TiO_2–ZrO_2 mixed oxide as a support for hydrotreating catalyst

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Pure TiO_2, ZrO_2 and TiO_2–ZrO_2 mixed oxides are prepared by urea hydrolysis. Hydrotreating catalysts containing 12 wt% molybdenum are prepared using these oxides and characterized by BET surface area, pore volume, XRD and oxygen chemisorption. It is observed that oxides produced by the method of urea hydrolysis have higher surface area as compared to those available commercially. With increasing zirconia content in the mixed oxide, the surface area increases and a maximum value is obtained for a mixed oxide having Ti and Zr molar ratio of 65/35. XRD results indicate that mixed oxides are poorly crystalline in nature. Thiophene hydrodesulfurization, cyclohexene hydrogenation and tetrahydrofuran hydrodeoxygenation are taken as model reactions for evaluating catalytic activities. It is found that both O_2 uptake and catalytic activities increase with increasing zirconia content in mixed oxide and reach maximum values for the 12 wt% Mo/TiO_2–ZrO_2 (65/35) catalyst. With further increases in zirconia content, O_2 uptake and catalytic activities decrease and the lowest values are observed for the pure ZrO_2 supported catalyst.

KEY WORDS: molybdenum; TiO_2–ZrO_2; XRD; O_2 chemisorption; HDS; HYD; HDO

1. Introduction

To meet the challenges related to the hydrodesulfurization (HDS) of various petroleum fractions, development of a new generation of catalysts is necessary. In this connection, the support of the hydrotreating catalyst plays an important role. Most of the HDS catalysts employed for industrial applications are molybdenum based promoted with cobalt or nickel and supported on alumina. Less attention has been given towards commercial application of other supports, such as ZrO_2 or TiO_2. Both ZrO_2 and TiO_2 seem to be promising HDS supports, as indicated by our earlier work as well as work carried out by other researchers [1–4].

However, one of the disadvantages in using these supports for commercial application is their poor thermal stability and low surface area. In addition, during reaction conditions phase transformations of ZrO_2 and TiO_2 supports have also been observed. Moreover, at high-temperature and high-pressure conditions, the surface area of the supports reduces drastically. To overcome the thermal instability and reduction in surface area of both titania and zirconia, the use of their mixed oxides has attracted attention of researchers in recent years [5–10]. The other interesting feature of the TiO_2–ZrO_2 mixed oxide is the presence of both acidic and basic sites.

Daly et al. [11] studied the hydrodesulfurization reaction over Co–Mo catalysts supported on TiO_2–ZrO_2 mixed oxides. They found that the co-ordinated unsaturated sites (CUS) are easier to form in mixed oxide support than on Al_2O_3 support and the concentration of CUS sites is larger in mixed oxide support. They reported that TiO_2–ZrO_2 supported catalysts are prone to deactivate faster as compared to Al_2O_3 supported catalysts. Weissman et al. [12] and Wang et al. [13] have also reported higher HDS and HDN activities of a TiO_2–ZrO_2 mixed oxide supported catalyst than that of an alumina supported one.

The present work has been conducted to study the nature of TiO_2–ZrO_2 supported Mo based catalysts and their performances towards various hydrotreating reactions such as thiophene hydrodesulfurization, cyclohexene hydrogenation (HYD) and tetrahydrofuran hydrodeoxygenation (HDO). For this purpose, different TiO_2–ZrO_2 mixed oxide supports were prepared by varying their TiO_2 content. TiO_2 and ZrO_2 pure supports were also prepared for comparing the results. XRD, and low-temperature oxygen chemisorption techniques were used to characterize molybdenum catalysts.

