript{2} mol h\textsuperscript{-1} g\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-A</td>
<td>0.63</td>
<td>0.32 0.23 0.08</td>
<td>0</td>
<td>14.32</td>
<td>10.7</td>
</tr>
<tr>
<td>W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-B</td>
<td>0.73</td>
<td>0.37 0.24 0.12</td>
<td>0.60</td>
<td>8.24</td>
<td>7.72</td>
</tr>
<tr>
<td>Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-C</td>
<td>0.65</td>
<td>0.34 0.19 0.12</td>
<td>1.82</td>
<td>2.5</td>
<td>6.39</td>
</tr>
<tr>
<td>Ni-W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-D</td>
<td>0.78</td>
<td>0.37 0.22 0.19</td>
<td>4.70</td>
<td>6.13</td>
<td>4.0</td>
</tr>
<tr>
<td>W-Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-E</td>
<td>0.90</td>
<td>0.40 0.34 0.16</td>
<td>2.25</td>
<td>9.48</td>
<td>6.21</td>
</tr>
<tr>
<td>Ni-W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-F</td>
<td>1.02</td>
<td>0.38 0.59 0.05</td>
<td>4.54</td>
<td>4.23</td>
<td>6.56</td>
</tr>
</tbody>
</table>

*Strong > 100kJ mol\textsuperscript{-1}, Medium 100-75 kJ mol\textsuperscript{-1}, Weak < 75 kJ mol\textsuperscript{-1}.

Fig. 2—Microcalorimetric curves of Ni-W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts

Moreover, nickel facilitates the reduction of WO\textsubscript{3} to WO\textsubscript{2}. The H\textsubscript{2} consumption in Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-C is 8.05 a.u while Ni-W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-D has 20.77 a.u which is higher than the total H\textsubscript{2} consumption of sample B (tungsten only) and C (nickel only) together. This suggests that H\textsubscript{2} consumption is not a simple addition as would have been in the case of physical mixtures of W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-B and Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-C catalysts, but an indicative of bimetallic interactions between Ni and W species. In sample W-Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-E a lower value of H\textsubscript{2} consumption 15.96 a.u was observed than sample D (20.77 a.u), because in the latter the nickel on the top is facilitating the reduction. On the other hand sample F has shown almost the same value (19.48 a.u) of H\textsubscript{2} consumption as in D.

Oxygen chemisorption — The commercial hydro-treating/hydrocracking catalysts contain high metal loading, above 15 wt%, where the active components are not only confined to surface monolayer, but also exist in the form of lumps, interrupted monolayer or in the sub surface layer of support inaccessible to oxygen adsorbate. Chemisorption is purely a surface phenomenon confined to monolayer only, but due to the presence of fairly large concentrations of bulk metal oxides, bulk phase oxidation can also take place. On the reduced/sulphided catalyst, the chemisorption of O\textsubscript{2} is a rapid process followed by slow oxidation which require diffusion of adsorbate molecule from surface to the bulk. Choice of pretreatment conditions and the temperature of adsorption are extremely important to get reliable values of oxygen chemisorption without any significant bulk phase oxidation. Low temperature oxygen chemisorption (LTOC) has been extensively used for the determination of metal area of hydrotreating catalysts. Both static and dynamic methods for Mo at 298K\textsuperscript{13-15} and for WS\textsubscript{2} at 195K\textsuperscript{16} have been reported. Bodrero and Bartholomew\textsuperscript{13} have found that O\textsubscript{2} uptakes under dynamic conditions at 298 K are in excellent agreement with static adsorption at 195K. Oxygen chemisorption is thus dependent on the temperature of adsorption\textsuperscript{15,17}. The preliminary investigations on Ni W/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} under dynamic mode indicate good precision of O\textsubscript{2} chemisorption at 273K rather than at ambient temperature where the scattering is greater. Moreover, at room temperature, the O\textsubscript{2} contribution to bulk oxidation is also possible.
Hydrotreating catalysts are used in sulphided form in industry. The catalyst after sulphidation essentially require a post sulphidation high temperature treatment (>673 K) in the flow of carrier gas or in vacuum\textsuperscript{15}. The anion vacancies which are probably the adsorption sites are to be created\textsuperscript{16}. It may be pointed out that \(H_2S\) is adsorbed at the same site as oxygen\textsuperscript{14,18} and quantitative removal of \(H_2S\) takes place above 673K\textsuperscript{19}.

