Hydrogen Generation by Ammonia Decomposition Using Co Supported on Mg/La Mixed Oxide: Effect of Calcination Atmosphere of Support

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ABSTRACT

In this investigation the effect of calcination atmosphere of the support for Co catalyst and its activity in ammonia decomposition (AD) is explored. Mg/La mixed oxide supports (Mg/La = 3) were prepared by co-precipitation from nitrates solutions. The precipitates (support precursor) were either calcined in air, nitrogen or vacuum at 450°C followed by impregnation with 5 wt. % Cobalt. The calcined supports and the supported cobalt catalysts were characterized using nitrogen adsorption, X-ray powder diffraction (XRD), temperature-programmed reduction (H2-TPR) scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Catalyst activity tests were performed in a fixed bed quartz reactor. It was found that the catalyst activity in AD is highest for support calcined in nitrogen followed by that calcined in vacuum while lower activity was exhibited for support calcined in air. This activity pattern is positively correlated with high surface concentration of Co and high Co support interaction as found from XPS and TPR measurements respectively.

Keywords: ammonia decomposition, mixed oxides, hydrogen generation, cobalt catalysts.

1 INTRODUCTION

Generation of CO free hydrogen by ammonia decomposition (AD) is more attractive from practical and economical point of view compared to other process. Much research has been devoted to the investigation of Group VIII metals (Ru, Ni, Ir, Fe, Co and Rh) or metal carbide/nitrides (MoNx, VCx, MoCx, VNx, etc.) as catalytic materials for AD [1-3]. Previous studies showed that Ru supported on multi wall carbon nanotubes (MWCNTs) is the most active catalyst for AD [3]. Unfortunately, MWCNTs as a support suffered from many drawbacks such as high cost, methanation of carbon at high temperatures and low metal support interaction. In addition the high price and limited availability of Ru makes it uneconomical for large scale applications. Therefore, developing a cheap and affordable active catalyst for AD is highly desirable. Many studies reported that support basicity plays a crucial rule in AD thus the tailoring of the basic strength of mixed oxides supports with proper

treatment could be used to design better catalysts [4-6] for AD.

In this investigation, the effect of calcination atmosphere of the support on AD for Co supported on Mg/La mixed oxide is explored. Further insight on the effect of such treatment on the morphology and catalyst support interaction of this catalyst is also discussed.

2 EXPERIMENTAL

Mg/La mixed oxide support (Mg/La = 3) were prepared by co-precipitation from Mg and La nitrates solutions under high super saturation conditions using a mixture of KOH and K₂CO₃. The obtained precipitate is then filtered and divided into three equal portions. All portions were calcined at 450 °C but in different atmospheres. The samples were designated as ML-air, ML-N2 and ML-vac, when calcined in air, N₂ or under vacuum, respectively. For comparison Mg/La mixed oxide support with the same Mg-La ratio was prepared using only KOH for precipitation followed by calcination in air at 450 °C. This support was designated as ML-OH. The prepared supports were impregnated with Co from aqueous cobalt nitrate solution using a rotary evaporator under reduced pressure to obtain 5 wt.% loading of Co. Impregnated precursors of the catalysts were dried in an oven overnight at 100°C followed by calcination at 500°C for 5 hours under nitrogen flow to obtain the final catalyst used in AD. The supported cobalt catalysts were designated as 5CML-air, 5CML-vac, 5CML-N2 and 5CML-OH.

2.1 Catalyst Characterization

The BET surface areas of the calcined supports and of the supported cobalt catalysts were determined by N₂ adsorption at -196 °C using a Quantachrome Nova200e apparatus. Prior to the experiments, the samples were outgassed at 400°C for 4 h. X-ray powder diffraction (XRD) patterns of the samples were recorded on EQUINOX 1000, Inel (France) using Co K α radiation (λ =1.789 Å) between 10 -115° at 40kV and 30 mA. Temperature-programmed reduction (H₂-TPR) experiments were performed using the quantachrome pulsar automated chemisorptions analyzer equipped with a thermal conductivity detector (TCD). Prior to measurement, 100 mg of the sample to be tested was loaded into U-tube sample holder and pretreated in a flow of helium at 120°C for 60 minutes to remove the adsorbed impurities and moisture. After cooling down to 50°C, the flow of He was switched to a flow of 5% H₂ in N₂ (15 cm³ min⁻¹). The temperature of sample was then ramped at a rate of 5°C min⁻¹. The morphologies of all samples were investigated using field emission scanning electron microscopy (FE-SEM, QUANTA FEG450, FEI) using ETD Everhart Thornley Detector (HV mode) and solid-state back scattering electron detector (VCD).