2. Experimental

The homogeneous precipitation procedure was used to prepare mixed oxide supports. A series of titania and zirconia mixed oxides with varying molar ratio were prepared by this method. Appropriate amounts of $TiCl_4$ and $ZrOCl_2$ were dissolved in distilled water and sufficient amount of urea was added. The solution was refluxed for 2–3 h at 95 °C. Precipitation was completed when pH of the solution reached an approximate value of 7. The precipitate was then filtered and washed with deionized water to remove chloride ions. The solid obtained was dried overnight at 120 °C and then calcined at 450 °C for 5 h. Pure TiO_2 and ZrO_2 were also prepared using the same method. All

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the supports were crushed and sieved to 18–40 BSS mesh (average particle size 0.72 mm) before using for impregnation of Mo. The incipient wetness method was used to load 12 wt% Mo on these supports. An appropriate amount of ammonium heptamolybdate (AR Grade, Fluka) was dissolved in a predetermined volume of distilled water based on the pore volume of the support. The impregnated catalysts were dried in air at 120 °C overnight and then calcined at 450 °C for 6 h.

A conventional static volumetric high-vacuum (up to 10^{-6} Torr) glass unit was used for BET surface area and low-temperature oxygen chemisorption (at −77 °C). Nitrogen gas was used for determination of BET surface area. The oxide precursors were sulfided *in situ* at 400 °C for 2 h by passing hydrogen through CS_2 bubblers kept at 27 °C, at a rate of 40 ml min^{-1}, prior to oxygen chemisorption measurements. 0.2–0.3 g of catalyst was taken for each oxygen chemisorption measurement. The details of the experimental procedure used for oxygen chemisorption studies are described elsewhere [14].

The total pore volume was measured in a Quantachrome, Autoscan instrument using a mercury penetration method.

X-ray diffraction studies were carried out on pure supports as well as on molybdenum oxide catalysts in a Rigaku model D-Max 111B X-ray diffractometer.

The catalytic functionalities of molybdenum sulfide catalysts were tested using different model compounds, viz. thiophene for hydrodesulfurization (HDS), cyclohexene for hydrogenation (HYD) and tetrahydrofuran for hydrodeoxygenation (HDO). In a typical experiment about 0.2 g of a catalyst sample secured between two plugs of quartz wool inside the gas reactor (Pyrex glass tube, 0.8 cm i.d.) was sulfided at 400 °C for 2 h. Sulfiding was carried out using a mixture of 10% CS_2 and 90% H_2 as similar to the chemisorption measurement before studying the reactions. After the sulfidation at 400 °C for 2 h the temperature was maintained at the reaction temperature and CS_2/H_2 gas flow was stopped. The catalyst was flushed at this temperature with H_2 until no CS_2 could be detected in the effluent gas. Thiophene or cyclohexene or tetrahydrofuran feed was introduced through the gas bubblers. H_2 flow rate was around 40 ml/min.

First-order rates were calculated according to the equation $x = r(W/F)$, where r is rate in mol h^{-1} g^{-1}, x the fractional conversion, W the weight of the catalyst in g and F the flow rate of the reactant in mol h^{-1}. The conversions were kept low to avoid diffusional limitations.

3. Results

3.1. Surface area and pore volume

The BET surface area was measured for pure TiO_2, ZrO_2 and their mixed oxides as well as for 12 wt% Mo loaded catalysts. Mo loading of 12 wt% was chosen since maximum activities were reported corresponding to this loading of Mo [10]. The results are given in table 1. In our earlier studies, we used commercial ZrO_2 (Harshaw) and TiO_2 (Norton) supports having surface area of 43 and 101 m^2 g^{-1}, respectively [1,2]. In the present study, the surface areas of zirconia and titania were found to be 86 and 151 m^2 g^{-1}, respectively. It is observed that both pure supports prepared by the urea hydrolysis method have higher surface area than commercially available supports.

It is also noted from table 1 that with the addition of zirconia to titania the surface area of the supports increases sharply and reaches a maximum value for a mixed oxide having Ti and Zr molar ratio of 65/35. The surface area of this mixed oxide support (having Ti/Zr = 65/35) is around 254 m^2 g^{-1}. In literature, it was also found that the mixed oxides exhibit much higher surface area than their single oxide counterparts [11]. With the addition of further amounts of zirconia to titania the surface areas of mixed oxides slowly decrease. The surface areas of catalysts having 12 wt% Mo supported on these oxides also show similar behavior. But with addition of 12 wt% Mo on the oxides supports a substantial decrease of surface area of catalysts is observed.

