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Effect of Loading on the Physicochemical Properties of Alumina Supported Co/Mo Bimetallic Nanocatalysts

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Abstract: The present research deals with the synthesis of cobalt bimetallic Co/Mo nanocatalysts supported on alumina. The nanocatalysts were prepared by wet impregnation method. The samples were characterized in terms of reducibility, dispersion and particle size using Temperature Programmed Reduction (TPR), Transmission Electron Microscopy (TEM) and BET-surface area analysis. H_2-TPR analysis of Co/Al_2O_3 indicated three temperature regions at 380°C (low temperature), 680°C (medium temperature) and 900°C (high temperature). The incorporation of molybdenum into cobalt nanocatalysts shifted the reduction temperatures towards higher temperature but the percentage of species being reduced at low temperature increased also incorporation of molybdenum reduce the crystallinity but decreased the metal particle size of the catalysts. Increasing metal loading from 5 to 10 %wt increased the reducibility of bimetallic nanocatalysts.

Key words: Bimetallic nanoparticles, Fischer-Tropsch synthesis, cobalt, molybdenum

INTRODUCTION

Fischer-Tropsch (FT) synthesis is a process which deals with the conversion of syngas derived from coal, biomass and natural gas into diesel fuels consisting of paraffins, olefins, alcohols and aldehydes with a high cetane number and is environmentally friendly (Dry, 1999). As a matter of fact, due to limited petroleum reserves and environmental restrictions, FT-synthesis is gaining more attention nowadays. The FT-synthesis is considered as a surface-catalyzed polymerization reaction. During this process, CO is adsorbed on transition metal surface and hydrogenated producing CH_x monomers which consequently propagate to produce products consisting of hydrocarbons and oxygenates with a broad range of functionalities and chain lengths (Brady and Pettit, 1980).

All the group VIII elements show considerable activity for this process. Among them Co, Fe and Ru displayed the highest activity (Tavasoli *et al*., 2005). Due to their high activity for FT-synthesis, high selectivity to linear products, more stability towards deactivation, low activity towards water-gas shift (WGS) reaction and low cost compared to Ru based catalysts, cobalt based catalysts are the preferred choice for FT-synthesis (Iglesia, 1997; Jacobs *et al*., 2002).

In many heterogeneous reactions the active phase are dispersed on a support which not only act as a carrier but may also contribute to the catalytic activity. Al_2O_3, SiO_2 and TiO_2 are the commonly used supports for cobalt-based catalysts (Sundaramurthy *et al*., 2008; Jacobs *et al*., 2004).

The incorporation of a second metal component to the catalysts may result in the geometric or electronic modification of the catalysts which may result in the modification of adsorption characteristics of the catalysts. Cooper and co-workers (Cooper *et al*., 2007) have used bimetallic Co-Mo for the FT-reaction. They found that incorporation of molybdenum to cobalt catalysts increases the acid-site strength causing them to be selective to lower hydrocarbons compared to mono-metallic cobalt catalysts.

This study deals with the synthesis and characterization of cobalt and molybdenum mono- and bimetallic nano-catalysts supported on γ-alumina. Effect of incorporation of molybdenum to cobalt catalysts and metal loading in terms of reducibility, dispersion, crystallinity and particle size distribution are presented.

MATERIALS AND METHODS

Catalysts synthesis: All the monometallic and bimetallic nano-catalysts were prepared using the wet impregnation method with 5 and 10 wt.% loading. These catalysts are assigned as M%/Alumina (where M represents metal

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impregnated). Before impregnation alumina (Merck, BET 190 m^2g^{-1}) was calcined at 500°C for 6 h. For each catalyst, required amounts of the precursor salts i.e., $Co(NO_3)_2.6H_2O$ (≥98%, Fluka) and $(NH_4)_6Mo_6O_{24}.4H_2O$ (99-101% , Fischer-Scientific) were dissolved in deionized water and added to the support dropwise with constant stirring followed by drying in an oven at 120°C overnight and calcining at 500°C for 6 h with the temperature ramping of 5°C min^{-1}.

Catalyst characterization: The reduction behaviour of the catalysts was studied using TPDRO1100 MS equipped with thermal conductivity detector. 0.5 g catalyst was placed in the U-shaped quartz tube. The catalyst samples were degassed in a flow of nitrogen at 200°C to remove traces of water and cooled down to room temperature. TPR was performed using 5% H_2/N_2 with a flow rate of 20 cm^3min^{-1} and heating from 40 to 900°C at 10°C min^{-1}. Morphology of the catalyst samples was characterized using transmission electron microscopy (Philip Tecnai 20, accelerating voltage: 200 kv). Samples were prepared in ultrasonic dispersion of n-hexane and the suspensions were dropped onto a copper grid. The surface area, pore volume and average pore size distribution of the catalyst samples were measured using N_2-adsorption (Micromeritics, ASAP 1000).

