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Mixed oxide supported hydrodesulfurization catalysts—a review

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Abstract

Support effects form important aspect of hydrodesulfurization (HDS) studies and mixed oxide supports received maximum attention in the last two decades. This review will focus attention on studies on mixed oxide supported Mo and W catalysts. For convenience of discussion, these are divided into Al_2O_3 containing mixed oxide supports, TiO_2 containing mixed oxide supports, ZrO_2 containing mixed oxide supports and other mixed oxide supports containing all the rest. TiO_2 containing mixed oxides received maximum attention, especially TiO_2–Al_2O_3 supported catalysts. A brief discussion about their prospects for application to ultradeep desulfurization is also included. An overview of the available literature with emphasis on research carried out in our laboratory form the contents of this publication.

Keywords: Mixed oxide supports; Hydrodesulfurization CoMo; NiMo catalysts; Support effects; Hydrodeoxygenation; Hydrogenation

1. Introduction

Increasing awareness of the impact of environmental pollution by automobiles has shifted the responsibility of pollution control to the refiner's side. As a consequence stringent fuel specifications for gasoline and diesel fractions resulted. In the case of diesel fuels the sulfur level is expected to be lowered to 50–10 ppm range in large part of developed and developing countries by the end of this decade [1,2]. In order to reach 50 ppm level from the existing 500 ppm sulfur specification, it was reported that the catalytic activity needs to be increased by four to five times that of the present ones [3]. In order to achieve this goal many approaches have been followed among which variation of support is an important one. The support effects are studied for other reasons such as understanding the role played by support in dispersing the active components and promoters and altering the catalytic functionalities through metal–support interaction [4–7]. Many materials have been tried as supports to Mo and W active components. Some of which are SiO_2 [8], MgO [9], ZrO_2 [10,11], TiO_2 [12,13], carbon [14–16], zeolites like Na–Y [17], USY [17], mesoporous materials like MCM-41 [18–20], HMS [21,22], SBA-15 [23] clays, pillared clays [24] and mixed oxides derived from above-mentioned oxides. Some of the oxides like TiO_2, ZrO_2 showed outstanding activities [12,13]. However, the low surface area, limited thermal stability and unsuitable mechanical properties prevented their commercial exploitation. With an aim to overcome these disadvantages mixed oxides of these materials with γ-Al_2O_3 have been used as supports to take advantage of favorable characteristics of both the systems [25–28]. Some systems containing SiO_2, MgO, ZrO_2, B_2O_3 have also figured in the studies in order to understand the role of support in hydrotreating reactions [6].

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Overall a number of mixed oxide supports containing M and W active components and Co or Ni promoters have been studied for hydrodesulfurization (HDS), hydrogenation (HYD), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO), etc. TiO_2–Al_2O_3 system has been extensively studied because of its commercial prospects [27,28]. Others such as ZrO_2–TiO_2, ZrO_2–Al_2O_3 [29], ZrO_2–Y_2O_3 [30–32], SiO_2–Al_2O_3 [33–39], and Al_2O_3–B_2O_3 [39–43] also received considerable attention. Systems such as ZrO_2–SiO_2 [44], TiO_2–SiO_2 [45], MgO–Al_2O_3 [29], MgO–SiO_2 [39], SiO_2–CeO_2 [46], and TiO_2–MnO_2 [47] also figured in some investigations related to exploratory studies. A review of available literature on this systems will be discussed with special emphasis on research carried out in our group. The available literature is grouped into Al_2O_3 containing mixed oxides, TiO_2 containing mixed oxides, ZrO_2 containing mixed oxides, and other mixed oxide systems, comprising of all others where limited information is only available, for the convenience of discussion.

2. Al_2O_3 containing mixed oxides

2.1. SiO_2–Al_2O_3 supported catalysts

Mo, CoMo, NiMo, NiW, W, supported SiO_2–Al_2O_3 mixed oxides studied extensively by a number of authors on various aspects like structure, texture and catalytic activities [33–39,48]. One of the variables studied is the composition of the support. The structure of MoO_3 phase as a function of support composition was also studied. The dispersions were evaluated using ESCA and oxygen chemisorption, which indicated that the dispersion of molybdenum decreases with the increase of SiO_2 in the support. The active ‘OH’ groups on the surface were estimated and the concentration of such groups closely followed the activity variation. The decrease in availability of active OH groups is probably responsible for the observed decrease in dispersion, as it is well known that molybdenum interacts with basic hydroxyl groups on the surface of the support [39].

The three functionalities HDS, HYD and hydrocracking as measured using model compounds, varied in three different ways as a function of composition of the support. The HDS of thiophene dropped sharply, HYD of 1-hexene decreased linearly while hydrocracking of isooctene increased with SiO_2 in the support to reach a maximum at 75 wt.% SiO_2 in the support [38]. Liu et al. [49] studied HDS of dibenzothiophene, HYD of naphthalene, C–N bond cleavage of indole on the same catalysts at elevated pressure and concluded similar results are obtained in this case also. This clearly shows that support indeed influence the activities and the support effect is different for different functionalities indicating that the functionalities originate from different set of sites. While HDS and HYD are related to supported MoS_2 phase, the hydrocracking is largely due to the protonic acidity of the SiO_2–Al_2O_3 support. Similar results are also obtained on W/SiO_2–Al_2O_3 [37].

2.2. B_2O_3–Al_2O_3 mixed catalysts

B_2O_3–Al_2O_3 supported Co–Mo catalysts received considerable attention in recent years. Murali Dhar et al. [38] studied the effect of boron on HDS, or HYD, and hydrocracking and did not observe any beneficial effects for HDS, HYD, but the hydrocracking activity is increased. Dubois and Fujueda [40] studied 3 wt.% Co–10 wt.% Mo/3 wt.% B_2O_3–Al_2O_3 for VGO hydrotreatment. They observed that there is no effect on HDS and HDN but cracking activity sharply improved. Ramirez Diaz et al. [41] characterized Al_2O_3–B (x) supports, where x varied from 0 to 2.0 wt.%, and observed that there are some beneficial effects by boron addition to thiophene HDS and optimum boron composition is 0.8 wt.%. They attributed the increase in HDS activity due to increase in octahedral cobalt and decrease of tetrahedral cobalt in the catalysts. Li et al. [42,43] characterized Ni–Mo/Al_2O_3–B_2O_3 catalysts using XRD, EXAFS techniques and dibenzothiophene (DBT) HDS. Their studies indicated that 2 mol% of B_2O_3 in Al_2O_3 is the optimum level. The presence of boron was found to increase the conversion of DBT to biphenyl slightly and this was attributed as due to increase of acidity. Lecrenay et al. [50] also reported beneficial effects of B_2O_3 inclusion in Al_2O_3 support for gas oil hydrotreatment. Flego et al. studied Al_2O_3–B_2O_3 system for thiophene HDS and concluded that acidity of support influences the activity. Al_2O_3–B_2O_3 system was studied under industrially relevant conditions [52] using atmospheric gas oil and found that these systems are superior to laboratory prepared Al_2O_3 supported catalysts and maximum activity for HDS is obtained at Al/B ratio of 3.5. From these studies it appears that only marginal beneficial effects are observed due to B_2O_3 inclusion in the Al_2O_3 support and this is largely due to increase in acidity of the system.

