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 Al₂O₃ containing mixed oxide supports, TiO₂ containing mixed oxide supports, ZrO₂ containing mixed oxide supports and other mixed oxide supports containing all the rest. TiO₂ containing mixed oxides received maximum attention, especially TiO₂–Al₂O₃ 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 SiO₂ [8], MgO [9], ZrO₂ [10,11], TiO₂ [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 TiO₂, ZrO₂ 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-Al₂O₃ have been used as supports to take advantage of favorable characteristics of both the systems [25–28]. Some systems containing SiO₂, MgO, ZrO₂, B₂O₃ 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\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} system has been extensively studied because of its commercial prospects [27,28]. Others such as ZrO\textsubscript{2}–TiO\textsubscript{2}, ZrO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} [29], ZrO\textsubscript{2}–Y\textsubscript{2}O\textsubscript{3} [30–32], SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} [33–39], and Al\textsubscript{2}O\textsubscript{3}–B\textsubscript{2}O\textsubscript{3} [39–43] also received considerable attention. Systems such as ZrO\textsubscript{2}–SiO\textsubscript{2} [44], TiO\textsubscript{2}–SiO\textsubscript{2} [45], MgO–Al\textsubscript{2}O\textsubscript{3} [29], MgO–SiO\textsubscript{2} [39], SiO\textsubscript{2}–CoO\textsubscript{2} [46], and TiO\textsubscript{2}–MnO\textsubscript{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\textsubscript{2}O\textsubscript{3} containing mixed oxides, TiO\textsubscript{2} containing mixed oxides, ZrO\textsubscript{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\textsubscript{2}O\textsubscript{3} containing mixed oxides

2.1. SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} supported catalysts

Mo, CoMo, NiMo, NiW, W, supported SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} in the support to reach a maximum at 75 wt.% SiO\textsubscript{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\textsubscript{2} phase, the hydrocracking is largely due to the protonic acidity of the SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} support. Similar results are also obtained on W/SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} [37].

2.2. B\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} mixed catalysts

B\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}–B\textsubscript{2}O\textsubscript{3} catalysts using XRD, EXAFS techniques and dibenzothiophene (DBT) HDS. Their studies indicated that 2 mol.% of B\textsubscript{2}O\textsubscript{3} in Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3} inclusion in Al\textsubscript{2}O\textsubscript{3} support for gas oil hydrotreatment. Flego et al. studied Al\textsubscript{2}O\textsubscript{3}–B\textsubscript{2}O\textsubscript{3} system for thiophene HDS and concluded that acidity of support influences the activity. Al\textsubscript{2}O\textsubscript{3}–B\textsubscript{2}O\textsubscript{3} system was studied under industrially relevant conditions [52] using atmospheric gas oil and found that these systems
are superior to laboratory prepared Al$_2$O$_3$ 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$_2$O$_3$ inclusion in the Al(O) support and this is largely due to increase in acidity of the system.

2.3. ZrO$_2$–Al$_2$O$_3$ mixed oxides supported catalysts

ZrO$_2$–Al$_2$O$_3$ 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$_2$O$_3$ supported CoMo catalysts show higher activities compared to γ-Al$_2$O$_3$ supported catalysts and similar results were also reported by Zhao et al. [56] with 12 wt.% ZrO$_2$–Al$_2$O$_3$ catalysts for FCC gasoline desulfurization. Damyanova et al. [53] studied ZrO$_2$–Al$_2$O$_3$ in 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$_2$O$_3$ supported one. Lecenay et al. [50] employed NiMo/ZrO$_2$–Al$_2$O$_3$ for HDS of 4,6-dimethyl dibenzothiophene, gasoil and LCO. They have concluded that this catalyst exhibited higher HDS activity compared to commercial NiMo/Al$_2$O$_3$ catalyst.

