ELSEVIER

Catalysis Today 28 (1996) 159–166

CATALYSIS TODAY

Niobia–alumina supported hydroprocessing catalysts: relationship between activity and support surface acidity

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Abstract

Two classes of Mo–Ni catalysts, surface niobium–aluminum oxides and mixed niobium–aluminum oxides, were examined for hydroprocessing of gas-oils. Niobia containing surface and mixed oxides are known to have increased surface acidities as compared to the component oxides; support surface acidity, in turn, may enhance gas-oil sulfur and nitrogen removal activities. Maximum rates of sulfur and nitrogen removal occurred for surface oxide catalysts containing 5 wt.-% Nb_2O_5, corresponding to the Nb–Al surface oxide support composition reported to have the highest Lewis acidity. Maximum activities, normalized on a surface area basis, occurred at a support composition of 80 wt.-% Nb_2O_5 for the mixed oxide series. Surface acidities of the Nb_2O_5–Al_2O_3 supports were measured by temperature programmed reaction study of adsorbed [^{18}O]ethanol; the desorption temperature of the ether dehydration product is a relative measure of Lewis acidity. Using this method, the highest surface acidity was found on the mixed oxide supports containing 80 wt.-% Nb_2O_5. For both series of catalysts, the compositions exhibiting the greatest degree of hydrotreating activity improvement corresponded to those exhibiting the highest surface acidity. Addition of niobia to alumina readily permits surface modifications to hydroprocessing catalysts for obtaining maximum hydroprocessing activity.

Keywords: Niobia–alumina supported hydroprocessing catalysts; Surface acidity

1. Introduction

Growing world-wide demands for cleaner transportation fuels and upcoming requirements for cleaner burning off-road fuels is dramatically challenging the petroleum refining industry. In the current climate of reducing costs and minimizing capital investment, a practical method of meeting improved quality fuel needs is to optimize refinery performance; specifically, improving the operations of hydroprocessing units that produced finished products. Hydroprocessing, or hydrotreating, is a heterogeneous catalytic process in which crude oil fractions are contacted with hydrogen at elevated pressures and temperatures, in order to remove impurities, primarily sulfur and nitrogen, and convert aromatic compounds to their corresponding naphthenic compounds, for production of gasoline and diesel range products.

An improved hydroprocessing catalyst will result in improved hydroprocessing unit utilization, either by permitting increased throughput at the same operating conditions or increased impurity removal at the same or less severe operating conditions. Recent findings have shown that hydroprocessing catalysts with supports of increased surface acidity have a higher activity, using both non-metal and metal alkoxide surface modified supports and transition

SSDI 0920-5861(95)00222-7

Table 1
Composition of gas-oils and corresponding catalyst test conditions

Gas oil	I	II
Density (cm^3/g)	0.845	0.865
Gravity (°API)	35.9	32.0
Sulfur (wt.-%)	1.37	0.716
Nitrogen (wppm)	83	480
Reaction conditions		
Temperature (°C)	300	300
Pressure (psig)	400	800
Pressure (bar)	27.6	55.2
Vol. liquid per vol. catalyst per h. (1/h)	2.0	2.0
Vol. H_2 per vol. catalyst (sccm/cm^3)	9.0	12.0
H_2 rate (scf/bbl)	1500	2000

metal mixed oxide supports [1–3]. Commonly employed hydroprocessing catalysts consist of active metals, such as molybdenum and nickel or cobalt, supported on alumina extrudates. Addition of niobia to alumina is known to result in increased surface acidities [4–6]. This work reports the results of using alumina modified with niobia, Nb_2O_5, both as a surface oxide (deposited onto an alumina support) and as a mixed oxide (mixed with alumina prior to forming a support) as supports for Mo–Ni hydroprocessing catalysts. The surface acidities of the catalysts and their activities for removal of sulfur and nitrogen from gas oils were compared.

