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Performance, characterization, and surface acidity of zirconium modified hydroprocessing catalysts

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Gas-oil hydrodesulfurization activity of Ni–Mo/Al_2O_3 catalysts was significantly improved when prepared with zirconium alkoxide, but lowered when prepared with Zr nitrate. IR of CO adsorption on reduced catalysts, and LRS and XPS of calcined catalysts show that the addition or zirconium does not effect the metal oxide structure. IR of pyridine adsorption and ^{27}Al NMR both show greatly enhanced Lewis and Brønsted acidities of the Zr alkoxide modified materials as compared to unmodified samples. These results point to the strong influence of surface acidity on activity in hydroprocessing catalysts.

Keywords: Hydrotreating; zirconium; aluminum-27 nuclear magnetic resonance spectroscopy; infrared spectroscopy; pyridine adsorption; hydrodesulfurization

1. Introduction

New US regulations will require increased quantities of low sulfur transportation fuels. Removal of S will greatly increase the efficiency of vehicular catalytic converters as well as reduce SO_x emissions. These changes will require refineries to hydrotreat larger amounts of naphthas and gas oils to low sulfur gasoline and diesel fuel products, in the range of 50 ppm S for gasolines and 0.05 wt% S for diesel fuel.

Any added advantage hydroprocessing catalysts can give to improving hydrodesulfurization (HDS) processing will result in proportionally larger increases in processing throughput under more severe conditions, and lower long term operating costs. To this end we have investigated improved activity hydroprocessing catalysts. We found that by modifying conventional catalysts with zirconium, an enhancement in HDS activity occurs.

A number of characterization techniques, including solid-state ^{27}Al nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR) of adsorbed CO and pyridine, laser Raman spectroscopy (LRS), and X-ray photoelectron spectroscopy (XPS), were used to elucidate the behavior of conventional and zirconium modified Ni–Mo/Al_2O_3 catalysts tested for the hydrodesulfurization of light gas oil.

2. Experimental

Conventional catalysts were prepared by sequential incipient wetness deposition of $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$, followed by $Ni(NO_3)_2\cdot 6H_2O$, onto a γ-Al_2O_3 support. Each metal compound, Mo, Zr, or Ni, was deposited in a single step followed by drying and calcining; Ni was deposited last in all cases. Drying was conducted at 110°C for 3 h, in vacuum, with a nitrogen purge, while calcining was conducted by heating to 500°C in 3 h, holding at 500°C for 3 h, then allowing the sample to cool overnight, all in flowing air at a nominal rate of (10 cm^3 air)/(cm^3 catalyst) min. The γ-Al_2O_3 (20/40 mesh) has a surface area of 265 m^2/g and pore volume of 0.7 cm^3/g. Catalysts were modified with either zirconyl nitrate ($ZrO(NO_3)_2\cdot xH_2O$), deposited either before or after Mo deposition by aqueous incipient wetness, or zirconium alkoxides, either 70% Zr *n*-propoxide ($Zr(C_3H_7OH)$) in 1-propanol, diluted approximately 25/75 vol% in ethanol, deposited onto Al_2O_3 before Mo deposition, or Zr *n*-butoxide–butanol complex ($Zr(OC_4H_9)_4\cdot C_4H_9OH$) diluted approximately 25/75 vol% in hexanes, after Mo deposition. We have observed no difference in various samples prepared using the different Zr alkoxides. Alkoxide deposition was performed in an inert atmosphere using solvents dried over molecular sieves. The same metal loadings, based on Al_2O_3, were used in all of the catalysts prepared, approximately 5 wt% Ni, 10 wt% Mo, and 4 wt% Zr. Catalysts were characterized by X-ray diffraction (XRD) and surface area measurements.