The total pore volume was measured and results are also given table 1. It is noticed that the 12% Mo/TiO_2 catalyst has maximum pore volume and with the addition of zirconia to titania, the total pore volume of catalysts gradually decreases and it reaches lowest value for the 12% Mo/ZrO_2 catalyst.

3.2. X-ray diffraction

The X-ray diffractograms of pure TiO_2, ZrO_2 and mixed oxide supports are presented in figure 1. It may be noted

Table 1
Surface area, total pore volume and O_2 chemisorption of TiO_2, ZrO_2 and mixed oxide supported catalysts.

Catalyst	BET SA ($m^2\,g^{-1}$)		Total pore volume ($cm^3\,g^{-1}$)	O_2 uptake ($\mu mol\,g_{cat}^{-1}$)
	a	b		
12Mo/TiO_2	151	98	0.3784	32
12Mo/TiO–ZrO_2 (Ti/Zr = 85/15)	181	109	0.3276	40
12Mo/TiO–ZrO_2 (Ti/Zr = 65/35)	254	158	0.3013	55
12Mo/TiO–ZrO_2 (Ti/Zr = 50/50)	239	146	0.2487	51
12Mo/TiO–ZrO_2 (Ti/Zr = 25/75)	225	131	0.2141	44
12Mo/ZrO_2	86	59	0.1972	20

[a] Surface area of pure support.

[b] Surface area of molybdenum catalyst.

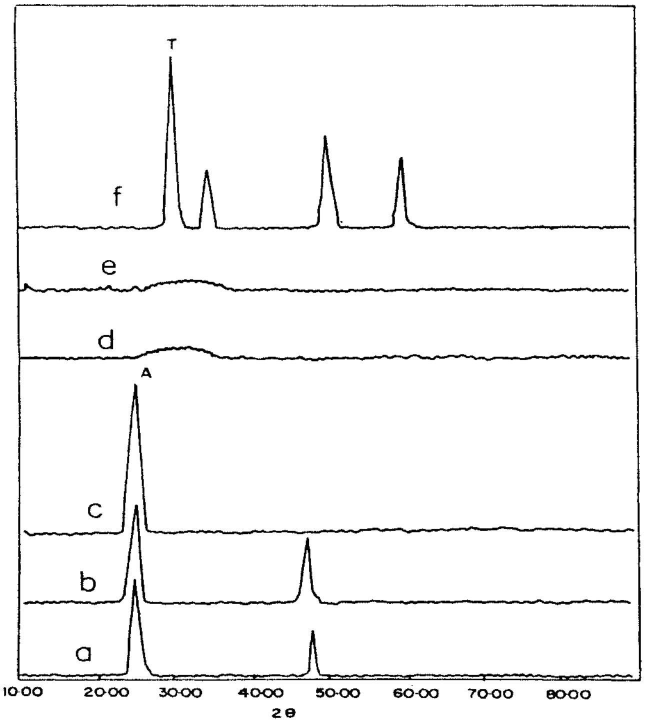

Figure 1. X-ray diffractograms of oxides: (a) TiO_2, (b) Ti/Zr = 85/15, (c) Ti/Zr = 65/35, (d) Ti/Zr = 50/50, (e) Ti/Zr = 25/75 and (f) ZrO_2.

from the diffractograms that in TiO_2 and TiO_2–ZrO_2 mixed oxides prepared with Ti/Zr = 85/15 and 65/35, the anatase phase of titania is observed. Peaks due to zirconia are not found in these oxides. The mixed oxides having Ti/Zr molar ratio of 50/50 and 25/75 are observed as X-ray amorphous. Pure ZrO_2 is tetragonal in phase. The amorphous nature of mixed oxides in the vicinity of 1/1 is also reported by other researchers [5].