2. Experimental

Catalysts were tested in upflow packed-bed tubular reactors using two different gas-oil feeds, listed in Table 1. Prior to testing catalysts were exposed to 10% H_2S in H_2 at 9 sccm (standard cm^3 per min) per cm^3 of catalyst at 300°C and about 1 bar (15 psig), heating to temperature in 2 h. After sulfiding, catalysts were exposed to gas-oil and pressure increased to reaction conditions; once the catalyst was completely covered with liquid, gas flow was switched to 100% H_2 as specified in Table 1. At no point were the catalysts not exposed to sulfur after heating was commenced. Gas-oil I, and the corresponding reaction conditions, were used for the surface oxide catalysts, gas-oil II and corresponding conditions were used for the mixed oxide catalysts. After 18 h at process conditions, sufficient for the system to reach steady state, liquid product samples were analyzed for sulfur content by X-ray fluorescence and nitrogen content by pyrolysis. Liquid mass recovery was close to 100%.

Surface oxide niobia–alumina catalysts were prepared by depositing hexane solutions of niobium ethoxide onto granular, 20 × 40 mesh, high-surface area γ-Al_2O_3, in an inert atmosphere to incipient wetness. The alumina was vacuum dried and stored in an anhydrous environment prior to use. After Nb deposition, the supports were dried, in vacuum, for 16 h at 110°C, then heated in air (calcining) for 3 h at 500°C. In separate steps, ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, were deposited onto the supports, followed by drying and calcining. For some catalysts, Nb was deposited before Mo and Ni, indicated by 'S1'; other catalysts were made with deposition sequence Mo–Nb–Ni, indicated by 'S2', the notation 'S1-4' indicates a niobia–alumina surface oxide catalyst containing nominally 4 wt.-% Nb_2O_5, with Nb deposited before Mo. Catalysts prepared and compositions obtained are listed in Table 2.

Mixed oxide niobia–alumina catalysts were prepared by blending niobic acid and activated alumina powder with a 10 wt.-% solution of oxalic acid in water, until a thick paste was obtained; niobic acid has been previously characterized [7,8]. The paste was extruded through a 1/8 in. (3 mm) die and the extrudates dried and calcined. Mo and Ni were added as before. Catalysts prepared and compositions obtained are listed in Table 2. The nomenclature 'M80' indicates a catalyst with a niobia–alumina mixed oxide support containing 80 wt.-% Nb_2O_5.

Alumina and mixed oxide supported finished catalysts were characterized for surface area using nitrogen adsorption by the BET method and crystalline phases identified by X-ray diffraction using Cu Kα radiation; these results are listed in Table 2. Used catalysts were Soxhlet extracted with toluene for 48 h to remove residual oil and then dried prior to characterization.

Surface acidity was qualitatively determined for the mixed oxide supports using a recently developed temperature-programmed reaction study (TPRS) method [9]. Dried supports were exposed to [^{18}O]ethanol vapor for 1 h; about 2 mg of the alcohol bearing support was loaded into a temperature programmed probe of a mass spectrometer and heated from 25 to 300°C at 25°C/min at a pressure of 1×10^{-7} Torr. Ether desorption products were measured as a function of mass/charge ratio and time (temperature) of desorption by the mass spectrometer.

Table 2
Characterization and activity of surface and mixed oxide Mo–Ni/Nb_2O_5–Al_2O_3 catalysts

Catalyst	Nb order	Nb_2O_5 (wt.-%)	R_S [a]	R_N [a]
S-0	–	–	1.01	11.7
S1-4	1	3.6	1.20	23.9
S1-6	1	5.7	{1.04}	{14.4}
S1-9	1	8.5	1.13	22.6
S2-7	2	6.7	{0.96}	17.2
S2-10	2	9.6	1.16	23.2
S2-12	2	12.0	0.97	18.9

Catalyst	Nb_2O_5 (wt.-%)	SA (m^2/g)	Phase	R_S [b] ($\times 100$)	R_N [b]
M100	100	14	TT	0.83	0.59
M80	78	40	TT	1.13	1.42
M60	58	54	trace TT	1.03	0.94
M40	38	90	trace TT + γ	0.65	0.86
M0	0	220	A, trace γ	0.54	0.75

[a] Measured with gas-oil I

[b] Measured with gas-oil II.