Catalysts were tested in a fixed-bed co-current up flow reactor, operated at 300°C, 27.6 bar (400 psi), 2.0 liquid hourly space velocity (cm^3 liquid per cm^3 catalyst per hour), and 100% H_2 at a rate equivalent to 270 standard cm^3 of gas per cm^3 of liquid, equivalent to 1500 standard cubic feet per barrel. Prior to testing catalysts were sulfided in situ with 10% H_2S in H_2 at 300°C for 3 h. Liquid product samples were collected after equilibrium was reached, about 16 h. Products were analyzed for S content by X-ray fluorescence according to ASTM D2622. Liquid feed is light straight run gas oil containing 1.37 wt% sulfur, with a density of 0.87 g/cm^3 (35.9° API gravity), 30 vol% aromatic content, and 248°C initial boiling point, 280°C midpoint and 342°C endpoint.

Mo $3d_{5/2}$, Ni $2p_{3/2}$, Zr $3d_{5/2}$, Al 2p, C 1s, and O 1s binding energies and surface atomic fractions of calcined catalysts were measured by XPS. Mo bands were observed by LRS of calcined catalysts. Adsorbed moisture prevented observation of Al and Ni bands by LRS.

The IR instrumentation, pretreatment and CO adsorption procedures were as described [1]. Pyridine adsorption was done by exposing the reduced sample to 16 Torr pyridine for 30 min at 150°C followed by evacuation for 30 min at 150°C and then at 300°C for 1 h. A 1 min exposure to 17 Torr H_2O and evacuation for 30 min at 300°C was completed prior to measurement.

Solid state ^{27}Al NMR spectra were obtained on a Varian VXR-400 superconducting spectrometer equipped with a Chemagnetics solids accessory. Magic angle spinning (MAS) was employed at a spin rate of $\sim$ 6 kHz. The resonance frequency of ^{27}Al at 7.04 T is 78.3 MHz. Cross polarization spectra (CPMAS) [2–4] were obtained using a contact time of 0.2–0.5 ms and a recycle delay of 1 s. Chemical shifts are reported relative to a solid sample of $KAl(SO_4)_2$. The cross polarization experiment involves the transfer of proton magnetization to Al atoms in dipolar contact with the proton, within 7 Å. Thus, the technique is surface selective with signal observed only from those surface Al atoms associated with hydroxyl groups, both surface tetrahedral and octahedral Al are observed. Single pulse magic angle spinning (SPMAS) experiments were performed to measure signal from all Al present, primarily from the bulk γ-Al_2O_3.

3. Results and discussion

No changes in surface area, pore volume, or crystallinity were noted between the zirconium modified and unmodified Ni–Mo/Al_2O_3 catalysts, regardless of the Zr precursor. HDS activity testing, summarized in table 1, reveals that zirconium nitrate or butoxide modifiers affect HDS activity differently. The Zr butoxide modified catalyst has a significantly higher activity, regardless of the deposition order of the metals, than both the unmodified or the Zr nitrate modified catalyst. Zirconium nitrate modified catalysts were always less active than the unmodified catalysts.

Alkoxides react with surface hydroxyl groups on support surfaces, resulting in direct support metal–oxygen–alkoxide metal bonds after calcining. Examples include V_2O_5 grafted onto TiO_2 [5–7] and Nb_2O_5 stabilized on SiO_2 [8,9]. We initially thought that this type of surface modification, through the interaction of Zr alkoxide with Al_2O_3, affected the structure of the supported Mo and Ni oxides, and then the subsequently formed sulfides on the finished catalyst, in such a way as to

Table 1
HDS activity of unmodified and Zr modified Ni–Mo/Al_2O_3 catalysts, expressed as pseudo-first order rate constant, in h^{-1}

Composition	Deposition sequence	
	Zr–Mo–Ni	Mo–Zr–Ni
Ni–Mo	4.3	4.3
Ni–Mo–Zr nitrate	3.4	3.6
Ni–Mo–Zr alkoxide	5.1	4.6

increase activity. Conversely, no such reaction is thought to occur from a relatively inert species such as zirconium nitrate.