We have examined Mo, CoMo [29] supported on ZrO$_2$–Al$_2$O$_3$ 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 °C also showed similar trend. Both Mo, CoMo supported on ZrO$_2$–Al$_2$O$_3$ exhibited higher activities compared Al$_2$O$_3$ supported catalysts. The composition variation of the support indicated that ZrO$_2$–Al$_2$O$_3$ (1:1) gave maximum activity for HDS, HYD functionalities. The TPR results indicated that the reducibility increased with introduction of ZrO$_2$ into Al$_2$O$_3$. 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$_2$O$_3$ system

As mentioned earlier, TiO$_2$ supported systems exhibited higher activities compared to Al$_2$O$_3$ 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$_2$O$_3$, SiO$_2$, etc. and forming mixed oxides of TiO$_2$ with other oxides such as Al$_2$O$_3$, SiO$_2$, ZrO$_2$. Among these mixed oxides TiO$_2$–Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ as supports for MoO$_3$ and WO$_3$ catalysts. TiO$_2$–Al$_2$O$_3$ supports can be prepared by various ways like coprecipitation, chemical vapor deposition, grafting, impregnation, etc. techniques [25,62]. All these methods lead to TiO$_2$–Al$_2$O$_3$ 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 \(\text{Al}_2\text{O}_3\). Zhaobin et al. \[62,63\] compared \(\text{TiO}_2–\text{Al}_2\text{O}_3\) precipitation, impregnation and grafting techniques for dispersion of \(\text{TiO}_2\) over \(\text{Al}_2\text{O}_3\) and found that grafting technique gives best dispersion of \(\text{TiO}_2\) over \(\text{Al}_2\text{O}_3\). This observation is based on the results obtained by using a battery of characterization techniques like XPS, TEM, XRD, TPD and grafting techniques for dispersion of TiO\(_2\) over Al\(_2\)O\(_3\). This observation is 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 \(\gamma\)-\(\text{Al}_2\text{O}_3\) supported catalysts. They also concluded that metal–support interactions are weak on \(\text{TiO}_2–\text{Al}_2\text{O}_3\) supported ones. Their catalytic activity studies indicated that modification of \(\text{Al}_2\text{O}_3\) by TiO\(_2\) improves HDS and HYD activities. They studied \(\text{TiO}_2–\text{Al}_2\text{O}_3\) supports containing maximum of 40 wt.% TiO\(_2\) 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 \(\text{Al}_2\text{O}_3\) decreases the interaction between MoO\(_3\) and the support. Ramirez Diaz et al. \[41\] considered full range of \(\text{TiO}_2–\text{Al}_2\text{O}_3\) 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\(_2 + \text{Al}_2\text{O}_3\) 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\(_2 + \text{Al}_2\text{O}_3\) 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\(_2 + \text{Al}_2\text{O}_3\) 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\(_2–\text{Al}_2\text{O}_3\) supports with different loadings of TiO\(_2\) using chemical vapor deposition technique. They studied up to 14 wt.% TiO\(_2\). The examination of IR spectra in hydroxyl region, which indicated the formation of \(\text{Al}–\text{O}–\text{Ti}\) linkages during the CVD process. From XPS data, Ti 2p/Al 2p ratio also indicated homogeneous distribution of TiO\(_2\).\[46\] The Mo 3d binding energy in oxide as well as sulfided state indicated better sulfidability of TiO\(_2–\text{Al}_2\text{O}_3\) supported catalysts compared to \(\text{Al}_2\text{O}_3\). The TiO\(_2–\text{Al}_2\text{O}_3\) formulations are intermediate in reduction and sulfidation behavior compared to \(\text{Al}_2\text{O}_3\) 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 \(\gamma\)-\(\text{Al}_2\text{O}_3\). They carried out HDS of dibenzothiophene and methyl substituted dibenzoanthiophenes which gave useful information about their utility in deep desulfurization application. These authors concluded that TiO\(_2–\text{Al}_2\text{O}_3\) supported catalysts are more efficient in converting 4,6-dimethyl dibenzoanthiophene, 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\(_2–\text{Al}_2\text{O}_3\) supported MoO\(_3\) catalysts as well as CoMo and NiMo catalysts by ammonium 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/\(\text{Al}_2\text{O}_3\) formation on \(\text{Al}_2\text{O}_3\) rich formulations. HRTEM results indicated that crystallites are shorter in length on mixed oxide supports compared to that over \(\gamma\)-\(\text{Al}_2\text{O}_3\). 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 up to TiO$_2$–Al$_2$O$_3$ (1:1) composition and beyond this region Ti–O–Ti linkages are seen. Mo supported on TiO$_2$–Al$_2$O$_3$ is more reducible and sulfidable compared to γ-Al$_2$O$_3$, but the behavior is intermediate between γ-Al$_2$O$_3$ and pure TiO$_2$ supported ones. There was no complete agreement on activities, every body in general agree that TiO$_2$–Al$_2$O$_3$ supported catalysts are more active than γ-Al$_2$O$_3$ 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$_2$O$_3$ supported catalysts 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 are similar to γ-Al$_2$O$_3$ 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 support characteristics, of course depends upon the technique and the amount of Ti ions that can be incorporated into γ-Al$_2$O$_3$ without formation of separate phases, depends upon the preparation method, and for a given preparation method, the chosen conditions and TiO$_2$/Al$_2$O$_3$ ratio are important. Homogenous 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$_2$O$_3$ compositions studied are of reasonably high surface area. As the Al$_2$O$_3$ content increases the XRD results indicated that TiO$_2$ lines broaden which indicates that TiO$_2$ dispersion in Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$] = 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 MoTiO$_2$–Al$_2$O$_3$ (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$_2$O$_3$ via various TiO$_2$–Al$_2$O$_3$ ratios Ti–O–Al bonding is likely to increase and since ESCA results by Ramirez Diaz et al. [41] demonstrated up to TiO$_2$/[TiO$_2$ + Al$_2$O$_3$] = 0.5 maximum number of Ti ions are present on the surface. The TiO$_2$–Al$_2$O$_3$ (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	extsubscript{2} crystallites. Therefore, the maximum dispersion of MoS	extsubscript{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	extsubscript{2} as a function of support composition. The intermediate values of kHYD/kHDS and kHYD/kHDO suggest that the MoS	extsubscript{2} supported on mixed oxides have characteristics of both the pure supports, viz. TiO	extsubscript{2} and Al	extsubscript{2}O	extsubscript{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	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} (1:1) composition.