All S series catalysts have 3.8 wt.-% NiO and 11.6 wt.-% MoO_3; M series: 5 wt.-% NiO, 12.3 wt.-% MoO_3, based on total weight of finished catalysts. For all catalysts, Nb_2O_5 wt.-% is based on $Nb_2O_5 + Al_2O_3$ support weight only. Order is position of niobium in metals deposition sequence. SA, surface area, of catalysts prior to testing; all S series catalysts have a surface area of about 220 m^2/g. Phases identified, prior to testing, from X-ray diffraction as TT-$Nb_2(O,Y)_{5+n}$ (TT) or primarily amorphous (A) with some γ-Al_2O_3 (γ). R_S: g S removed per m^2 catalyst per h; R_N: wppm N removed per m^2 catalyst per h; values in {} considered unreliable due to experimental error, not plotted. R_S and R_N calculated using fresh catalyst parameters.

3. Results and discussion

3.1. Niobia–alumina surface oxides

Sulfur and nitrogen removal activities of molybdenum–nickel niobia–alumina surface oxide catalysts using gas-oil I are tabulated in Table 2 and plotted in Fig. 1. Although limited data were obtained, the following trends are apparent: sulfur removal activity rises then falls with increasing niobia loading, reaching a maximum at loadings of about 5 wt.-% Nb_2O_5. Nitrogen removal activities in general increase with increasing niobia loadings. There appears to be no trend with respect to niobium deposition order, indicating that a possible interaction of the supported metals, Nb and Mo, do not influence catalytic activities. While the reported activities are calculated on a surface area basis, equivalent trends are expected on a weight basis, for the surface oxide samples only, as the 'S' series of catalysts had nearly the same sur-

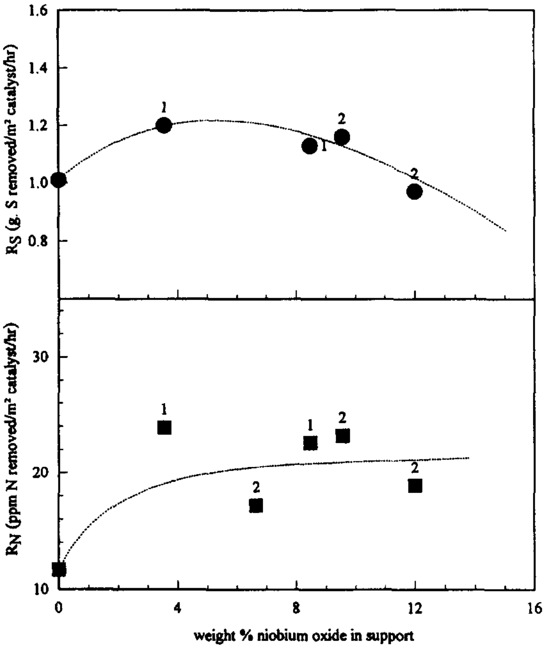

Fig. 1. Rates of sulfur (●) and nitrogen (■) removal from gas-oil I as a function of support Nb_2O_5 content of Mo–Ni/Nb_2O_5–Al_2O_3 surface oxide catalysts. Numbers next to data points indicate position of niobium in metals deposition sequence.