The results of LTOC are displayed in Table 1. Ni/SiO\(_2\)-Al\(_2\)O\(_3\)-C has shown higher \(O_2\) uptake (1.82 mL STP/g) as compared to W/SiO\(_2\)-Al\(_2\)O\(_3\)-B (0.60 mL STP/g). Tungsten trioxide is reduced to \(WO_2\) only at around 773K and not to metallic tungsten. This tungsten (\(WO_3\)) dispersed on the support would contribute less towards LTOC as compared to nickel catalyst-C which is in the form of finely dispersed nickel species. Moreover, in tungsten borne catalyst with 19wt% loading, some metal could be in inaccessible locations as indicated earlier. The bimetallic catalyst with nickel on the top Ni-W/SiO\(_2\)-Al\(_2\)O\(_3\)-D has higher LTOC than the catalyst-E in which order of impregnation of metals was reversed. This is in accordance with the fact that in catalyst-D, nickel species are more abundantly available and located in easily accessible positions. Tungsten species in catalyst-E on the top, because of their inherent character of adsorbing less oxygen as seen in sample-B and probably the nickel species are covered under tungsten are the factors making a cumulative effect on the catalyst culminating to a low LTOC. Commercial catalyst-F has shown a comparable value with catalyst-D.

**Acidity and acid strength distribution**

The microcalorimetric curves of differential heats of adsorption versus amount of ammonia adsorbed for Ni-W/SiO\(_2\)-Al\(_2\)O\(_3\) catalysts are shown in Fig. 2. The ordinate represents the strength of acid sites (kJmol\(^{-1}\)) while the abscissa indicate the surface coverage by ammonia molecules i.e. the concentration of the acid sites (mmolg\(^{-1}\)). The parent SiO\(_2\)-Al\(_2\)O\(_3\)-A carrier has shown the presence of strong acid sites of sufficiently high strength (142 kJ mol\(^{-1}\)). The similar initial differential heat of \(NH_3\) adsorption on silica-alumina has been reported in literature\textsuperscript{20}. On incorporation of W or Ni and W in the support, not only the strength of strong acid sites has increased (~154-164 kJ mol\(^{-1}\)) but their concentration has also improved. The differential heats of adsorption versus surface coverage are stepwise curves indicating that the surface adsorption sites are energetically heterogeneous. These steps correspond to the clusters of acid sites of different strength\textsuperscript{21}. Based on the acid strength, the entire curve has been divided into three regions on a differential heat acidity scale; the strong corresponding to >100 kJ mol\(^{-1}\), medium from 100-75 kJ mol\(^{-1}\) and the weak acid sites <75 kJmol\(^{-1}\). The total acidity and acid strength data derived from Fig. 2. are displayed in Table 1. The SiO\(_2\)-Al\(_2\)O\(_3\)-A support has shown predominantly strong and medium strength acidity. Incorporation of nickel on SiO\(_2\)-Al\(_2\)O\(_3\) has not affected the acid strength distribution. On the other hand, addition of W to the carrier has not only increased the total acidity but also has increased the concentration of strong and medium acid sites (Catalyst-B). The Catalyst-E, where W is on the top has demonstrated an enhancement in the population of stronger sites and more pronoucnecelly the medium acid sites as compared to Catalyst-D where Ni is on the top. Tungsten trioxide is known to be acidic in nature and has therefore imparted additional acidity both to the support and the catalysts as evident from the acidity of Catalyst B and E. Catalyst-F has almost a comparable concentration of strong acid sites but has shown a considerable increase in the medium strength acidity.

**Catalytic activity**

The catalytic activity of various catalysts for the hydrogenation of cyclohexene and cumene cracking are shown in Table 1. The major product of the hydrogenation was cyclohexane with some methyl cyclopentene obtained due to occurrence of isomerization reaction also. Similar product distribution was also reported with sulphided Co(Ni) Mo/Al\(_2\)O\(_3\) catalysts by Ramirez et al.\textsuperscript{22}. In cumene cracking the major product was benzene with little propene.

A perusal of the data given in Table 1 indicate a high rate of cyclohexene conversion for the SiO\(_2\)-Al\(_2\)O\(_3\)-A support. This is attributed to the isomerization reaction to methyl cyclopentene occurring probably on Brönsted acid sites of medium and strong strength present on the support surface\textsuperscript{22}. W/SiO\(_2\)-Al\(_2\)O\(_3\)-B has demonstrated fairly good hydrogenation activity as the major product was cyclohexane. On the other hand Ni/SiO\(_2\)-Al\(_2\)O\(_3\)-C has shown a low rate of hydrogenation, despite of the fact that it has shown a high \(O_2\) chemisorption. Tungsten species have shown better hydrogenation activity than nickel. The dispersion of tungsten (\(WO_3\)) as reflected from LTOC is
low as compared to nickel. Nevertheless, these tungsten sites are good enough to provide an effective hydrogenation function. It is well established that W ions in WS₂ crystal are the active sites for hydrogenation. The accepted views reveal that the active sites for hydrogenation reside at the edge planes of MoS₂ or WS₂ and the generation of active sites is the result of some configurations of Mo or W ions and sulphur vacancies creating some coordinatively unsaturated sites (CUS) or anion vacancies for the adsorption of the feed molecules. Hydrogenation over Ni₅S₂ has been reported much slower than over either WS₂ or Ni-W-S²⁻.