Physical characterization methods aimed at understanding the changes brought about by Zr addition found no differences in the Mo or Ni oxide structures between the modified and unmodified calcined catalysts, regardless of whether Zr nitrate or alkoxide is used. The Zr deposition order had no measurable effect on the structure of the metals. XPS atomic surface coverage and binding energies for Mo, Zr, Ni and Al were the same for all of the catalysts. The average values for the binding energies were 232.8 eV for Mo, 182.8 eV for Zr, 856.4 eV for Ni and 74.5 eV for Al, all referenced to Al 2p at 74.5 eV, all are close to the values expected for the fully oxidized species [10].

Laser Raman spectroscopy of supported Mo in the calcined catalysts found a major band at around 953 cm^{-1} for unmodified and Zr nitrate and alkoxide modified catalysts. This corresponds to a polymeric species, similar to Mo_7O_{24} or Mo_8O_{27}, associated with water due to rehydration of the sample after exposure to atmosphere following calcining [11]. IR of CO adsorption of Zr alkoxide modified reduced $Ni-Mo/Al_2O_3$ catalysts (Zr loadings of 0.0–3.0 wt%) is illustrated in fig. 1. Also examined, but not illustrated, was the influence of Zr alkoxide precursor on Ni/Al_2O_3 and on Mo/Al_2O_3 CO adsorption. Similar behavior was found for

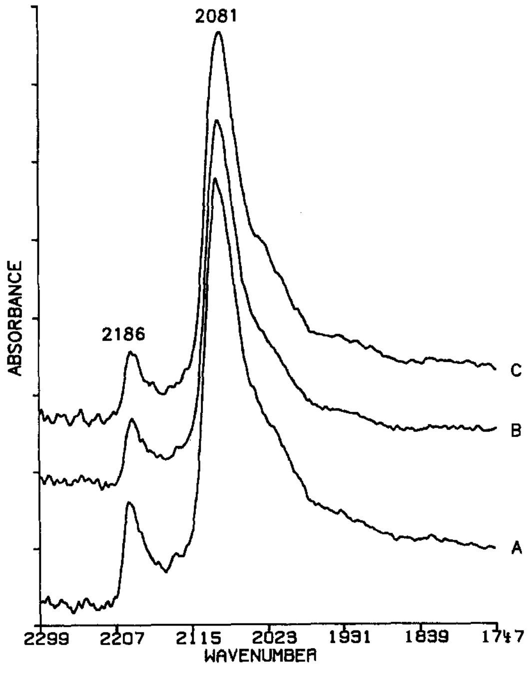

Fig. 1. IR spectra of CO adsorbed onto reduced Zr alkoxide–$Ni-Mo/Al_2O_3$ as a function of Zr loading: (A) 0, (B) 2.0, (C) 3.0 wt%. These results show no change to the Ni and Mo structures due to Zr modification.

all three cases. No change in relative intensity or position of the various CO adsorption IR bands were observed. The observed adsorptions corresponded to those commonly observed for CO on Ni at 2081 cm^{-1}, and on Mo at 2186 cm^{-1} [12].

The CO adsorption results, taken together with the XPS and LRS data, indicate that there is no difference in the state of Mo or Ni between the zirconium alkoxide or nitrate modified and unmodified Ni–Mo/Al_2O_3 calcined catalysts. These findings lead to the hypothesis that Mo and Ni on the different catalysts may have similar structures in the sulfided state, regardless of type and presence of zirconium modifier.

A series of characterizations was completed to more fully understand the interaction of zirconium alkoxide with Ni–Mo/Al_2O_3 catalysts; and in particular, the interactions between zirconium alkoxide and alumina that lead to higher hydrotreating activity. No further work was done with zirconium nitrate catalysts. The loss of activity of these samples was believed to be due to a detrimental physical interaction between zirconium nitrate and the catalyst.