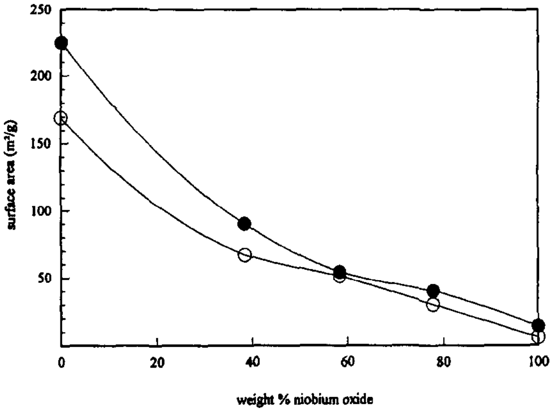

Fig. 2. Surface areas of Mo-Ni/Nb_2O_5-Al_2O_3 mixed oxide catalysts as measured by N_2 BET, prior to activity testing (●) and after activity testing and toluene extraction (○).

face areas (220 m^2/g) and densities (0.60 g/cm^3).

A potential explanation for the observation of increasing hydroprocessing activity with increasing niobia content could be changes in molybdenum dispersion brought on by surface modification. However, similar polymolybdate species are observed for MoO_3 supported on Al_2O_3 or Nb_2O_5; upon sulfiding, these polymeric species transform into MoS_2, leaving considerable portions of the support exposed for either Al or Nb oxide supports [10–15]. This suggests that the niobia–alumina interaction and not a possible niobia–molybdenum interaction, is responsible for the changes in activity, especially in light of the insensitivity of the reactivity to Nb deposition order. However, reports on the behavior of niobium–molybdenum–aluminum surface oxide systems were not found.

The trends illustrated in Fig. 1 are remarkably similar to trends in Lewis and Brønsted acidities observed for niobia–alumina surface oxides [4,5]. On a per gram basis, maximum Lewis acidity was found to occur at about 5 wt.-% Nb_2O_5, with increasing loadings of Nb_2O_5 the amount and strength of Lewis acid sites decreases, eventually falling below that measured for unmodified alumina; also observed was an increase in Brønsted acidity with increasing Nb content, starting at about 5 wt.-% Nb_2O_5, although the concentration of Brønsted acid sites is much less than that of Lewis acid

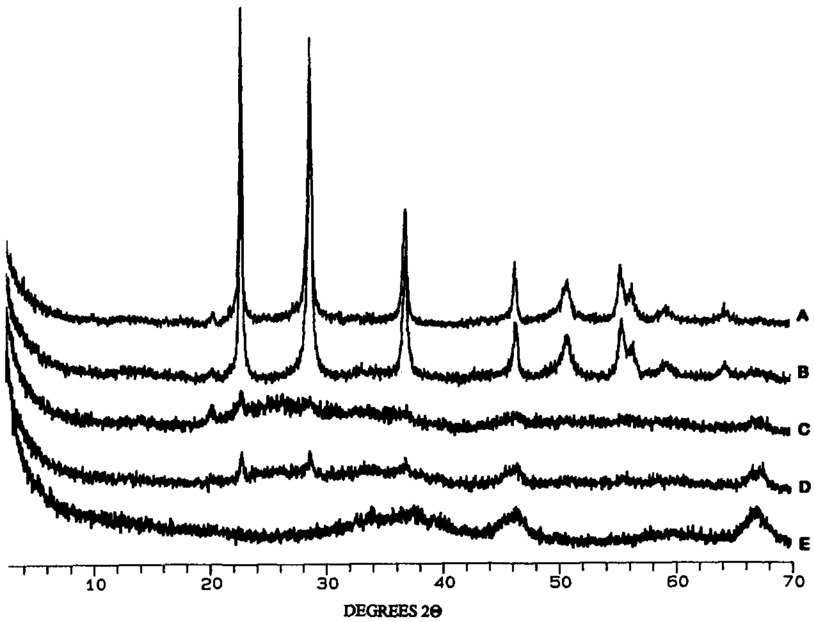

Fig. 3. X-ray diffraction spectra of Mo-Ni/Nb_2O_5-Al_2O_3 mixed oxide catalysts, after exposure to activity testing. Major diffraction intensities correspond to TT-$Nb_2(O,Y)_{5+n}$. Spectra correspond to samples A: M100, B: M80, C: M60, D: M40 and E: M0. Identical results were found for the same series of catalysts prior to activity testing.

sites. These results were found to be independent of niobium deposition methods [16].