2.3. ZrO_2–Al_2O_3 mixed oxides supported catalysts

ZrO_2–Al_2O_3 supported molybdenum catalysts promoted by Co and Ni received considerable attention for HDS of thiophene, 4,6-dimethyl dibenzothiophene and also real feed stocks [51,53–55]. The support preparation methods are varied and the materials were thoroughly characterized by FTIR, ESCA, TPR methods. Flego et al. [51] reported that ZrO_2–Al_2O_3 supported CoMo catalysts show higher activities compared γ-Al_2O_3 supported catalysts and similar results were also reported by Zhao et al. [56] with 12 wt.% ZrO_2–Al_2O_3 catalysts for FCC gasoline desulfurization. Damyanova et al. [53] studied ZrO_2–Al_2O_3 in great detail using temperature-programmed reduction (TPR), FTIR, XPS techniques and concluded that Zr in the support influences the reducibility and dispersion of molybdenum positively. Analysis of peak shape and binding energies from XPS results, Nag et al. indicated that metal–support interactions is weak on ZrO_2 supported catalysts. The increase in reducibility in these systems may be due to weaker metal–support interaction compared to γ-Al_2O_3 supported one. Lecrenay et al. [50] employed NiMo/ZrO_2–Al_2O_3 for HDS of 4,6-dimethyl dibenzothiophene, gasoil and LCO. They have concluded that this catalyst exhibited higher HDS activity compared to commercial NiMo/γ-Al_2O_3 catalyst.

We have examined Mo, CoMo [29] supported on ZrO_2–Al_2O_3 on a series of catalysts containing 0–14 wt.% Mo and found out 8 wt.% Mo as optimum Mo loading. Oxygen uptakes obtained at $-77\,^{\circ}C$ also showed similar trend. Both Mo, CoMo supported on ZrO_2–Al_2O_3 exhibited higher activities compared Al_2O_3 supported catalysts. The composition variation of the support indicated that ZrO_2–Al_2O_3 (1:1) gave maximum activity for HDS, HYD functionalities. The TPR results indicated that the reducibility increased with introduction of ZrO_2 into Al_2O_3. It appears that increase in reducibility and consequent increase in anion vacancies as observed by oxygen chemisorption seems to be responsible for the increase in activity in this system.

3. Ti containing mixed oxide systems

3.1. TiO_2–Al_2O_3 system

As mentioned earlier, TiO_2 supported systems exhibited higher activities compared to Al_2O_3 supported Mo and CoMo systems. However, thermal instability, low surface area and poor mechanical properties came in their way of commercial exploitation. In order to overcome these disadvantages and also get more insight into the role played by the Ti, in Ti containing supports, a number authors followed several methods like grafting of TiO_2 on γ-Al_2O_3, SiO_2, etc. and forming mixed oxides of TiO_2 with other oxides such as Al_2O_3, SiO_2, ZrO_2. Among these mixed oxides TiO_2–Al_2O_3 systems received maximum attention while several authors also studied TiO_2–ZrO_2 and TiO_2–SiO_2 is comparatively less studied. Our results on these three systems will be discussed after reviewing the results presented by different authors in the literature.

TiO_2–Al_2O_3 supports with varying TiO_2 contents were studied by a number of investigators with respect to their physico-chemical properties [25,26,57–66] as well as, as supports to metal catalysts [57–66]. There is also considerable literature on TiO_2–Al_2O_3 as supports for MoO_3 and WO_3 catalysts. TiO_2–Al_2O_3 supports can be prepared by various ways like co-precipitation, chemical vapor deposition. grafting, impregnation, etc. techniques [25,62]. All these methods lead to TiO_2–Al_2O_3 supports of high surface area. However, some physico-chemical properties like acidity are reported to be highly dependent on preparation method of the support material. Variation of physico-chemical properties and acidity as a function of preparation method was studied by Rodenas et al. [65] and found that the samples prepared by urea hydrolysis are less acidic compared to samples prepared by ammonia precipitation. They observed surface enrichment of alumina in the case of samples prepared by urea hydrolysis and also noted considerable differences in oxidizing and reducing properties. Lahousse et al. [59] studied acid base properties of support prepared by hydrolysis of alkoxides of Al and Ti ions of varying composition and observed that Brønsted and Lewis acidity is maximum in the vicinity of 50–60 mol% of Al_2O_3. Zhaobin et al. [62,63] compared TiO_2–Al_2O_3 precipitation, impregnation and grafting techniques for dispersion of TiO_2 over Al_2O_3 and found that grafting technique gives best dispersion of TiO_2 over Al_2O_3. This observation is based on the results obtained by using a battery of characterization techniques like XPS, TEM, XRD, TPD of ammonia, etc.

Now considering TiO_2–Al_2O_3 as a support for molybdenum containing catalysts with reference to hydrotreating reactions, Delmon and coworkers [62,63] were one of the earliest researchers to report on this system. They have employed XRD, AEM, XPS, and TPR techniques and evaluated HDS and HYD activities on catalysts using supports prepared by precipitation, impregnation and grafting techniques and made a series of interesting observations. They observed that the type of Mo^{6+} species present on the catalyst system depended on the coverage by TiO_2. They also observed from TPR that the hydrogen consumption increases with TiO_2 content, which suggests that TiO_2 helps molybdenum to reduce to lower valence states than on γ-Al_2O_3 supported catalysts. They also concluded that metal–support interactions are weak on TiO_2–Al_2O_3 supported ones. Their catalytic activity studies indicated that modification of Al_2O_3 by TiO_2 improves HDS and HYD activities. They studied TiO_2–Al_2O_3 supports containing maximum of 40 wt.% TiO_2. Zhaobin et al. [64] from their temperature-programmed sulfiding studies on Mo/TiO_2–Al_2O_3 catalysts containing upto 25.4 wt.% of Al_2O_3 and found that presence of titania reduces sulfiding temperature by 80–100 °C and also the sulfiding as indicated by laser Raman spectroscopic studies was complete on titania rich samples. They have concluded that presence of TiO_2 on the surface of Al_2O_3 decreases the interaction between MoO_3 and the support. Ramirez Diaz et al. [41] considered full range of TiO_2–Al_2O_3 compositions as support for MoO_3 in relation to oxide as well as sulfided state and catalytic activity. They concluded that the supports with low TiO_2 contents, titanium ions will be bonded mainly via Ti–O–Al bridges. At higher titanium contents higher proportion of Ti–O–Ti bonds are found. They also observed that above $TiO_2/[TiO_2 + Al_2O_3]$ ratio 0.5, formation of greater number of Ti–O–Ti bonds. Their studies also indicated that Al/Ti ratio measured by ESCA are close to theoretical values but however beyond $TiO_2/[TiO_2 + Al_2O_3]$ ratio of 0.5 these supports showed lower values than the theoretical value. They observed that intrinsic HDS activity is maximum around $TiO_2/[TiO_2 + Al_2O_3]$ ratio of 0.95. They studied these catalysts in detail by acidity measurements using IR spectra of adsorbed pyridine. They observed a relationship between acidity and HDS activity. Pophal et al. [25] studied TiO_2–Al_2O_3 supports with different loadings of TiO_2 using chemical vapor deposition technique. They studied upto 14 wt.% TiO_2. The examination of IR spectra in hydroxyl region, which indicated the formation of Al–O–Ti linkages during the CVD process. From XPS data, Ti 2p/Al 2p ratio also indicated homogeneous distribution of TiO_2. The Mo 3d binding energy in oxide as well as sulfided state indicated better sulfidability of TiO_2–Al_2O_3 supported catalysts compared to Al_2O_3. The TiO_2–Al_2O_3 formulations are intermediate in reduction and sulfidation behavior compared to Al_2O_3 and TiO_2. This was concluded from S/Mo ratio of the supports. They concluded that sulfidation on mixed oxide supports is more efficient over composite supports than over γ-Al_2O_3. They carried out HDS of dibenzothiophene and methyl substituted dibenzothiophenes which gave useful information about their utility in deep desulfurization application. These authors concluded that TiO_2–Al_2O_3 supported catalysts are more efficient in converting 4,6-dimethyl dibenzothiophene, which is more difficult molecule to desulfurize. They have also suggested that on these catalysts the HDS mechanism is different. Oleguin et al. [66] studied TiO_2–Al_2O_3 supported MoO_3 catalysts as well as CoMo and NiMo catalysts by ammonia TPD, UV-Vis diffuse reflectance spectroscopy, high-resolution electron microscopy and thiophene and benzothiophene HDS. Their characterization results indicated that there is an increase in Co/Al_2O_3 formation on Al_2O_3 rich formulations. HRTEM results indicated that crystallites are shorter in length on mixed oxide supports compared to that over γ-Al_2O_3. They observed an increase in intrinsic activity at high titania contents. They noted that support modifications has pronounced effect on thiophene HDS compared to benzothiophene HDS contrary to that observed by Pophal et al. [25] that these catalysts are good for deep desulfurization.