3.2. Promotional effect

Promotional effect of both cobalt and nickel were investigated on 8 wt.% Mo on TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{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	extsubscript{2}–Al	extsubscript{2}O	extsubscript{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	extsubscript{2}/γ-Al	extsubscript{2}O	extsubscript{3} the promotional effect is small. The small promotional effects may be attributed to formation of CeTiO	extsubscript{3}, NiTiO	extsubscript{3} type of surface compounds and also may be due to CoMoO	extsubscript{4} formation. On γ-Al	extsubscript{2}O	extsubscript{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	extsubscript{2} support the promotional effect for HDS is 39% and for NiMo/TiO	extsubscript{2} it is 103%. It appears that on Ti containing supports, Ni is a better promoter compared to cobalt. Overall, CoMo/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} is 50% more active than conventional CoMo/γ-Al	extsubscript{2}O	extsubscript{3} formulation, and NiMo/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} (1:1) is 100% more active than that of conventional NiMo/Al	extsubscript{2}O	extsubscript{3} formulation. It clearly shows that TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} supported CoMo, NiMo catalysts are superior to conventional CoMo, NiMo supported on γ-Al	extsubscript{2}O	extsubscript{3}.

3.3. Variation of Mo loading

We have varied Mo content on MoS	extsubscript{2}/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} (1:1) from 2 to 14 wt.% [58]. The MoS	extsubscript{2}/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{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	extsubscript{3}/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{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 8wt.% Mo/TiO	extsubscript{2}–Al	extsubscript{2}O	extsubscript{3} catalysts.](attachment://image.png)
techniques. The XRD results indicated that up to 8 wt.% MoO₃ loading molybdenum is very well dispersed and above this loading there is evidence for the formation of MoO₃ 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 MoO₃ is more reducible on TiO₂–Al₂O₃ compared to Al₂O₃ but less reducible compared to TiO₂, thereby showing intermediate reduction behavior compared to the constituent oxides. The variation of H₂ consumption per Mo indicated that there are two types of phases characterized by two different reduction behaviors and the transition point is 8 wt.% MoO₃. The oxygen uptakes on sulfided catalysts increased with increase of MoS₂ loading up to 8 wt.% MoO₃ and then decreased. The surface coverage increased up to 8 wt.% MoO₃ 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 up to 8 wt.% MoO₃ and increases rapidly with further increase of molybdenum loading. All these results suggest that there are two distinct regions below and above 8 wt.% MoO₃. The small crystallite size in both oxide and sulfided state suggest that molybdenum is present in monolayer dimensions up to 8 wt.% Mo loading and beyond this region large crystallites of MoS₂ 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 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 TiO₂–Al₂O₃ 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 MoO₃ and these patches grow in number up to 8 wt.% MoO₃. At this concentration, all sites available to bind MoO₃ to TiO₂–Al₂O₃ are exhausted and further addition of molybdenum results in three-dimensional MoO₃ 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 MoS₂ patches with coordinatively unsaturated sites or anion vacancies. These vacancies increase in number as the number of MoS₂ patches increase with Mo loading up to 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 MoS₂ on TiO₂–Al₂O₃ support.