RESULTS AND DISCUSSION

H_2-Temperature Programmed Reduction (TPR) profiles: The reducibility of the calcined catalysts was studied by H_2-Temperature Programmed Reduction (TPR). It is a very useful tool which reveals the reduction behavior of different oxidized phases of the catalysts. In some cases it also gives useful information about the metal particle size, metal dispersion and metal to support interaction.

As shown in Fig. 1, three peaks were observed in case of 5% Co/Al_2O_3. The peak appearing at 381°C was due to the reduction of Co_3O_4 to CoO. The second peak appearing at 710°C can be attributed to the reduction of CoO to Co° (Berge *et al*., 2000). While the peak present at high temperature is usually attributed to the reduction of very small particles and the reduction of metal and support mixed oxides. As shown in Fig. 1, the catalyst 5% Mo/Al_2O_3 showed typical reduction pattern for Mo species. The larger peak at 467°C can be attributed to reduction of Mo^{6+} to Mo^{4+} while the one at 638°C was due to the reduction of Mo^{4+} to lower species (Khodakov *et al*., 2007). The peak appearing at higher temperature may be due to the reduction of smaller particles and mixed oxides of metal and support.

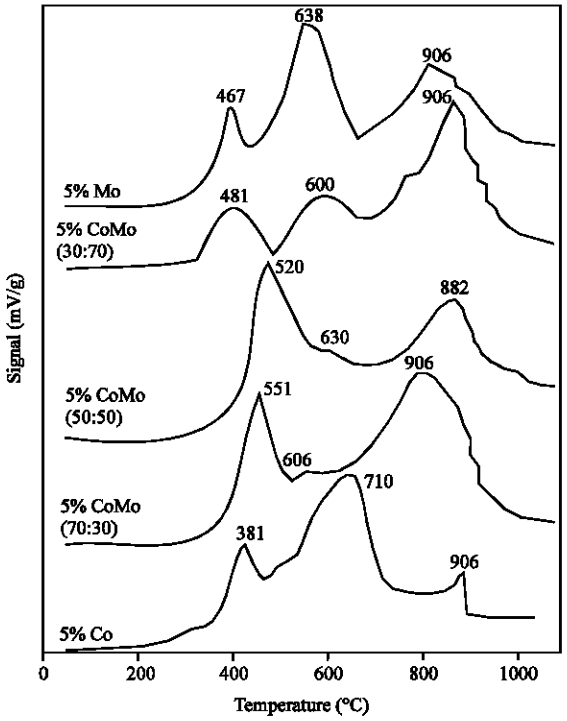

Fig. 1: TPR profiles of the catalysts

As shown in Fig. 1, for the 5% CoMo (70:30)/Al_2O_3 catalyst when molybdenum was incorporated to cobalt catalysts a significally different reduction behavior was displayed. This was different from either of the monometallic nano-catalysts. The first reduction peak shifted to 520°C (increased by 36%) while the second reduction peak appeared at 630°C (decreased by 11%). The peaks appearing at 520 and 630°C can be attributed to the reduction of bimetallic $CoMoO_4$ and $MoAlO_4$ (Chen and Adesina, 1994; Rodriguez *et al*., 1999; Chen and Liu, 1991). With further increase in the amount of Mo incorporated for the catalyst 5% CoMo(70:30)/Al_2O_3, first reduction peak is increased by 44.6% (551°C) while the second reduction peak decreased by 14.6% (606°C) but greater percentage of the species were reduced at 551°C. When the Mo content was more increased for the catalyst 5% CoMo(30:70)/Al_2O_3, though the reduction occurred at lower temperature (first and second peaks appeared at 481 and 606°C, respectively) as shown in the Fig. 1, but majority of the species were reduced at higher temperature. Interaction of Mo to Co catalysts shifted the reduction temperatures slightly to higher temperatures and reduced the degree of dispersion but percentage of the species reduced at relatively low temperatures increased. This effect was more pronounced for the catalyst 5% CoMo(50:50)/Al_2O_3, in case of