Overall the literature data indicated that Al–O–Ti linkages are formed upto TiO_2–Al_2O_3 (1:1) composition and beyond this region Ti–O–Ti linkages are seen. Mo supported on TiO_2–Al_2O_3 is more reducible and sulfidable compared to γ-Al_2O_3, but the behavior is intermediate between γ-Al_2O_3 and pure TiO_2 supported ones. There was no complete agreement on activities, every body in general agree that TiO_2–Al_2O_3 supported catalysts are more active than γ-Al_2O_3 supported ones. But they differ on the composition of TiO_2 in the support where the maximum activity occurs [67,68].

We have prepared a series of TiO_2–Al_2O_3 supports with varying TiO_2 contents by urea hydrolysis method at 90 °C. The precipitate obtained by urea hydrolysis was calcined at 550 °C after drying at 110 °C overnight. The CoMo, NiMo catalysts were prepared by incipient wetness method [58]. These are of high surface area in the range 117–194 m^2/g. These surface areas as are similar to γ-Al_2O_3 but higher than that of TiO_2 supported catalysts (59 m^2/g). The X-ray diffraction results indicated that well defined anatase peaks are only seen on TiO_2 rich samples. At a Mo loading of 8 wt.% there is no indication for any characteristic lines due to MoO_3. The TPR data indicated reducibility is more in TiO_2 rich samples. Oxygen uptakes also pass though a maximum as a function of TiO_2 content. The maximum occurs at Mo/TiO_2–Al_2O_3 (1:1) composition. The dispersion as measured by oxygen chemisorption of the catalysts also showed maximum at this composition. The crystallite sizes evaluated using oxygen chemisorption data showed a minimum at this composition. Various catalytic functionalities HDS, HYD and HDO also passes though a maximum at the same support composition suggesting that increase in dispersion is indeed responsible for increase of activity.

3.1.1. *Mode of active phase formation and catalytic action*

In order to understand the total working of the system as a function of TiO_2 content the right starting point is support preparation itself. As discussed earlier the supports can be prepared by various methods like impregnation, grafting, and coprecipitation by ammonia or urea hydrolysis, etc. techniques. The support characteristics, of course depends upon the technique and the amount of Ti ions that can be incorporated into γ-Al_2O_3 without formation of separate phases, depends upon the preparation method, and for a given preparation method, the chosen conditions and TiO_2/Al_2O_3 ratio are important. Homogeneous precipitation using urea hydrolysis is employed in the case of our samples. Pure titania easily sinters and comparatively of low surface area. However, all TiO_2–Al_2O_3 compositions studied are of reasonably high surface area. As the Al_2O_3 content increases the XRD results indicated that TiO_2 lines broaden which indicates that TiO_2 dispersion in Al_2O_3 is increasing. However, since X-ray visible crystallites of anatase are of dimensions greater than 50 Å in size, this is not likely to be the phase where the maximum amount of MoO_3 is located, as the support surface area offered by this phase is only small compared to other phases. There is another phase where well dispersed Ti in Al_2O_3 matrix with Ti–O–Al bonds. Since our sample the 1:1 composition is more likely to have maximum Al–O–Ti bonds because of high surface area and also as the XPS results by Ramirez Diaz et al. [61] also showed that $TiO_2/[TiO_2 + Al_2O_3] = 0.5$, Ti/Al ratios by XPS are close to theoretical ones, therefore it is likely that Ti–O–Al linkages are maximum on the surface of Mo/TiO_2–Al_2O_3 (1:1). Assuming this to be the case the highly dispersed molybdenum should be located on these ions. The oxygen chemisorption results show that molybdenum selectively interacts with only part of the surface. Therefore, the molybdenum, based on the literature data likely to interact with hydroxyl groups of suitable energy on these ions. The literature reported on Mo/various oxides suggests that these likely hydroxyl groups interacting are most basic ones. The TPR studies indicated that mixed oxide supported catalysts are intermediate in reduction behavior between Al and Ti. This suggests that both Ti and Al ions are involved in binding the supported molybdenum. As we move from TiO_2 to Al_2O_3 via various TiO_2–Al_2O_3 ratios Ti–O–Al bonding is likely to increase and since ESCA results by Ramirez Diaz et al. [41] demonstrated upto $TiO_2/[TiO_2 + Al_2O_3] = 0.5$ maximum number of Ti ions are present on the surface. The TiO_2–Al_2O_3 (1:1) is expected to accommodate most of the MoO_3 through its hydroxyl groups, and in such a case the dispersion is expected to be maximum at this composition. The oxygen chemisorption on the sulfided catalysts indeed showed maximum dispersion and small crystallite sizes at this composition.

The catalytic activities for various functionalities also followed the same trends since the active sites for various functionalities are related to dispersion.

In the case of promoted catalysts the promoters are likely to be located at the edges of MoS_2 crystallites. Therefore, the maximum dispersion of MoS_2 is likely to accommodate maximum amount of edge sites. In promoted catalysts also more or less similar variations of activities are observed. Small variations are likely due to surface morphology of MoS_2 as a function of support composition. The intermediate values of kHYD/kHDS and kHYD/kHDO suggest that the MoS_2 supported on mixed oxides have characteristics of both the pure supports, viz. TiO_2 and Al_2O_3. Morphological changes can significantly effect HYD selectivity as it is well known that HYD and C–S bond cleavage takes place on different sites and morphological changes can alter the ratio of such sites. It appears that the mixed oxide supports increase the number of sites as well as effects the activity per site. The optimum number of sites and activity per site occurs at TiO_2–Al_2O_3 (1:1) composition.