### 3.4. Titania–zirconia mixed oxide supported molybdenum catalysts

In the literature there is considerable interest on TiO₂–ZrO₂ 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 TiO₂–ZrO₂ 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/TiO₂–ZrO₂ and Co–Mo/Al₂O₃ 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 Al₂O₃ support and CUS sites are more in concentration on this mixed oxide support. They further reported that TiO₂–ZrO₂ supported catalysts are prone to deactivate faster in comparison to Al₂O₃ supported ones. The deactivation of mixed oxide is quicker may be due to presence of stronger acidic sites compared to Al₂O₃ support. The deactivation has also been reported to occur by pore plugging.
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 catalyst is higher than that of TiO$_2$, ZrO$_2$ and Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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 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 sulfidized 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
observed on TiO₂ rich formulations but no ZrO₂ lines were seen in any composition, except in pure ZrO₂. At 12 wt.% Mo loading no MoO₃ lines are seen on any of the ZrO₂–TiO₂ compositions indicating that molybdenum is well dispersed on the ZrO₂–TiO₂ compositions studied. The catalytic functionalities HDS, HYD and HDO all increased with the increase of zirconia content in the support up to 35 mol% ZrO₂ and then started decreasing (Fig. 3). In other words for this method of preparation TiO₂–ZrO₂ (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 ZrO₂ or TiO₂ (Fig. 4). It is clear from these studies that TiO₂ (65:35) containing 12 wt.% Mo is the best composition for all three functionalities and it is also clear that ZrO₂–TiO₂ can accommodate more molybdenum in highly dispersed form than γ-Al₂O₃ 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 ZrO₂–TiO₂ (65:35), the Mo loading is varied from 2 to 16 wt.% [38]. XRD measurements suggested that there are no lines due to MoO₃ up to 14 wt.% Mo loading. There is a faint indication for the presence of MoO₃ strong lines at this loading, indicating that MoO₃ is well dispersed up to 12 wt.% Mo loading on these catalysts. The TPR results indicated that reducibility of MoO₃ increases up to 12 wt.% and then levels off. The ESCA results also indicated the Iₘo/Iₜi + I₉ₓ ratio increased up to 12 wt.% Mo, indicating that the dispersion is increasing up to 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
is a measure of dispersion of molybdenum sulfides, it may be taken that MoO₃ is well dispersed and present in monolayer dimensions up to this loading. The catalytic functionalities for the three reactions HDS of thiophene, HYD of cyclohexene and HDO of furan all increased up to 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 through dispersion. This is also supported by linear correlations between O₂ uptake and functionalities passing through origin, obtained on these samples. The results of TiO₂–ZrO₂ as a function of Mo loading are very similar to Mo/TiO₂–Al₂O₃ 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 TiO₂–SiO₂ support prepared by homogeneous precipitation technique [75]. The surface area of this TiO₂–SiO₂ support of varying TiO₂/SiO₂ ratios ranged between 300 and 380 m²/g. One this support, 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.% TiO₂ in SiO₂ and at higher TiO₂ contents the activity decreases. The activities however were higher than either pure TiO₂ or SiO₂ supported catalyst. Hydrogenation functionality however is very high on SiO₂ and the HYD activity decreases with the increase of TiO₂ in SiO₂. 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 TiO₂ content in the support. It is interesting that the promotional effects in TiO₂–SiO₂ are higher than, TiO₂–Al₂O₃ and TiO₂–ZrO₂ supported molybdenum catalysts.