Fig. 2 illustrates pyridine adsorption on reduced Al_2O_3 impregnated with 0–10 wt% zirconium as alkoxide. Pyridine adsorption gives a qualitative assessment of the relative proportions of Lewis and Brønsted acid sites on Al_2O_3 surfaces [13]. Unmodified Al_2O_3 has Lewis acid sites producing bands at 1562 and 1449 cm^{-1}. There is a dramatic increase in the number of both Lewis and Brønsted acid sites

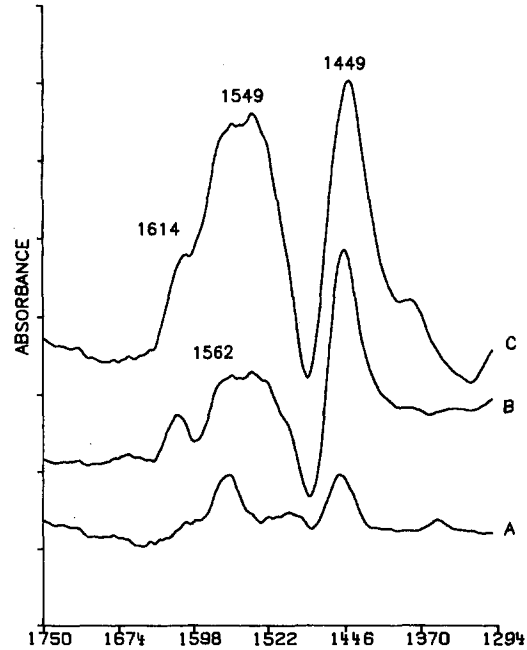

Fig. 2. IR spectra of pyridine adsorbed onto reduced Zr alkoxide/Al_2O_3 samples as a function of Zr loading: (A) 0, (B) 4.0, (C) 10.0 wt%.

with the addition of Zr alkoxide, as evidenced by the increase in intensity of the bands at 1562 and 1449 cm^{-1}, and the growth of a band corresponding to Brønsted acid sites at 1549 cm^{-1}.

The results of SPMAS and CPMAS ^{27}Al NMR experiments on the Al_2O_3 support, calcined Al_2O_3 supported Zr alkoxide, and the Zr alkoxide–Mo–Ni/Al_2O_3 catalyst listed in table 1 are illustrated in fig. 3. Both bulk and surface Al in γ-Al_2O_3 support material, spectra A and B, have tetrahedral (T_d) resonances at about the same chemical shift, 65–70 ppm. However, a Zr alkoxide modified Al_2O_3, spectrum C, shows an upfield shift in the surface Al T_d resonance to 60 ppm, which is even more pronounced in the spectrum of the completed Zr butoxide–Mo–Ni/Al_2O_3 catalyst, D, having been shifted to a value of 50 ppm. This upfield shift is likely due to an increase in acidity of surface hydroxyl groups, leading to a greater shielding of tetrahedral surface Al coordinated to these hydroxyl groups, or to the formation of five-coordinated surface Al, seen as the intensity between the T_d and O_h signals in curves C and D [14,15]. In either case, these differences indicate a qualitative increase in surface acidity of the zirconium alkoxide modified Al_2O_3 compared to the unmodified Al_2O_3. In contrast, similar CPMAS experiments on the two zirconyl nitrate modified samples had spectra similar to curve B of fig. 3, indicating that the presence of zirconium, deposited as the nitrate, does not cause an interaction leading to a shift of Al T_d resonance.

Further evidence for the formation of five coordinated surface Al with associated Lewis acidity, upon reaction with zirconium butoxide, is presented in fig. 4.