3.2. Promotional effect

Promotional effect of both cobalt and nickel were investigated on 8 wt.% Mo on TiO_2–Al_2O_3 (1:1) support and are shown in Fig. 1. The model reactions used are thiophene HDS, cyclohexene HYD, and furan HDO. It can be seen that in TiO_2–Al_2O_3 system cobalt causes 27% increase in HDS and 33.5% HYD activity at 3 wt.% cobalt level. In the case of nickel the increase in HDS is 47.6% and for HYD it is 21.5%. Compared to MoS_2/γ-Al_2O_3 the promotional effect is small. The small promotional effects may be attributed to formation of $CoTiO_3$, $NiTiO_3$ type of surface compounds and also may be due to $CoMoO_4$ formation. On γ-Al_2O_3 supported catalysts there is 139% increase in HDS for cobalt and 142% for nickel at 3 wt.% level. In the case of CoMo/TiO_2 support the promotional effect for HDS is 39% and for NiMo/TiO_2 it is 103%. It appears that on Ti containing supports, Ni is a better promoter compared to cobalt. Overall, CoMo/TiO_2–Al_2O_3 is 50% more active than conventional CoMo/γ-Al_2O_3 formulation, and NiMo/TiO_2–Al_2O_3 (1:1) is 100% more active than that of conventional NiMo/Al_2O_3 formulation. It clearly shows that TiO_2–Al_2O_3 supported CoMo, NiMo catalysts are superior to conventional CoMo, NiMo supported on γ-Al_2O_3.

3.3. Variation of Mo loading

We have varied Mo content on MoS_2/TiO_2–Al_2O_3 (1:1) from 2 to 14 wt.% [58]. The MoS_2/TiO_2–Al_2O_3 catalysts were characterized by low temperature oxygen chemisorption and catalytic activities for various functionalities using model reactions like thiophene HDS, cyclohexene HYD and furan HDO. The oxide precursors MoO_3/TiO_2–Al_2O_3 and pure support were characterized by XRD, BET surface area, pore volume and temperature-programmed reduction

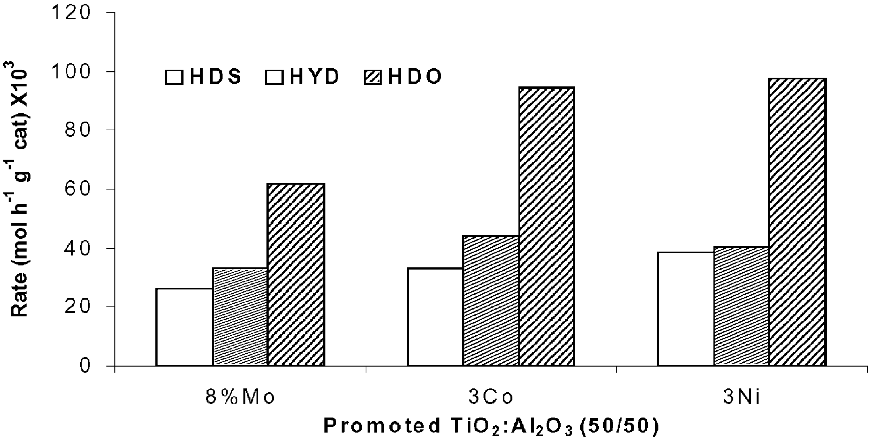

Fig. 1. Effect of promoters on reaction rates of 8 wt.% Mo/TiO_2–Al_2O_3 catalysts.

techniques. The XRD results indicated that upto 8 wt.% MoO_3 loading molybdenum is very well dispersed and above this loading there is evidence for the formation of MoO_3 crystallites, which can be noted from the diffractograms, and whose concentration increased with further increase of Mo loading. The temperature-programmed reduction behavior indicated that MoO_3 is more reducible on TiO_2–Al_2O_3 compared to Al_2O_3 but less reducible compared to TiO_2, there by showing intermediate reduction behavior compared to the constituent oxides. The variation of H_2 consumption per Mo indicated that there are two types of phases characterized by two different reduction behaviors and the transition point is 8 wt.% MoO_3. The oxygen uptakes on sulfided catalysts increased with increase of MoS_2 loading up to 8 wt.% MoO_3 and then decreased. The surface coverage increased up to 8 wt.% MoO_3 and started decreasing rapidly above this point. The crystallite size calculated from oxygen uptakes indicated that the size is small (∼35 Å) and this crystallite size is more or less constant upto 8 wt.% MoO_3 and increases rapidly with further increase of molybdenum loading. All these results suggest that there are two distinct regions below and above 8 wt.% MoO_3. The small crystallite size in both oxide and sulfided state suggest that molybdenum is present in monolayer dimensions upto 8 wt.% Mo loading and beyond this region large crystallites of MoS_2 are present. Since the surface coverage is small even at the monolayer completion at 8 wt.% Mo, it can be construed that the monolayer is not a continuous monolayer but it is in the form of patches characterized by an average size of 35 Å. These monolayer patches are likely to be formed by interaction of oxomolybdenum species with surface hydroxyl groups of TiO_2–Al_2O_3 support [6]. It is not possible to distinguish to which of two ions in the support the hydroxyl group is linked but the intermediate behavior of reduction suggests that it is likely that both ions are involved. Therefore, it appears that the molybdenum first interacts with surface hydroxyl groups of suitable strength and forms patches of MoO_3 and these patches grow in number upto 8 wt.% MoO_3, at this concentration all sites available to bind MoO_3 to TiO_2–Al_2O_3 are exhausted and further addition of molybdenum results in three-dimensional MoO_3 crystallites. In the sulfided state also similar behavior is observed as can be noted from variation of oxygen uptakes and related parameters like crystallite size as well as variation of catalytic functionalities. The reductive sulfiding creates MoS_2 patches with coordinatively unsaturated sites or anion vacancies. These vacancies increase in number as the number of MoS_2 patches increase with Mo loading upto the completion of sulfided monolayer. Beyond this point a rapid crystallite growth decreases the anion vacancies at higher loadings. Since it is well known [69] that oxygen chemisorption takes place on anion vacancies and also that the activities are related to these vacancies [6], both catalytic properties and oxygen chemisorption are related to anion vacancies, and it is not surprising that a linear correlation exists between catalytic activity for these functionalities on samples containing 2–14 wt.% Mo and oxygen uptakes (Fig. 2). However, since the correlation is obtained with all the functionalities it is clear that oxygen chemisorption is not specific to any one of the functionalities but is related to general state of dispersion of MoS_2 on TiO_2–Al_2O_3 support.

3.4. Titania–zirconia mixed oxide supported molybdenum catalysts

In the literature there is considerable interest on TiO_2–ZrO_2 supported mixed oxides as supports for HDS and related reactions [70]. Daly et al. [47] studied the HDS reaction over Co–Mo catalysts supported on TiO_2–ZrO_2 mixed oxides. They prepared the mixed oxide supports by homogeneous precipitation method using urea hydrolysis. They found that the mixed oxide supports have higher surface areas than their single oxide counterparts. They observed from NO chemisorption and temperature-programmed desorption studies of Co–Mo/TiO_2–ZrO_2 and Co–Mo/Al_2O_3 that the molybdenum–support interaction is weaker in mixed oxide support. They also found that the coordinately unsaturated (CUS) sites are easy to form in mixed oxide support than that on Al_2O_3 support and CUS sites are more in concentration on this mixed oxide support. They further reported that TiO_2–ZrO_2 supported catalysts are prone to deactivate faster in comparison to Al_2O_3 supported ones. The deactivation of mixed oxide is quicker may be due to presence of stronger acidic sites compared to Al_2O_3 support. The deactivation has also been reported to occur by pore plugging.