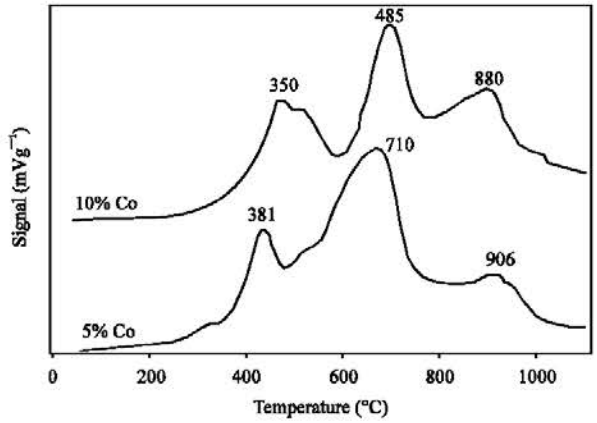

Fig. 2: TPR profiles of 5% Co/Alumina

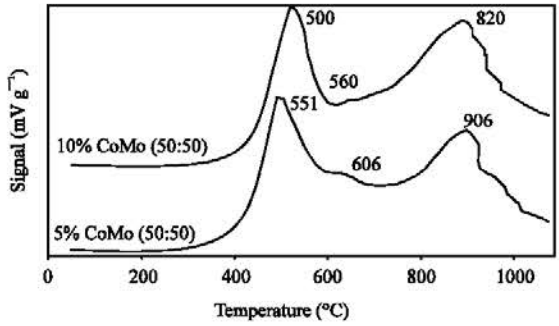

Fig. 3: TPR profiles of 5% CoMo (50:50)/Alumina and 10% CoMo (50:50)/Alumina

5 wt.% Co/Al_2O_3 only 34% of the chemisorbed hydrogen was consumed at 350°C but with incorporation of Molybdenum, 60% of chemisorbed hydrogen was consumed in the region from 551 to 606°C.

Increase in loading from 5 to 10 wt.% enhanced the reduction which could be attributed to the increase in metal particle size with increase in metal loading as evident from the TEM images. As shown in the Fig. 2, for the catalyst 10% Co/Al_2O_3 increase loading from 5 to 10 wt.% all the three reduction peaks shifted to lower reduction temperatures. Reduction peaks appeared at 350, 485 and 880°C which are reduced by 8.13, 31.69 and 3% respectively. This behavior was pronounced for the bimetallic nano-catalysts also. For the catalyst 10% CoMo (50:50)/Al_2O_3, as shown in the Fig. 3, reduction occurred at 500, 560 and 820°C, respectively much lower than 5% CoMo(50:50)/Al_2O_3 catalyst.

Transmission Electron Microscopy (TEM): Figure 4 shows the Transmission Electron Microscopy (TEM) images for the 5 wt.% Co(I)/Al_2O_3 catalyst. Average particle size of the catalysts was calculated from the TEM images are summarized in Fig. 5 and 6.

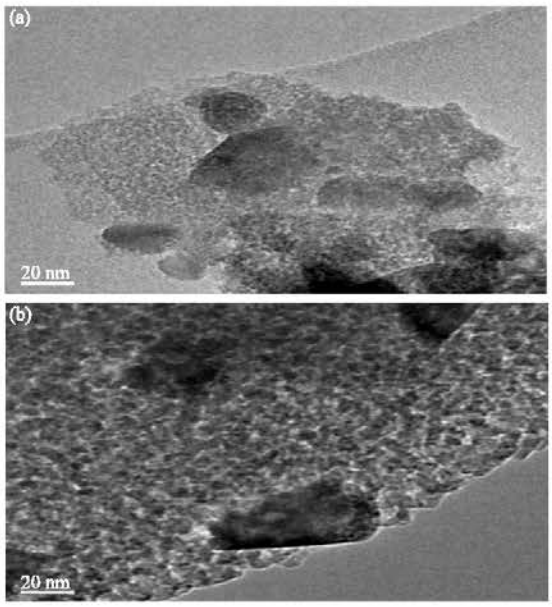

Fig. 4: TEM images of the catalysts. (a) 5% Co/Alumina and (b) 5% CoMo (50:50)/Alumina