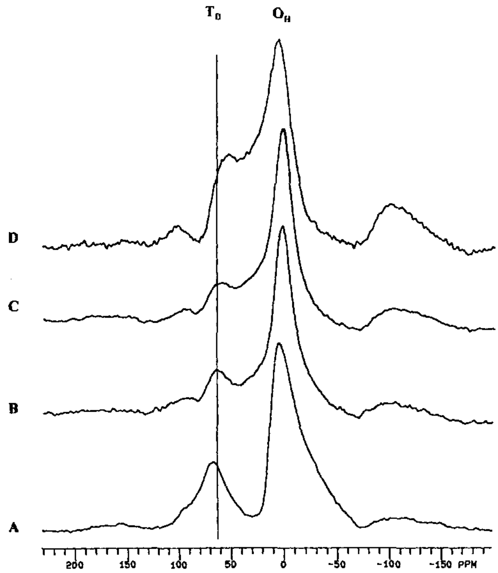

Fig. 3. ^{27}Al NMR of Al_2O_3 (A, B), Zr (added as butoxide) 3.0 wt%/Al_2O_3 (C), and Zr alkoxide–Mo–Ni/Al_2O_3 (D). A is a SPMAS spectrum illustrating chemical shifts of octahedral (O_h) and tetrahedral (T_d) Al resonances. B, C, and D are CPMAS spectra selectively showing surface Al.

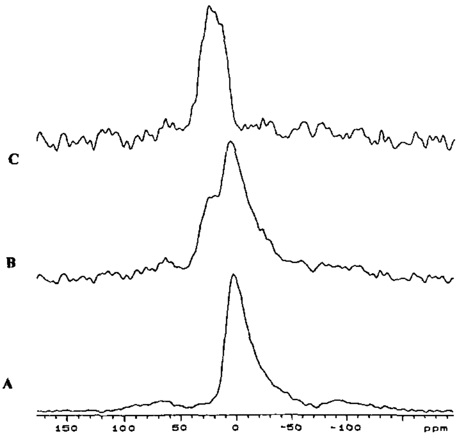

Fig. 4. ^{27}Al NMR CPMAS spectra of Zr (added as butoxide) 3.0 wt%/Al_2O_3 dried at 110°C (A) and the same sample after calcining at 500°C (B). C is the difference of spectra A and B, illustrating the appearance of a resonance at about 40 ppm, attributable to five-coordinated surface Al.

The first two spectra are of zirconium butoxide deposited on alumina, before and after calcining. Before calcining no interaction between the alkoxide and the alumina surface hydroxyl groups is observed by NMR, but after calcining, a chemical reaction between the two results in the direct Zr–O–Al bond formation, as noticed previously [5–9]. Additionally, this reaction results in some surface Al appearing in a modified state, as revealed by the pyridine adsorption studies and as shown in fig. 4. The difference of the two NMR spectra, spectra C, clearly indicates the presence of a resonance at a chemical shift of 40 ppm, which is attributed to five-coordinated alumina having Lewis acid functionalities [16,17]. These NMR results clearly show that the addition of zirconium butoxide results in the formation of modified surface Al with increased surface Brønsted and Lewis acid sites.

The IR data indicate an increase in both Lewis and Brønsted acidity, complimentary NMR data indicate that the presence of Zr, when deposited as an alkoxide, on the Al_2O_3 modifies or creates new Brønsted and Lewis acid sites on the catalyst surface. One mechanism by which this can occur is by a polarizing effect between grafted Zr and nearby hydroxyl groups attached to adjacent tetrahedral Al. Drawing protons away causes an increase in negative charge on their associated Al, resulting in increased shielding and the upfield shift seen in the CPMAS NMR spectra. Additional increases in acidity can arise from the introduction of Zr, where those tetrahedrally coordinated oxygens attached to Zr, not bonded either to adjacent Zr or the Al surface, exist as surface hydroxyl groups.

The IR, XPS, and LRS data indicate that the addition of Zr to Ni–Mo/Al_2O_3 does not noticeably alter the Ni–Mo oxide structure; however, the addition of Zr, in the form of alkoxide, increases the number of Lewis and Brønsted acid sites associated with the supported surface, a substantial number of which must continue to exist after the sulfiding procedure and occur on the active form of the catalyst. These results lead us to conclude that the increased density of acid sites enhances the reactivity of the Zr alkoxide modified catalysts.