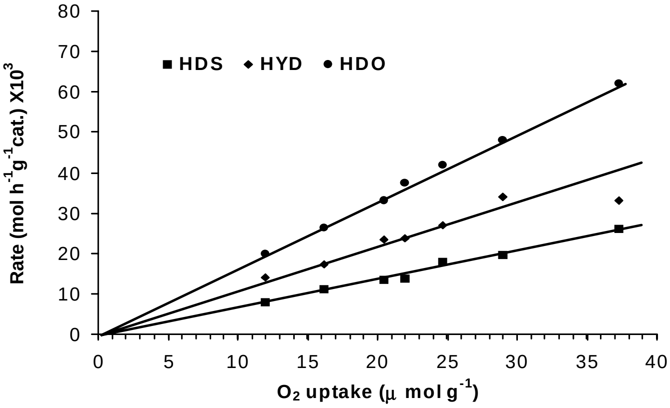

Fig. 2. Correlation between O_2 uptake and activity on MoS_2 on TiO_2–Al_2O_3 (1:1).

Weissman et al. [71] prepared Mo and Ni–Mo hydrotreating catalysts supported on TiO_2–ZrO_2 by supercritical fluid (SCF) extraction method. They studied the HDS and HDN activities of the sulfided catalysts at 300 °C temperature and used light straight-run gas oil as a feed for activity study. They observed that HDN activity of the mixed oxide supported catalysts is higher than that of TiO_2, ZrO_2 and Al_2O_3 supported catalysts. The higher HDN activity on mixed oxide supported catalyst may be due to acidic nature of support. It is reported that the acidic sites of the catalysts facilitate the HDN reaction [71]. They also observed that Ni–Mo catalysts supported on mixed oxide showed greater HDS and HDN activities, on surface area basis than the equivalent Al_2O_3 supported ones. They concluded that the higher activities of mixed oxide supported catalysts may be due to the better dispersion or smaller particle size than that of Al_2O_3 supported catalyst. The smaller crystal size leads to greater number of CUS sites or anion vacancies. These anion vacancies or CUS sites are responsible for HDS catalytic activities and hence mixed oxide supported catalysts showed higher activities.

Miciukiewiez et al. [72] studied Raman spectroscopy on 12 wt.% MoO_3 catalyst supported on TiO_2–ZrO_2 mixed oxide. The TiO_2–ZrO_2 mixed oxide (1:1 molar ratio) was prepared by coprecipitation method and the surface area of this catalyst is very high (~349 m^2/g). After calcination at 550 °C, the mixed oxide was found to be amorphous. They reported that the dispersed Mo species on the mixed oxide support may be identified as polymeric molybdenum species.

Wang and Chang [73] studied the HDS reaction of dibenzothiophene and HDN of aniline reaction over Co–Mo on TiO_2–ZrO_2–V_2O_5 catalysts and over Co–Mo on γ-Al_2O_3 catalysts. The reactions have been carried out in a continuous flow microreactor at 240–350 °C and 355 MPa. It was found that Ti/Zr/V supported catalysts had higher HDS and HDN activities than Al_2O_3 supported catalysts. The Ti/Zr/V-supported catalysts were also more active than the commercial catalyst (HR-306) in HDS of petroleum feed stocks.

In our laboratory [74] we have prepared a series of catalysts using TiO_2–ZrO_2 supports [70,74]. The variables studied were the support composition and Mo loading. On a single support having optimum catalytic activity, Mo loading was varied from 2 to 14 wt.%. The supports were prepared by homogeneous precipitation technique. The BET surface areas varied 181–225 m^2/g. The pore volumes ranged from 0.38 to 0.21. An amount of 12 wt.% MoO_3 was deposited on each composition TiO_2–ZrO_2 support. This wt.% Mo was chosen, as this was the composition at which the maximum activity as a function of Mo loading was obtained. Low temperature oxygen chemisorption, catalytic activities were evaluated on sulfide catalysts. Various functionalities studied were the thiophene HDS, cyclohexene HYD and furan HDO. The oxide precursors were examined by XRD measurement. These results indicated that anatase lines of TiO_2 were

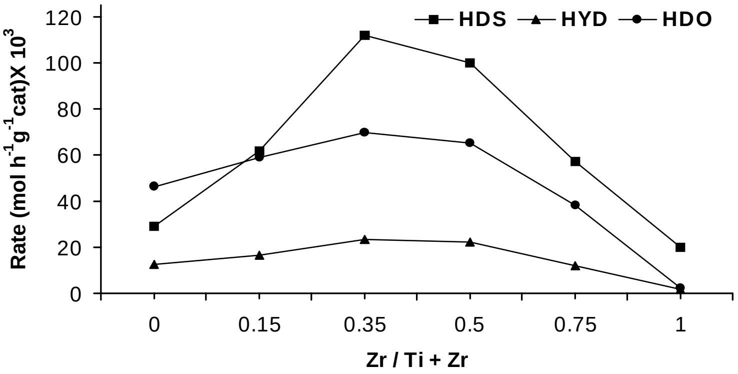

Fig. 3. Variation of rate on Mo supported catalysts as a function of $ZrO_2/ZrO_2 + TiO_2$ ratio.

observed on TiO_2 rich formulations but no ZrO_2 lines were seen in any composition, except in pure ZrO_2. At 12 wt.% Mo loading no MoO_3 lines are seen on any of the ZrO_2–TiO_2 compositions indicating that molybdenum is well dispersed on the ZrO_2–TiO_2 compositions studied. The catalytic functionalities HDS, HYD and HDO all increased with the increase of zirconia content in the support upto 35 mol% ZrO_2 and then started decreasing (Fig. 3). In other words for this method of preparation TiO_2–ZrO_2 (65:30) is the optimum composition of the support. It is interesting to see that the kHYD/kHDS, kHDO/kHDS and kHDO/kHYD all show intermediate values compared to either pure ZrO_2 or TiO_2 (Fig. 4). It is clear from these studies that TiO_2 (65:35) containing 12 wt.% Mo is the best composition for all three functionalities and it is also clear that ZrO_2–TiO_2 can accommodate more molybdenum in highly dispersed form than γ-Al_2O_3 support. It is well known that 8 wt.% Mo is the Mo level that results in maximum activity on this support.