Oxygen adsorbs selectively on edge or corner sites. The distribution of sites on edge, corner and basal planes affect the adsorption site density which in turn depends upon the preparation procedure of the catalyst. The hydrogenation activity is controlled by the dispersion of tungsten and the dispersion of nickel is not the key structural factor controlling the hydrogenation activity. Promoter action of nickel could be due to a large density of nickel atoms in the edge positions of WS₂ and consequently facilitating the reduction of W species by an electronic transfer from Ni to W.

The Ni-W/SiO₂-Al₂O₃-D has high LTOC than catalyst W-Ni/SiO₂-Al₂O₃-E. The TPR profiles (Fig. 1) indicate a sharp low temperature peak at 760K indicating an easy reduction of predominantly nickel species with some W species the reduction of which has been facilitated by nickel. This could result in high dispersion of Ni species attributing high LTOC. But the hydrogenation activity is less probably due to scanty availability of active W species. On the other hand in catalyst-E, the reduction is difficult due to SMSI of W-dominated nickel species appeared as a small peak at 735K and have shown a low value of LTOC but fairly high hydrogenation activity.

The SiO₂-Al₂O₃-A carrier has shown reasonably good cracking activity for cumene conversion. This is due to the presence of sufficiently strong acid sites catalyzing the cracking reaction. On incorporation of W as in Catalyst-B, the cracking activity has decreased. It is interesting to note that although addition of W (WO₃) has enhanced the concentration of strong acid sites, this has not reflected in the corresponding increase in cracking activity. Cracking is known to proceed via a carbenium ion produced by the interaction of Brönsted acid sites. The acidity in the catalyst is due to hydroxyl groups associated with the support and it appears that by and large the cracking of cumene to benzene is due to this acidity. Incorporation of WO₃ to silica-alumina has created some additional acidity, probably the Brönsted type due to hydroxy groups associated with tungsten ions. It seems that this acidity has little influence on cracking reaction. It has also been reported that the hydroxyl groups associated with W are unstable and could be eliminated easily in H₂ atmosphere thus not contributing to cracking. Boorman et al. based on pyridine absorption i.r. bands on Co(Ni) Mo/Al₂O₃ have distinguished two different types of PyH⁺ bands, one ascribed to Brönsted sites on alumina and other to hydroxyl groups on Mo. Alumina hydroxyl groups are replaced by Mo species during preparation. But the acidity of the remaining alumina hydroxyls is increased by the influence of Mo species if these hydroxyls reside on the Mo itself but located at the chain terminating Mo atoms.

The cumene cracking activity is higher in catalyst W-Ni/SiO₂-Al₂O₃-E as compared to catalyst-D because of the higher number of strong acid sites in the former. The commercial Catalyst-F with strong acidity almost same to catalyst D and E and a high population of medium acid sites has shown cracking activity almost equal to catalyst-E. Strong acid sites play prominent role in the cracking reaction rather than the medium strength sites. It may be stated that the catalyst W-Ni/SiO₂-Al₂O₃-E (W-on top) has demonstrated excellent hydrogenation and cracking functions.

**Conclusions**

The silica-alumina support has exhibited a fairly good number of strong and medium acid sites. While the addition of nickel has little effect on the acidity, incorporation of W on silica-alumina has created some new strong acid sites. The cumene cracking activity seems to be primarily due to the hydroxyl groups of the carrier. Enhanced strong acidity on addition of W has not demonstrated a saluting effect on cracking activity. Dispersion of tungsten and not of nickel is the key structural factor for the hydrogenation activity of cyclohexene. Ni/Si-Al has easy reducibility and high LTOC while W/Si-Al has difficult reduction and a low oxygen chemisorption. But the anion vacancies which are the seat for catalytic activity, generated in the tungsten catalyst are sufficient to provide a promising hydrogenation function. In the bimetallic Ni-W catalyst in which W is on the top has shown superior hydrogenation and cracking activity.
as compared to the catalyst where Ni is on the top.

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