Taking into account possible variations in intrinsic surface acidity between different sources of Al_2O_3, the surface acidity results of Datka et al. [4] and Jehng and Wachs [5] compare favorably with the present catalytic activity results. The changes in sulfur removal activity can be directly associated with changes in the acidity of the support, specifically, increase and then decrease in Lewis acidity as brought on by increasing amount of surface-phase Nb_2O_5. The increase, and then maintenance, of nitrogen removal activity may be a result of combined increases in Lewis and Brønsted acidities, as the total support surface acidity remains higher than unmodified alumina as Brønsted acidity continues to increase as Lewis acidity decreases with higher Nb_2O_5 loadings.

3.2. *Niobia–alumina mixed oxides*

Molybdenum–nickel niobia–alumina mixed oxide catalysts were characterized for surface area and crystallinity before and after catalyst testing, summary of the results are listed in Table 2 and presented in Figs. 2 and 3. A slight decrease in surface area and no change in crystallinity of individual samples was observed after catalytic testing; the change in surface area is attributable to residual unextracted carbonaceous matter filling some pore volume; catalyst testing does not seem to effect the physical state of the mixed oxide supports. Catalysts with higher niobium contents have lower surface areas, consistent with support crystallization and the appearance of TT-$Nb_2(O,Y)_{5+n}$ [17] with increasing Nb_2O_5 content. Catalysts with less than 60 wt.-% Nb_2O_5 are mostly amorphous, although there is evidence of γ-Al_2O_3 in some samples; the M80 and M100 samples contained well crystallized TT-$Nb_2(O,Y)_{5+n}$.

Niobia–alumina mixed oxide sulfur and nitrogen removal activities with gas-oil II are tabulated in Table 2 and plotted in Fig. 4. Nb_2O_5 single oxide supported catalysts have greater sulfur removal but lower nitrogen removal activities than the Al_2O_3 single oxide supported catalysts. Highest activities of both sulfur and nitrogen removal for all the M-series

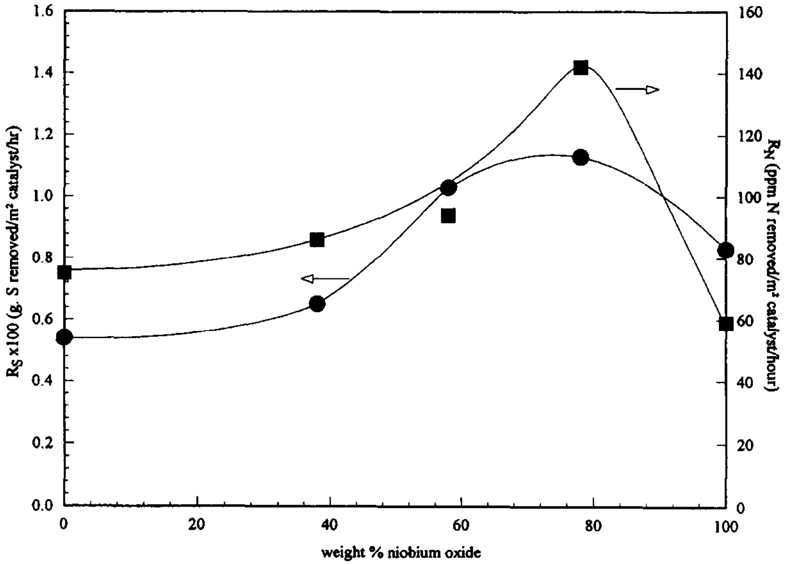

Fig. 4. Rates of sulfur (●) and nitrogen (■) removal from gas-oil II as a function of support Nb_2O_5 content for Mo–Ni/Nb_2O_5–Al_2O_3 mixed oxide catalysts. Curves represent best fits through data.

single and mixed oxide catalysts tested occurred for the M80 composition. Sulfur and nitrogen removal rates of M80 were about twice that of the Al_2O_3 supported catalyst, M0; as compared to M100, nitrogen removal was much more enhanced (2.4 times greater) on M80 than sulfur removal (1.4 times greater).