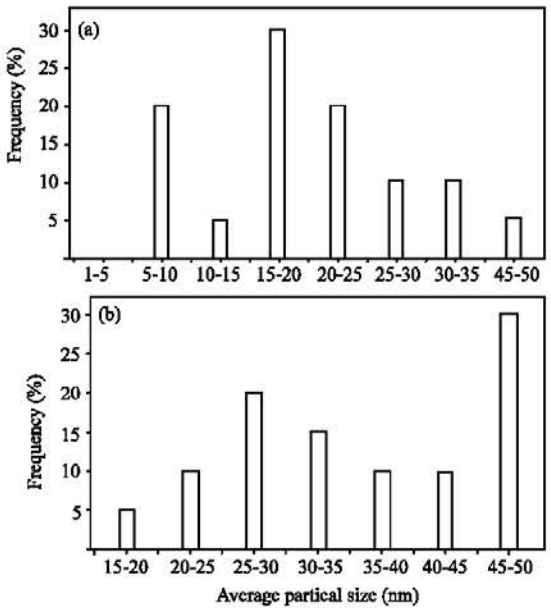

Fig. 5: TEM plots of the catalysts; (a) 5% and (b) 10% Co/Alumina

For 5 wt.% Co/Al_2O_3 shown in Fig. 5 (a), 30% of the particles were in size range from 15-20 nm. The increase in loading from 5 to 10 wt.% resulted in increase in metal particle size. For 10 wt.% Co/Al_2O_3 the metal particle size ranged from 45-50 nm (Fig. 5b).

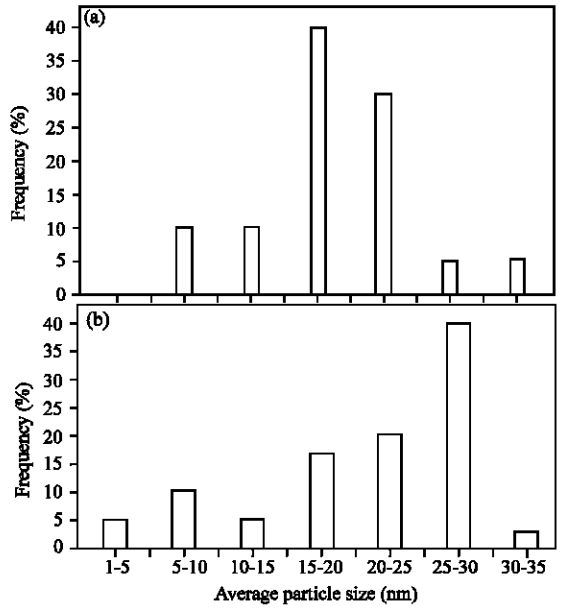

Fig. 6: TEM plots of the catalysts (a) 5% CoMo (50:50)/Alumina and (b) 10% CoMo (50:50)/Alumina

Table 1: Textural properties

No.	Species	BET Surface area (m^2g^{-1})	Total pore volume (cm^3g^{-1})	Average pore diameter (nm)
5% M/Alumina				
1	Alumina	190	0.1	9.8
2	5%C	180	0.267	7.5
3	5%Mo	130	0.2	6.9
4	5%CoMo (50:50)	107	0.221	8.2
10% M/Alumina				
1	10%Co	100.6225	0.242119	8.1
2	10%M	107.6394	0.229316	7.9
3	10%CoMo (50:50)	100.1427	0.223671	7.8

N_2-adsorption: Table 1 shows the BET surface area analysis of the catalysts. It was found that surface area of the 5% Co/Alumina and 5% Mo/Alumina was reduced by 5 and 31%, respectively, similarly pore volume and pore size of these catalyst samples were found to be less than the alumina, this could possibly be due to the blockage of the pores of the support with the metal particles. Greater reduction in the surface area of the bimetallic 5% CoMo/Alumina (43%) could be attributed due to the bigger metal particle size. Reduction in the surface area, pore volume and pore size was more pronounced for the catalysts with the increase in loading from 5 to 10 wt.%. For the 10% Co/Alumina surface area was reduced by 47% and for 10% Mo/Alumina it was found to be reduced by 43% while for the bimetallic 10% CoMo/Alumina the reduction was 45%. Pronounced reduction in the surface area for the catalysts with 10 wt.% metal loading could possibly be due to the blockage of the pore with the metal particles which are bigger in size than the catalysts with 5 wt.% metals loading.

CONCLUSIONS

It was found that incorporation of Mo (up to 50 wt.%) to the cobalt nano-catalysts increases the reduction temperature by approximately 44% but the percentage of species reducing at lower temperature increased with further increase in the amount of (up to 70 wt.%) Mo. TEM analysis revealed that bimetallic nano-catalyst resulted in better dispersion and decrease in the metal particle size. Surface area and pore volume were found to be lower for all the catalysts than the support, possibly due to the blockage of the support pores by the metal particles, this behavior was more pronounced for the bimetallic nano-catalysts.

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