Previous work [13,18–22] has shown that there is a direct relationship between Lewis and Brønsted acidity and hydroprocessing catalyst activity in both calcined and sulfided conventional (Ni–Mo or Co–Mo/Al_2O_3) hydrotreating catalysts. Compositions having the highest acidity correspond to those giving maximum activity. This acidity is thought to arise from sulfur vacancies on the sulfided metals, chiefly from the Mo component; the support was thought to contribute only about 20% of the measured acidity on the sulfided catalyst. However, the addition of promoters, Co and Ni, causes a decrease in acid sites from the unprompted catalyst, especially stronger and Brønsted sites. This decrease in acidity is both harmful, in limiting overall activity, and beneficial, in that the stronger sites are thought to be responsible for coking.

Several mechanisms have been proposed to account for the higher activity of mixed oxide supported Mo-based hydrotreating catalysts. Different active phase morphologies have been observed, by high-resolution transmission electron microscopy, on different types of supports. For example, smaller MoS_2 particles are observed on TiO_2 or ZrO_2 supports, as compared to Al_2O_3 or SiO_2 supports, these smaller particles are thought to have a greater number of active sites through increased exposure of MoS_2 crystallite edges [23,24]; however, the interpretation of particle sizes and distributions in these types of studies has recently been examined, the reported morphologies may be an artifact of support physical structure surface area and means by which electron microscopes create images, rather than support chemistry [25]. The catalysts of this work were prepared on the same Al_2O_3 support, discounting physical support effects on the observed activity differences. Additionally, we did not observe any differences in the oxide state of the catalysts, indicating a limited, if any, role of surface acidity on Mo dispersion.

Increased support acidity has been proposed to result in an increase in the number of active sites and an increase in the reactivity of these active sites associated with the MoS_2 phase. An increased electronegativity of the supported MoS_2 phase, induced by increased surface acidity of the support, has been used to explain increase in hydrotreating activity observed on mixed oxide supports [21]. Other work has shown that increased activity is not due to an electronic effect [23,26]. Other reports indicate that changes in support chemistry affect the reactivity of supported MoS_2, through an increased acidity of the MoS_2 active sites [22,26]; however, the supports of this work have the same composition, but exhibit a range of activity changes.

In the absence of any conclusive morphological differences between catalysts of different activities, either in this or previous work, we propose that support acidity may play an intrinsic role in hydrotreating catalyst performance; working in conjunction with any changes in supported MoS_2 caused by support modification. Addition of Zr alkoxide to Al_2O_3 increases both the Lewis and Brønsted acidity of the catalyst, which may account for the observed activity increase. These additional acid sites reside on the support and are associated with Zr attached to Al_2O_3. Undoubtedly this activity increase is associated with the observed modified surface hydroxyl groups, in a mechanism involving increased reactivity of the reactants. No direct measurement of acidity was done on the Zr nitrate modified catalysts; however, the NMR studies indicate that surface Al_2O_3 is unperturbed by Zr deposited as a non-interacting species. The observed decrease in HDS activity over the unmodified Ni–Mo catalyst may be due to physical blocking or suppression of active sites by Zr which is not associated with the support.

4. Conclusion

Zirconium modifiers to conventional Ni–Mo/Al_2O_3 hydrotreating catalysts either enhance or diminish activity. When added in the form of zirconium nitrate, the result is a decrease in HDS activity. Zr added in the form of a precursor that interacts with the support, such as Zr alkoxides, results in increased activity. In either case, investigations by LRS, IR, and XPS indicate no change in the structure of the active metals, demonstrating that Zr is not likely affecting the active sites for hydrodesulfurization.

However, IR of pyridine adsorption and ^{27}Al NMR reveal significant increases in surface Al_2O_3 Lewis and Brønsted acidity when Zr alkoxide is used. This indicates an indirect effect of Zr on activity, through modification of the support. Our results are consistent with the previous findings that increased acidity in hydrotreating catalysts results in higher HDS activity [13,18–22].

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