The X-ray diffraction studies are also carried out on 12 wt% molybdenum loaded on these mixed oxides. It is noticed from diffractograms (which are not shown here) that no molybdenum peak is observed for 12% Mo/TiO_2 and 12% Mo supported on mixed oxides. But presence of crystalline MoO_3 is observed on zirconia support. The formation of crystalline MoO_3 on zirconia support may be due to its low surface area compared to pure titania and mixed oxides. 12 wt% molybdenum is in excess of the amount necessary for the formation of a monolayer on this low surface area (86 $m^2\,g^{-1}$) of zirconia. Overall, mixed oxides are poorly crystalline and mostly amorphous in nature (particularly mixed oxide containing higher zirconia). Molybdenum oxide is also well dispersed on high surface area mixed oxides, since at 12% Mo loading on mixed oxide supports we did not observe any peaks due to crystalline MoO_3.

3.3. Oxygen chemisorption

The oxygen chemisorption was studied for 12 wt% Mo catalysts supported on pure TiO_2 and ZrO_2 as well as on mixed oxides. The results of the chemisorption studies are given in table 1. The O_2 uptake value increases with increase of zirconia content in the mixed oxides and reaches maximum for the mixed oxide having Ti/Zr molar ratio of 65/35. Beyond this, the O_2 uptake value decreases with increasing zirconia content in the mixed oxide and the lowest value is obtained for the zirconia supported catalyst.

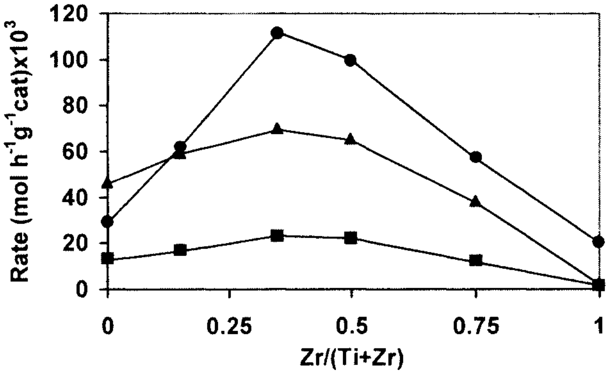

Figure 2. Variation of rate as a function of Zr/(Ti + Zr): (●) HDS, (■) HYD and (▲) HDO.

3.4. Activity studies

Hydrodesulfurization of thiophene, hydrogenation of cyclohexene and hydrodeoxygenation of tetrahydrofuran were chosen as model reactions for evaluating catalytic activities of 12 wt% molybdenum sulfide catalysts supported on mixed oxides and on its end members containing the same amount of molybdenum. It was mentioned earlier that 12 wt% Mo loading was taken for activity tests, since our earlier measurements showed that maximum activities occur at 12 wt%. The rates for all these three reactions were calculated and they are plotted against support composition in figure 2. It is observed from this figure that the rate of thiophene hydrodesulfurization increases sharply with increasing zirconia content in mixed oxide supports and reaches maximum for a Ti/Zr molar ratio 65/35. The 12 wt% Mo catalyst supported on TiO_2–ZrO_2 having equal proportion of each shows slightly lower HDS activity than the catalyst supported on TiO_2–ZrO_2 having Ti/Zr = 65/35. Above this support composition, the HDS activity steadily decreases with increasing zirconia concentration in mixed oxide. 12 wt% Mo loaded on ZrO_2 shows very low HDS activity.

The rates for hydrogenation of cyclohexene and hydrodeoxygenation of tetrahydrofuran are also calculated and these are plotted against zirconia content in the mixed oxide (see figure 2). The trends observed for both HYD and HDO activities are similar to that observed in case of HDS. But, with the increase in zirconia content in the mixed oxide, the HYD or HDO activity does not increase as sharply as it is observed in the case of HDS. For all three reactions, the maximum activity is found at 12 wt% Mo/TiO_2–ZrO_2 (65/35). The 12 wt% Mo/TiO_2–ZrO_2 (50/50) catalyst shows slightly lower activity than the catalyst with support composition 65/35. HDS activity is much higher than HYD and HDO activities. It is around five times higher than HYD and nearly two times higher than HDO at 12 wt% Mo/TiO_2–ZrO_2 (65/35).