An understanding of the activity behavior can be had through characterization of the support surface chemistry using TPRS. Ethanol undergoes dissociative adsorption, nucleophilic attack or dehydration when adsorbed onto activated alumina surfaces. Ethylene is produced from unimolecular dehydration and ethers are formed from bimolecular dehydration reactions of ethanol-derived alkoxides. When using ^{18}O labeled ethanol, the product $CH_3CH_2OCH_2CH_3$, $(Et)_2O$, forms on Brønsted acid sites or on Lewis acid sites with adsorbed water and the product $CH_3CH_2^{18}OCH_2CH_3$, $(Et)_2^{18}O$, forms on Lewis acid sites. Increase in Lewis acidity is revealed by more facile production of $(Et)_2^{18}O$, which is experimentally observed through lowered peak desorption temperatures [9,18,19]. Unfortunately, the qualitative nature of this method provides little information about the absolute number of acid sites.

The results of [^{18}O]ethanol TPRS experiments from niobia–alumina mixed oxides are listed in Table 3 and plotted in Fig. 5. $(Et)_2^{18}O$ desorption temperatures vary as a function of niobia content, the lowest desorption temperatures for both species occurred on the M80 composition. As stated above, lower desorption temperatures are associated with increased surface acidity. Increased acidity of mixed oxides, as compared to their single oxide components, is a well known phenomenon [20,21]; this TPRS method shows that niobia–alumina mixed oxides also exhibit increased surface acidity as compared to their single oxide constituents. Similar results were found for a mixed oxide system with Nb/Al molar ratio of 1:1, increased surface acidity was observed by IR and isopropanol dehydration, as compared to the single oxide components [22]. Desorption temperatures on M100 for both isotopomeric species were higher than on the other single oxide component, M0, showing that niobia has less Lewis acidity than alumina.

Table 3
Peak desorption temperatures and temperature changes of isotopomeric ether desorption products of [^{18}O]ethanol adsorbed onto $Nb_2O_5-Al_2O_3$ mixed oxide supports, as measured by mass spectrometry

Mass/charge ratio and parent molecule	59, 74, $(Et)_2O$	61, 76, $(Et)_2^{18}O$
Support	Peak desorption temperature (°C)	
M100	275 [b]	135 [m], 183 [b,m]
M80	160	117
M60	145	118
M40	148	129
M0	184	163
Support	Change in temperature (Δ°C)	
M100	+91	−28 [m], +20 [m]
M80	−24	−46
M60	−39	−45
M40	−36	−34
M0	0	0

[b] Indicates broad desorption peak. [m] Indicates bi-modal desorption peak. $(Et)_2O$ data presented for comparison only.

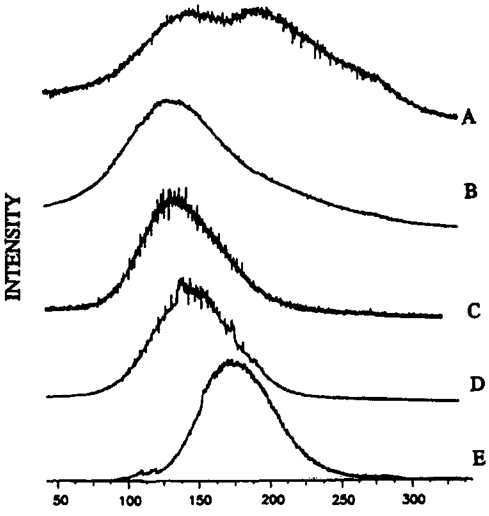

Fig. 5. Reconstructed partial chromatograms of temperature programmed desorption products of [^{18}O]ethanol adsorbed onto $Nb_2O_5-Al_2O_3$ mixed oxide supports, for mass/charge ratios of 61 and 76, corresponding to the $(Et)_2^{18}O$ product. Spectra correspond to samples A: M100, B: M80, C: M60, D: M40 and E: M0.