Molybdenum content on 15 wt.% TiO₂–SiO₂ was varied from 2 to 14 wt.%. XRD results indicated Mo is well dispersed in this catalysts up to 8 wt.% Mo loading. The low temperature oxygen chemisorption on the sulfided samples indicated that the uptakes increase up to 8 wt.% Mo on these catalysts (Fig. 6). It should be mentioned at this juncture that on TiO₂–ZrO₂, the O₂ uptake increase up to 8 wt.% and on SiO₂ increases only up to 4 wt.% The catalytic activities for HDS, HYD and HDO also increase up to 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 O₂ chemisorbs on anion vacancies and it is well known that anion vacancies on the active site are responsible for catalytic activity.
3.5. Comparison of three Ti containing mixed oxide supports

In this review three supports TiO$_2$–Al$_2$O$_3$, 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$_2$O$_3$ 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$_2$O$_3$ (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$_2$O$_3$-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$_2$O$_3$ 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$_2$O$_3$ > 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$_2$O$_3$ 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 TiO$_2$, SiO$_2$, SiO$_2$–TiO$_2$ (12:88), and Al$_2$O$_3$–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. 7. Effect of support on catalytic activity for various functionalities.](image-url)
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 Al2O3 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 TiO2–SiO2 supported molybdenum system. However, on Mo/TiO2–Al2O3 the promotional effect is not large in the case of both Co and Ni. A general observation is that on pure TiO2 and TiO2–Al2O3 supported systems the promotional effects for both the functionalities is only small, in agreement with the results reported earlier on Mo/TiO2 [67]. It is also clear that support influences the promotional action of Co.

### Table 1

Promotional effects on different supports

<table>
<thead>
<tr>
<th>Supported catalyst</th>
<th>Surface area (m²/g)</th>
<th>Catalytic activity</th>
<th>8 wt.% Mo promoted</th>
<th>3 wt.% Co–8 wt.% Mo promoted</th>
<th>3 wt.% Ni–8 wt.% Mo promoted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HDS</td>
<td>HYD</td>
<td>HDS</td>
<td>HYD</td>
</tr>
<tr>
<td>SiO2</td>
<td>340</td>
<td>5.6</td>
<td>17.07</td>
<td>11.8</td>
<td>60.0</td>
</tr>
<tr>
<td>TS (12.88)</td>
<td>312</td>
<td>11.39</td>
<td>8.19</td>
<td>36.4</td>
<td>32.2</td>
</tr>
<tr>
<td>TA (50:50)</td>
<td>129</td>
<td>26</td>
<td>33.1</td>
<td>33</td>
<td>44</td>
</tr>
<tr>
<td>TiO2</td>
<td>153</td>
<td>11.2</td>
<td>25.4</td>
<td>26.8</td>
<td>24.7</td>
</tr>
<tr>
<td>TeO2</td>
<td>59</td>
<td>6.4</td>
<td>12.4</td>
<td>8.9</td>
<td>22</td>
</tr>
<tr>
<td>TZ (65:35)</td>
<td>50.6</td>
<td>11.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Thiophene HDS, cyclohexene HYD; rate (mol h⁻¹ g⁻¹ cat.) × 10⁻³.