Coming to variation of Mo loading on ZrO_2–TiO_2 (65:35), the Mo loading is varied from 2 to 16 wt.% [38]. XRD measurements suggested that there are no lines due to MoO_3 upto 14 wt.% Mo loading. There is a faint indication for the presence of MoO_3 strong lines at this loading, indicating that MoO_3 is well dispersed upto 12 wt.% Mo loading on these catalysts. The TPR results indicated that reducibility of MoO_3 increases upto 12 wt.% and then levels off. The ESCA results also indicated the $I_{Mo}/I_{Ti} + I_{Zr}$ ratio increased upto 12 wt.% Mo, indicating that the dispersion is increasing upto this loading. Low temperature oxygen chemisorption studies indicated a maximum in oxygen uptakes occurred at 12 wt.% (Fig. 5). Since it is well established that oxygen chemisorption takes place on anion vacancies and oxygen chemisorption

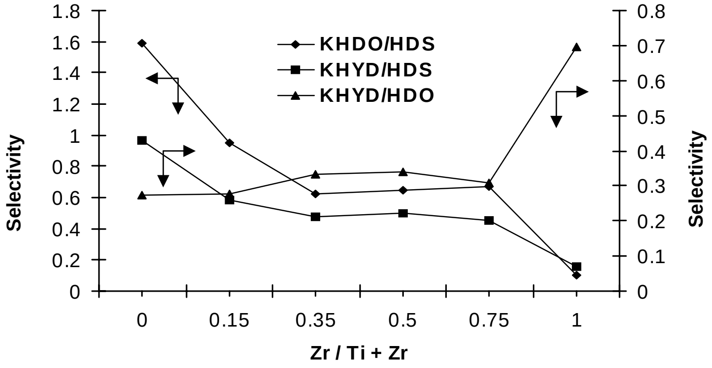

Fig. 4. Selectivity variation as a function of $ZrO_2/ZrO_2 + TiO_2$ ratio.

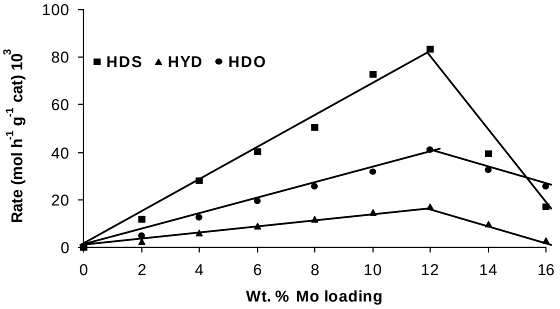

Fig. 5. Variation of rate as a function of Mo loading on TiO_2–ZrO_2 (65:35).

is a measure of dispersion of molybdenum sulfides, it may be taken that MoO_3 is well dispersed and present in monolayer dimensions upto this loading. The catalytic functionalities for the three reactions HDS of thiophene, HYD of cyclohexene and HDO of furan all increased upto 12 wt.% loading and then decreased. Similar variation of oxygen uptakes and the three catalytic functionalities suggest that these activity parameters are related to oxygen chemisorption though dispersion. This is also supported by linear correlations between O_2 uptake and functionalities passing through origin, obtained on these samples. The results of TiO_2–ZrO_2 as a function of Mo loading are very similar to Mo/TiO_2–Al_2O_3 and the explanation for activity variation given earlier equally applies to this system also.

In our attempts to understand the support effects in mixed oxides, we have studied catalysts based on TiO_2–SiO_2 support prepared by homogeneous precipitation technique [75]. The surface area of this TiO_2–SiO_2 support of varying TiO_2/SiO_2 ratios ranged between 300 and 380 m^2/g. One this supports, studies were carried out as a function of composition of the support at a fixed molybdenum content. These studies indicated that the HDS activity is maximum in the sample containing 15 wt.% TiO_2 in SiO_2 and at higher TiO_2 contents the activity decreases. The activities however were higher than either pure TiO_2 or SiO_2 supported catalyst. Hydrogenation functionality however is very high on SiO_2 and the HYD activity decreases with the increase of TiO_2 in SiO_2. The catalysts prepared using 3 wt.% Co or 3 wt.% Ni showed good promotional effects for all three the functionalities. These promoted catalysts followed same trends as the unprompted catalysts as a function of TiO_2 content in the support. It is interesting that the promotional effects in TiO_2–SiO_2 are higher than, TiO_2–Al_2O_3 and TiO_2–ZrO_2 supported molybdenum catalysts.

Molybdenum content on 15 wt.% TiO_2–SiO_2 was varied from 2 to 14 wt.%. XRD results indicated Mo is well dispersed in this catalysts upto 8 wt.% Mo loading. The low temperature oxygen chemisorption on the sulfided samples indicated that the uptakes increase upto 8 wt.% Mo on these catalysts (Fig. 6). It should be mentioned at this juncture that on TiO_2, the O_2 uptake increase upto 8 wt.% and on SiO_2 increases only upto to 4 wt.%. The catalytic activities for HDS, HYD and HDO also increase upto 8 wt.% and then starts decreasing. In the case of all the three functionalities excellent correlations were obtained between oxygen chemisorption and catalytic activities. This is expected since O_2 chemisorbs on anion vacancies and it is well known that anion vacancies on the active site are responsible for catalytic activity.

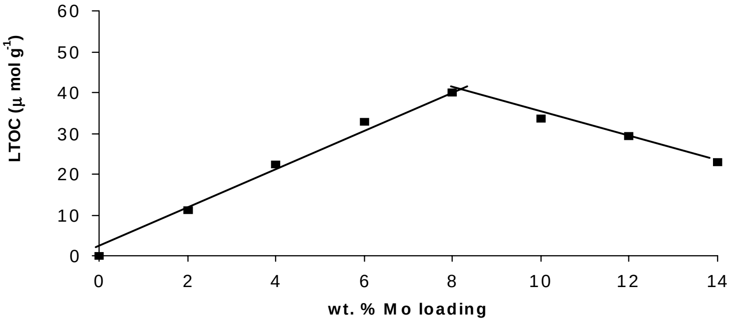

Fig. 6. Variation of O_2 chemisorption as a function of Mo loading on TiO_2–SiO_2 (12:88).

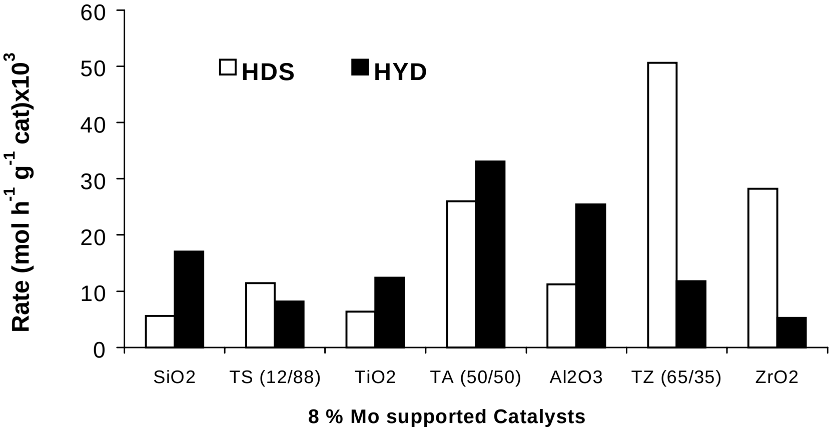

Fig. 7. Effect of support on catalytic activity for various functionalities.