Comparison of the [^{18}O]ethanol TPRS and gas-oil hydroprocessing activity results for the mixed oxides shows at least qualitative similarities. The mixed oxide support composition producing the greatest catalytic activity had the lowest ether desorption temperatures. This correspondence of data clearly indicates that support surface acidity plays a significant role in the activity of hydroprocessing catalysts. A comparison of R_S and R_N activities of M0, M80 and M100 samples with their corresponding $(Et)_2^{18}O$ desorption temperatures shows that relative Lewis acidity increases proportionally from M0 to M80. This behavior parallels the relative changes in catalytic activity: for R_S, M80 > M0 and M80 > M100, and for R_N, M80 > M0 and M80 ≫ M100. The qualitative conclusion of these comparisons is that an increase in support Lewis acidity increases both sulfur and nitrogen removal activities in the mixed oxide samples. Note that these activity results for the mixed oxide series are on a per surface area basis.

3.3. Role of surface acidity

That surface acidity plays a role in hydrotreating reaction mechanisms has been noted previously. Direct correlation between catalyst acidity, in either the sulfide, oxide or reduced state, and desulfurization and denitrogenation activity has been observed [23–28]. Noted is that changes in active metal morphology that may be brought on by increases in support acidity do not necessarily explain increased activity [23]. The two types of surface acidity, in conjunction with associated surface base sites, play different roles. While increasing Lewis acidity is thought to contribute to overall increase in activity, increased Brønsted acidity enhances catalysis of specific steps in denitrogenation only those involving nitrogen-containing carbonium-ion intermediates and hydrocracking [28–30].

Stronger Lewis acid sites can arise from more electronegative surface metal species, which can be created in mixed oxide systems from charge or oxygen coordination imbalances on surfaces [20]. For surface hydroxyl groups attached to surface metal species, M–O–H, increased electronegativity of a metal, which may be brought on by a surface mixed-oxide environment, results in stronger M–O bonds and weaker O–H bonds, leading to increased ability to donate H from surface-interacting water species. The speculation follows then that supports exhibiting increased Lewis acidity, can in a hydroprocessing environment, exhibit increased 'activation' of hydrogen from adsorbed water or perhaps hydrogen sulfide, which results in increased reaction rates in hydrogenation reactions including gas-oil desulfurization and denitrogenation. Increased Brønsted acidity, which is a result of a more nucleophilic surface, additionally enhances denitrogenation, as seen on the surface oxide samples. The behavior of the niobia–alumina surface oxide and mixed oxide supports described in this work, and Mo–Ni catalysts made from these supports are consistent with the creation and roles of Lewis and Brønsted acid sites on these series of catalysts.

4. Conclusions

Physical evidence indicates hydroprocessing activities of molybdenum–nickel catalysts made with surface and mixed oxide niobia–alumina supports varies as a function of support surface acidity. Both surface and mixed oxide supports show increased, then decreased acidity with increasing niobia content. The support compositions having maximum surface acidity corresponds to those having maximum hydroprocessing sulfur and nitrogen removal activities, for both series of supports. Further evidence suggests that while increased Lewis acidity leads to enhanced overall activity, increased Brønsted acidity further enhances nitrogen removal activity. Changes to surface acidity is a reflection of changing nature of surface metal species in a mixed or surface oxide environment as a function of varying oxide composition. Addition of niobia to alumina readily permits surface modifications to hydroprocessing catalysts for obtaining maximum hydroprocessing activity.