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$_2$Si ratio, whereas HYD activity showed maximum at 0.30 Zr/Zr$_2$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$_2$O$_3$ system

ZrO$_2$–Y$_2$O$_3$ supported catalysts were studied in considerable detail. Hamon et al. [30] reported Mo/ZrO$_2$–Y$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ than γ-Al$_2$O$_3$ suggesting that MoS$_2$ is better dispersed on Y$_2$O$_3$–Al$_2$O$_3$. They also suggested NiMoS of Type 2 is formed on Y$_2$O$_3$–Al$_2$O$_3$.

5. Other mixed oxides

Some mixed oxides like CeO$_2$–SiO$_2$ [46], Al$_2$O$_3$–P$_2$O$_5$ [50], Al$_2$O$_3$–Ga$_2$O$_3$ [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$_2$O$_3$ supported catalysts. Results on CoMo/Al$_2$O$_3$–B$_2$O$_3$ were reported by Flego et al. [51] indicated that this system exhibits lower activities for thiophene HDS than Al$_2$O$_3$ supported catalysts. Lecrenay et al. [50] reported CoMo/Al$_2$O$_3$–Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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. Al2O3–B2O3 mixed oxides supported catalysts were found to exhibit higher activity compared to γ-Al2O3 supported catalysts at an Al/B ratio of 3.5 [52]. Zhao et al. [56] reported TiO2–Al2O3 supported CoMo and NiMo catalysts showed superior activity for desulfurization of FCC gasoline compared to CoMo/γ-Al2O3 catalysts. However, they have reported that for the same feed under comparable condition ZrO2–Al2O3 supported catalysts showed lower activity. They attributed the higher activities to change in reducibility. Wei et al. [78] examined TiO2–Al2O3 supported NiMo catalysts for naphtha desulfurization and found that 14.6 wt.% TiO2 containing TiO2–Al2O3 supported NiMo catalysts exhibited superior activity compared to commercial NiMo/γ-Al2O3 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 dibenzothiophenones such as 4,6-dimethyl dibenzothiophene. They have also reported desulfurization reactivities with real feeds such as gas oil, light cycle oil under industrially relevant conditions. NiMo/TiO2–Al2O3 with TiO2 content 8 and 25 wt.% was considered. These catalysts showed superior activity for conversion of 4,6-dimethyl dibenzothiophene. They observed that use of TiO2 containing supports moderates inhibition by H2S and aromatics like naphthalene. HDS of light cycle oil (LCO) was found to be better on NiMo/TiO2–Al2O3. It was concluded that TiO2–Al2O3 supported catalysts prefer HYD pathway to direct desulfurization pathway.

Segawa and coworkers [27,28] studied TiO2–Al2O3 catalysts prepared by CVD method using 4,6-dimethyl dibenzothiophene. They have considered upto 13.2 wt.% TiO2 deposited on γ-Al2O3. These catalysts which have physical characteristics comparable to that of commercial catalysts, showed higher activities than γ-Al2O3 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.

Bonque et al. [79] used TiO2–Al2O3 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, sulphhydryl 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 MoS2 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 TiO2–Al2O3 system and to some extent ZrO2–Al2O3. 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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