3.5. Comparison of three Ti containing mixed oxide supports

In this review three supports TiO_2–Al_2O_3, TiO_2–ZrO_2 and TiO_2–SiO_2, containing active component molybdenum, are considered. Two parameters varied are composition of the support at fixed Mo content and variation of Mo content on a support of fixed composition. All the catalysts in the two cases were examined by XRD, oxygen chemisorption and other techniques. The catalytic activity for all the three functionalities were evaluated using model compounds and correlations were obtained between oxygen uptakes and all the three catalytic functionalities. First considering support composition variation, there are significant differences in catalytic behavior as a function of support composition, while TiO_2–Al_2O_3 the maximum in activity occurred at 50:50 ratio, on Mo/TiO_2–ZrO_2 it is 65:35, while on Mo/SiO_2–TiO_2 it is at 15 wt.% TiO_2. Therefore, it appears that the support composition where maximum beneficial effects occurred is specific to each system in question. Evidence from ESCA for maximum Ti–O–Al bonds in the case of TiO_2–Al_2O_3 (1:1) composition was noted in literature. In the case of TiO_2–SiO_2 the Si–O–Ti connectivity was found to be maximum at this composition [39]. It appears that formation of M–O–M bonds between the two metal ions involved, and their growth determines the fixation of molybdenum on the support. Oxygen uptakes obtained on this system were only rough guide of the trends in activities agreeing with earlier suggestion made by Zmierczak et al. [69] on SiO_2–Al_2O_3-based catalysts. It is interesting to note that for HDS reaction, Mo/TiO_2–ZrO_2 appears to be the best among the three supports, followed by Mo/TiO_2–Al_2O_3 and then Mo/SiO_2–TiO_2 [76]. However, it is interesting to note that HYD functionality did not follow the same trend, and in this case the order of decreasing activity is Mo/TiO_2–Al_2O_3 > Mo/TiO_2–ZrO_2 > Mo/TiO_2–SiO_2. As can be noted (Fig. 7) that in the case of TiO_2–ZrO_2 and TiO_2–Al_2O_3 the activities obtained are considerably higher than constituent single oxides indicating that a synergistic action of the two constituents of the support, induced in the supported phase an activity increase, probably due to metal–support interaction. It is interesting to note that on SiO_2–TiO_2 supported catalysts similar synergy is observed in the case of HDS but HYD activity is lower than both the Mo catalysts derived from SiO_2 or TiO_2. This is an instance where HDS and HYD are independently varied via support effect.

Promotional effect of Co and Ni on 8 wt.% molybdenum supported on γ-Al_2O_3, TiO_2, SiO_2, SiO_2–TiO_2 (12:88), and Al_2O_3–TiO_2 (50:50) for thiophene HDS and cyclohexene HYD. From the data shown in Figs. 8 and 9 and Table 1 it can be seen that the promotional effect indeed is present in all the systems studied. However, the extent of promotion is specific to each support and the functionality.

There are striking differences in promotional effects for each functionality, for example, SiO_2 supported Mo exhibits huge promotional effect for HYD,

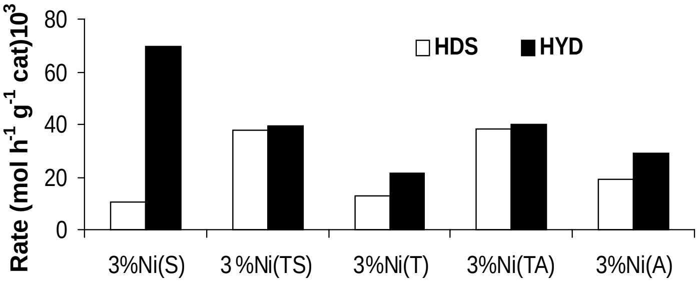

Fig. 8. Ni promotional effect on catalytic functionalities for different supports.

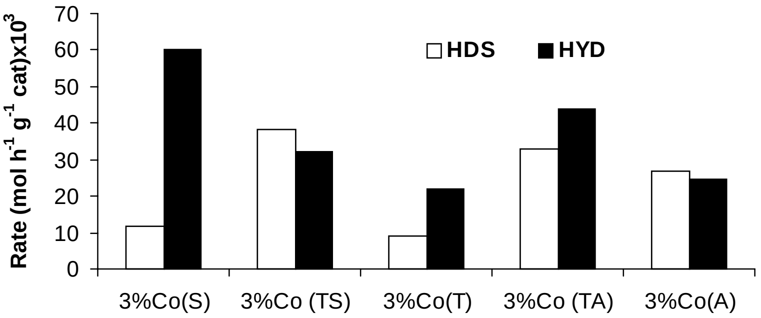

Fig. 9. Co promotional effect on catalytic functionalities for different supports.

whereas HDS is only increased to a small extent. In the case of Al_2O_3 support cobalt exhibited large promotional effect for HDS. The promotional effect of Co or Ni is similar on the mixed oxide systems presented in this investigation. It is interesting to note that there is large promotional effect for both for HDS and HYD in the case of TiO_2–SiO_2 supported molybdenum system. However, on Mo/TiO_2–Al_2O_3 the promotional effect is not large in the case of both Co and Ni. A general observation is that on pure TiO_2 and TiO_2–Al_2O_3 supported systems the promotional effects for both the functionalities is only small, in agreement with the results reported earlier on Mo/TiO_2 [67]. It is also clear that support influences the promotional action of Co

Table 1
Promotional effects on different supports

Supported catalysts[a]	Surface area (m^2/g)	Catalytic activity[b]					
		8 wt.% Mo		3 wt.% Co–8 wt.% Mo promoted		3 wt.% Ni–8 wt.% Mo promoted	
		HDS	HYD	HDS	HYD	HDS	HYD
SiO_2[c]	340	5.6	17.07	11.8	60.0	10.63	69.7
TS (12:88)	312	11.39	8.19	38.4	32.2	37.42	39.4
TA (50:50)	129	26	33.1	33	44	38.4	40.2
Al_2O_3	153	11.2	25.4	26.8	24.7	19.1	29.1
TiO_2	59	6.4	12.4	8.9	22	13	21.7
TZ (65:35)		50.6	11.8				

[a] TS = TiO_2–SiO_2; TA = TiO_2–Al_2O_3; TZ = TiO_2–ZrO_2.

[b] Thiophene HDS, cyclohexene HYD; rate (mol h^{-1} g^{-1} cat.) × 10^3.

[c] 4 wt.% Mo loading.

or Ni in a subtle way. This may be by altering the Mo edge sites on which the promoter atoms reside.

4. ZrO_2 containing mixed oxides supported catalysts

4.1. SiO_2–ZrO_2 supported catalysts

We have studied SiO_2–ZrO_2 supported Mo, CoMo, NiMo catalysts using thiophene HDS, cyclohexene HYD and cumene cracking reactions [44,75]. The variation of support composition and at a fixed support composition variation of Mo content, and at a fixed Mo content variation of Co or Ni were considered. Oxygen chemisorption was used to measure the anion vacancies or dispersion. The maximum in HDS activity was obtained at 0.15 wt.% Zr/Zr + Si ratio, whereas HYD activity showed maximum at 0.30 Zr/Zr + Si ratio. At a fixed support composition the maximum in HDS, HYD and HDO occurred at 6 wt.% Mo on the catalysts. Promotional effect of cobalt and nickel occurred at 3 wt.% Co or Ni on above-mentioned 6 wt.% Mo catalysts. Oxygen chemisorption was also showed similar trends indicating that dispersion Mo is maximum at this composition. The mixed oxides showed higher activities compared to component oxides indicating the superiority of mixed oxides as supports to Mo, CoMo active components.