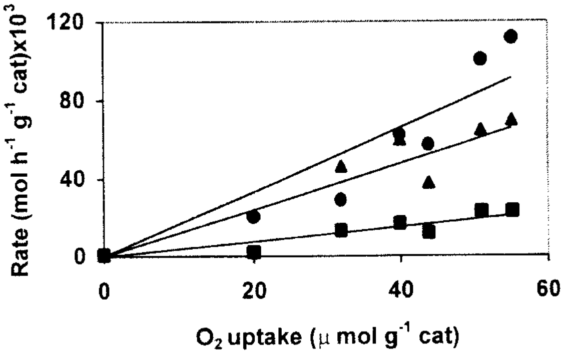

Figure 3. Correlation between rate of activity and O_2 uptake: (●) HDS, (■) HYD and (▲) HDO.

3.5. Correlation of oxygen chemisorption and activities

The rates for hydrodesulfurization, hydrogenation and hydrodeoxygenation are plotted against oxygen uptakes in figure 3. It is seen that the rates of HYD and HDO of molybdenum sulfided catalysts can be linearly correlated with oxygen chemisorption and straight lines passing through the origin are obtained for both cases. The relationship between HDS rate and oxygen chemisorption is comparatively scattered and an average line passing through the origin is drawn.

4. Discussion

Pure TiO_2, ZrO_2 and TiO_2–ZrO_2 mixed oxides were prepared by coprecipitation of titania and zirconia using the urea hydrolysis method. This method is superior to ammonia hydrolysis in terms of obtaining surface area and more homogeneity. In the ammonia hydrolysis method, the OH concentration changes during precipitation and due to this change the precipitate lacks uniformity. But when urea is used the OH concentration remains constant and the composition of the precipitate is uniform. In addition, a larger number of acid sites are generated when urea is used. The urea hydrolysis method also gives high surface area solids [11]. Among mixed oxide supports, TiO_2–ZrO_2 (65/35) mixed oxide is of higher surface area. On addition of 12 wt% Mo on oxide supports the surface area of the catalysts decreases substantially by about 30–40%. This may be due to blocking of support pore mouths by molybdenum atoms.

X-ray diffraction studies indicate that in mixed oxide support containing high concentration of titania only anatase phase is found. In the vicinity of 1/1 molar ratio, TiO_2–ZrO_2 oxide is X-ray amorphous. Molybdenum oxide is well dispersed on the high surface area mixed oxide supports, and hence we did not observe any peak due to crystalline MoO_3 at 12 wt% Mo. But presence of crystalline MoO_3 is seen on the zirconia supported catalyst. The formation of crystalline MoO_3 on the zirconia support may be due to its low surface area compared to mixed oxide supports and 12 wt% Mo is in excess amount necessary for the formation of a monolayer on this low surface area of zirconia.

The change which occurs when molybdenum is impregnated on mixed oxide support, is discussed below. According to Tanabe's hypothesis [15] the surface structure of TiO_2–ZrO_2 can be represented as (I) and (II) in figure 4. Both structures (I) and (II) contain acidic and basic sites. When molybdenum is impregnated on mixed oxide support and subsequently calcined, the molybdenum atom interacts with the more basic hydroxyl group of the support and a new structure is formed as shown in (III). It is obvious that all titania or zirconia ions do not contain OH groups and selective OH groups having a basic nature only participate in the process of fixing molybdenum on to the support.