References

[1] E.C. DeCanio and J.G. Weissman, Colloids Surf. A, in press.

[2] J.G. Weissman, E.C. DeCanio and J.C. Edwards, Catal. Lett., 24 (1994) 113.

[3] J.G. Weissman, E.I. Ko and S. Kaytal, Appl. Catal. A, 94 (1993) 45.

[4] J. Datka, A.M. Turek, J.M. Jehng and I.E. Wachs, J. Catal., 135 (1992) 186.

[5] J.M. Jehng and I.E. Wachs, Catal. Today, 8 (1990) 37.

[6] A.M. Turek, I.E. Wachs and E.C. DeCanio, J. Phys. Chem., 96 (1992) 5000.

[7] M Shirai, N. Ichikuni, K. Asakura and Y. Iwasawa, Catal. Today, 8 (1990) 57.

[8] K. Domen, A. Kudo, A. Tanaka and T. Onishi, Catal. Today, 8 (1990) 77.

[9] E.C. DeCanio, V.P. Nero and J.W. Bruno, J. Catal., 135 (1992) 444.

[10] N.Y. Topsøe and H. Topsøe, J. Catal., 139 (1993) 631.

[11] F. Luck, Bull. Soc. Chim. Belg., 100 (1991) 781.

[12] F.E. Massoth, Adv. Catal., (1978) 265.

[13] P. Grange, Cat. Rev. Sci. Eng., 21 (1980) 135.

[14] Y.S. Jin, A. Auroux and J.C. Vedrine, J. Chem. Soc., Faraday Trans. 1, 85 (1989) 4179.

[15] J.M. Jehng, A.M. Turek and I.E. Wachs, Appl. Catal. A, 83 (1992) 179.

[16] J.M. Jehng and I. E. Wachs, J. Mol. Catal., 67 (1991) 369.

[17] E.I. Ko and J.G. Weissman, Catal. Today, 8 (1990) 27.

[18] E.C. DeCanio, J.W. Bruno, V.P. Nero and J.C. Edwards, J. Catal., 140 (1993) 84.

[19] E.C. DeCanio, V.P. Nero and E.I. Ko, J. Catal., 146 (1994) 317.

[20] K. Tanabe, in J. R. Anderson and M. Boudart (Editors), Catalyst Science and Technology, Springer, New York, 1981, Chap. 5.

[21] K. Tanabe, T. Sumiyoski, K. Shibata, T. Kiyoura and J. Kitagawa, Bull. Chem. Soc. Jpn., 47 (1974) 1064.

[22] P.G. Pries de Oliveira, F. Lefebvre, M. Primet, J.G. Eon and J.C. Volta, J. Catal., 130 (1991) 293.

[23] J. Ramirez, L. Ruiz-Ramirez, L. Cedeno, V. Harle, M. Vrinat and B. Breysse, Appl. Catal. A, 93 (1993) 163.

[24] J. Laine, J. Brito and S. Yunes, Proc. 3rd Int. Conf. Chem. Uses Molybdenum, (1979) 98.

[25] M.O. Alias and V. Srinivasan, Chem. Sci., 102 (1990) 117.

[26] M.O. Alias and V. Srinivasan, Indian J. Chem., 29A (1990) 515.

[27] N.Y. Topsøe and H. Topsøe, J. Catal., 139 (1993) 641.

[28] S. Rajagopal, T.L. Grimm, D.J. Collins and R. Miranda, J. Catal., 137 (1992) 453.

[29] N.Y. Topsøe, H. Topsøe and F.E. Massoth, J. Catal., 119 (1989) 252.

[30] H. Shimada, T. Sato, Y. Yoshimura, J. Hiraishi and A. Nishijima, J. Catal., 110 (1988) 275.