4.2. ZrO_2–Y_2O_3 system

ZrO_2–Y_2O_3 supported catalysts were studied in considerable detail. Hamon et al. [30] reported Mo/ZrO_2–Y_2O_3 to be two times more active on per atom of Mo basis for biphenyl HYD. Vrinat et al. [31,32] further confirmed the superior activity of these catalysts for thiophene HDS. The observed increase in activity was attributed to the smaller size of particles as observed from HRTEM images. They have also examined NiMo/ZrO_2–Al_2O_3 by XPS and electron microscopy. These studies indicated that Mo is well dispersed and promoter ion did not alter the dispersion. The stacking of MoS_2 slabs and slab lengths were determined from electron microscopy data. These results showed that MoS_2 slab lengths are smaller in the case of ZrO_2–Y_2O_3 than γ-Al_2O_3 suggesting that MoS_2 is better dispersed on Y_2O_3–Al_2O_3. They also suggested NiMoS of Type 2 is formed on Y_2O_3–Al_2O_3.

5. Other mixed oxides

Some mixed oxides like CeO_2–SiO_2 [46], Al_2O_3–P_2O_5 [50], Al_2O_3–Ga_2O_3 [51] were reported as supports to CoMo active phase. Gulkova and Vit used SiO_2–CeO_2 as support to (P) CoMo system for HDS of thiophene and HDN of pyridine and reported that catalysts prepared SiO_2–CeO_2 has higher activities compared Al_2O_3 supported catalysts. Results on CoMo/Al_2O_3–B_2O_3 were reported by Flego et al. [51] indicated that this system exhibits lower activities for thiophene HDS than Al_2O_3 supported catalysts. Lecrenay et al. [50] reported CoMo/P_2O_5–Al_2O_3 system for HDS gas oil, light cycle oil as well as for 4,6-dimethyl dibenzothiophene and this system was found to be superior to Al_2O_3 supported systems.

5.1. Oxides and mixed oxides in mesoporous structure

So far the discussion has been on mixed oxides in the normal sense of the term. However, recently mesostructured oxides and mixed oxides are receiving considerable attention. Some of the interesting materials already tested are MCM-41 [77], Al-MCM-41 [77], HMS, Al-HMS [22,23], Ti-HMS, SBA-15 [23] as supports for Mo and W active components. All these materials showed comparable or several fold higher activities for HDS and related reactions. Although the structural stability of these materials at present is less than desirable there is considerable promise in literature reports to improve their stability. The fact that all these materials that showed promise, like ZrO_2–TiO_2, TiO_2–Al_2O_3 in principle can be synthesized in mesoporous form with very high surface areas and hopefully in thermally stable form, assures plenty of challenging topics of research area based on these materials in future.

6. Mixed oxides as supports in deep desulfurization catalysis

Oxide and mixed oxides supported catalysts for deep desulfurization will be dealt with in detail in the same issue by Segawa et al. However, a brief account is given here for completeness of the information. Al_2O_3–B_2O_3 mixed oxides supported catalysts were found to exhibit higher activity compared γ-Al_2O_3 supported catalysts at an Al/B ratio of 3.5 [52]. Zhao et al. [56] reported TiO_2–Al_2O_3 supported CoMo and NiMo catalysts showed superior activity for desulfurization of FCC gasoline compared to CoMo/γ-Al_2O_3 catalysts. However, they have reported that for the same feed under comparable condition ZrO_2–Al_2O_3 supported catalysts showed lower activity. They attributed the higher activities to change in reducibility. Wei et al. [78] examined TiO_2–Al_2O_3 supported NiMo catalysts for naphtha desulfurization and found that 14.6 wt.% TiO_2 containing TiO_2–Al_2O_3 supported NiMo catalysts exhibited superior activity compared commercial NiMo/γ-Al_2O_3 of comparable composition. They also found that sulfiding treatment is not necessary for these catalysts.

Deep desulfurization of diesel oil to 50 ppm sulfur level or lower depends on the ability of the catalyst to desulfurize alkyl dibenzothiophenes such as 4,6- and 4-alkyl dibenzothiophene. Desulfurization these model compounds in considerable detail were reported by Mochida and coworkers [50] and Segawa and coworkers [27,28] on Mo and NiMo/TiO_2–Al_2O_3. They have also reported desulfurization reactivities with real feeds such as gas oil, light cycle oil under industrially relevant conditions. NiMo/TiO_2–Al_2O_3 with TiO_2 content 8 and 25 wt.% was considered. These catalysts showed superior activity for conversion of 4,6-dimethyl dibenzothiophene. They observed that use of TiO_2 containing supports moderates inhibition by H_2S and aromatics like naphthalene. HDS of light cycle oil (LCO) was found to be better on NiMo/TiO_2–Al_2O_3. It was concluded that TiO_2–Al_2O_3 supported catalysts prefer HYD pathway to direct desulfurization pathway.

Segawa and coworkers [27,28] studied TiO_2–Al_2O_3 catalysts prepared by CVD method using 4,6-dimethyl dibenzothiophene. They have considered upto 13.2 wt.% TiO_2 deposited on γ-Al_2O_3. These catalysts which have physical characteristics comparable to that of commercial catalysts, showed higher activities than γ-Al_2O_3 supported catalysts at all support compositions. Based on detailed characterization studies using XPS and TPR they have attributed the higher activities to difference in reducibility behavior. Borque et al. [79] used TiO_2–Al_2O_3 supported CoMo and NiMo catalysts for HDS of gas oil and pyridine HDN and concluded that these catalysts performed on par with commercial catalysts.

7. Concluding remarks

Past two decades there has been intense activity from several parts of the world on oxides and mixed oxides as supports to Mo, CoMo, NiMo, W and NiW. These supports have been prepared using several methods and effect of preparation on physico-chemical properties are dealt with in considerable detail. The support and catalysts were characterized in few cases, most of the times only activity data is available to say that mixed oxide supported catalysts perform on par or better than commercial catalysts but there is not sufficient data to arrive at a consensus regarding the factors that are responsible for such increase in activity. Increase in anion vacancies or increase in dispersion or alteration of metal–support interactions gauged by reducibility and sulfidability are often reported as reasons. However, the alteration of structure, composition and energetics of the active site constituting anion vacancy, sulfhydryl groups, Mo and Co, by the support not known to any detail. Also there is no method available to measure the degree of interaction of MoS_2 with the support. It is not clear, what is the optimum interaction that is needed for a commercial application and how one can achieve it though modification of support composition, preparation methods, etc. This knowledge is needed to enable us to exploit the potential of these materials for commercial application.

Much less knowledge is available on the suitability of these materials for deep desulfurization of feed stocks such as naphtha, gas oil and light cycle oil. Sufficient knowledge is only available in the case of TiO_2–Al_2O_3 system and to some extent ZrO_2–Al_2O_3. Further studies using relevant molecules such as 4,6-dimethyl dibenzothiophene with several other mixed oxide supported catalysts, are needed in order to fully explore the potential of the mixed oxides for commercial exploitation. Exciting results are starting to come, on mesoporous material-based systems; the way the publications are coming out on this systems, is any indication, these materials will definitely figure in future investigations prominently.

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