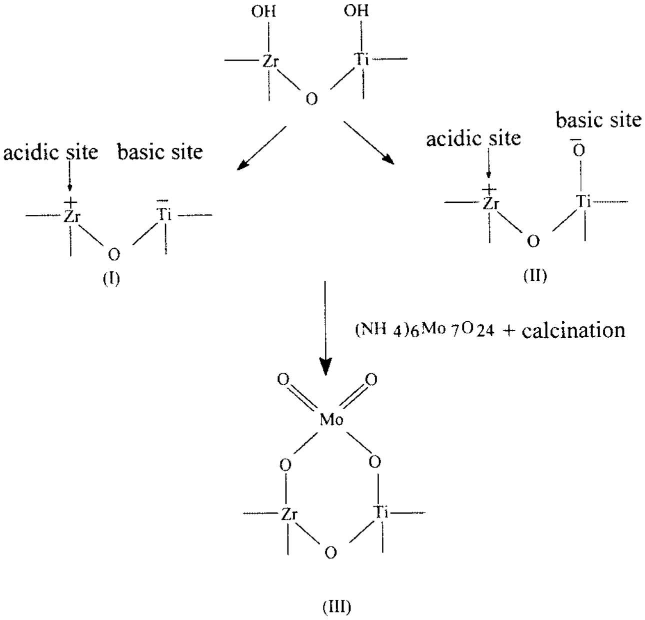

Figure 4. A schematic presentation of TiO_2–ZrO_2 structures and interaction with molybdenum oxide.

Oxygen uptake for 12 wt% Mo/TiO_2 catalyst is 32 μmol g_{cat}^{-1} and it increases with addition of ZrO_2 into mixed oxide support. O_2 uptake is maximum on 12 wt% Mo/TiO_2–ZrO_2 (65/35) catalyst. With further addition of zirconia into mixed oxide, oxygen uptake decreases sharply. Similar trends are also observed in activity studies. It is also observed that molybdenum catalysts supported on mixed oxides have better activities than that of single oxide supported catalysts. 12 wt% Mo/ZrO_2 shows low activity performance compared to mixed oxide based catalysts for all three reactions. Comparatively lower activity of Mo/ZrO_2 catalysts may be due to formation of crystalline MoO_3 on ZrO_2, which is also supported by XRD results. Daly et al. [11] reported that the higher initial activity of TiO_2–ZrO_2 mixed oxide supported catalysts was due to easy formation of coordinated unsaturated sites (CUS) on mixed oxide supported catalysts as compared to Al_2O_3 supported catalyst. In our present study, we observed higher oxygen chemisorption on mixed oxides supported catalysts as compared to single oxides supported catalysts. Oxygen chemisorption measures the CUS. Therefore, we can draw the same conclusion as Daly had that higher activity of mixed oxide supported catalysts might be due to formation of more CUS on mixed oxide supported catalysts as compared to single oxides supported catalysts.

A linear relationship between oxygen uptake and catalytic activity is obtained. Therefore, it is clear that oxygen chemisorption is related to catalytic functionalities. It is known that oxygen chemisorbs on co-ordinatively unsaturated sites such as anion vacancies on sulfided catalysts [16]. It is also well known that anion vacancies are responsible for HDS and related reactions on sulfided catalysts [17]. Therefore, it appears that the catalytic activities and oxygen uptakes are related through anion vacancies which are formed during sulfidation of catalyst. Since a linear relationship is obtained in all the three cases oxygen chemisorption is not specific to any one of the functionalities but may be related to general state of dispersion of molybdenum sulfide. Oxygen chemisorption cannot measure the degree of co-ordinative unsaturation. Different degree of co-ordinative unsaturation may be favorable for different reactions.

5. Conclusions

The following conclusions could be drawn from the present study:

- Urea hydrolysis method is suitable to prepare high surface area supports.
- TiO_2–ZrO_2 mixed oxide supports have higher surface area as compared to their pure counterparts.
- Oxygen chemisorption is a valuable technique for determination of active sites.
- Oxygen chemisorption cannot distinguish the different sites for different reactions.
- Mixed oxide supported catalysts show very high activities as compared to single oxide supported catalysts.
- Among TiO_2–ZrO_2 mixed oxides, the catalyst supported on mixed oxide having a composition of 65/35 shows the highest activities for all three reactions.

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