2.2 Activity Studies

Activity tests were performed in a fixed bed quartz reactor under atmospheric pressure (PID system, Eng &Tech, Spain). Prior to the reaction, a 100 mg of catalyst was reduced in a mixture of nitrogen and hydrogen flow at 500°C for 5 hours. After the catalyst activation, pure NH_3 gas was introduced into the reactor at a gs hourly space velocity (GHSV) of 6000 h⁻¹. Experiments were carried out at temperatures ranging from 300 - 550°C with successive rise of 50°C. Products analysis was performed by using an online gas chromatograph (GC-450 Varian, USA) equipped with a thermal conductivity detector and a Poropak Q column.

3. **RESULTS AND DISCUSSION**

3.1 Catalyst Characterization

The surface area results of supports and corresponding cobalt catalyst are displayed in Table 1. The ML-air, ML- N_2 and ML-vac, supports did not show much difference in their BET surface area while ML-OH support showed the higher surface area. It may be due to the lack of formation mixed oxide where the Mg/La mixed oxide generally have low surface area compared to individual oxides [7]. Impregnation of the support with cobalt resulted decrease in surface area for all supports.

| Supports/Catalyst | BET Surface area (m ² /g) | surface cobalt concentration (atom %) |
|----------------------------|--|---|
| ML-air/5CML-air | 59.7/37.2 | 2.64 |
| ML-N2/5CML -N ₂ | 41.5/32.7 | 3.32 |
| ML –Vac/5CML -Vac | 64.2/34.9 | 2.96 |
| ML-OH/5CMLa-OH | 76.0/45.7 | 2.56 |

Table 1: Surface area and XPS results of catalysts

The XRD patterns of freshly calcined supports in different atmospheres are portrayed in Figure1A where it is observed the presence of two types of lanthanum carbonate phases besides MgO phase. Support calcined under vacuum shows one type of lanthanum carbonate with major diffraction lines at $26.66^{\circ}, 34.46^{\circ}, 36.31^{\circ}$ and 52.29°

corresponding to the La₂CO₅ phase [PDF: 00-023-0320, tetragonal, a= 4.063Å, c = 13.5 Å]. On the other hand, the support calcined under N₂ atmosphere shows diffraction lines at 25.88°, 29.32°, 30.03°, 32.17°, 35.39°, 39.30°, 39.55°, 40.80°, 52.05°, 55.7°, 59.07°, 64.54° and 67.5° corresponding to La₂O₂CO₃ phase [PDF: 00-037-0804, hexagonal, a=4.075 Å and c=15.95 Å].



Figure 1. XRD patterns of (A) calcined supports, (B) calcined cobalt catalysts

When the support is calcined in air we can clearly see both phases but the hexagonal phase is more dominant compared to tetragonal phase. Conversely the support ML-OH is shows mainly a tetragonal phase as major component. From these results it could be concluded that there are two type lanthanum species, one is showing tetragonal La₂CO₅ phase having cell parameters a=4.06Å c= 3.5Å and the other one is showing hexagonal La₂O₂(CO₃) phase having cell parameters a=4.075Å and c=15.95Å. This might explain the presence of bulk form and mixed oxide form of lanthanum which is forming carbonates by exposure to air.

After impregnation with cobalt all calcined catalysts (in nitrogen) show only hexagonal La₂O₂CO₃ phase except

5CML-OH catalyst which is still showing two phases of lanthanum carbonate. No diffraction lines were observed for cobalt except for 5CML-OH. Low loading of and small crystal size of Co species may evade detection cobalt species by XRD for these catalysts.

XPS of Co 2p spectrum of cobalt catalysts are shown in Figure 2. It was found that CoO is the major surface species in calcined cobalt catalysts. The Co 2p3/2 binding energy of CoO in 5CML-N2 and 5CML-Vac catalysts is slightly higher than other catalysts which may indicate a stronger interaction between Co and the support for this catalyst. As seen in Table 1 the surface cobalt concentration (atom %) for the four catalysts follows the order, 5CML-N₂ > 5CML-Vac > 5CML-air > 5CML-OH which is in accordance with the trend observed for catalytic activity where higher surface concentration of Co results in higher catalytic activity.



Figure 2: Co 2p XPS spectra of cobalt catalysts with support calcined in different atmosphere (a) 5CML-OH, (b) 5CML-air, (c) 5CML-Vac, (d) 5CML-N₂

TPR patterns are presented in Figure 3. Three major reduction peaks are obtained, the first peak is a relatively narrow and strong and extending from 250-380°C, the second peak is broad and extending from 380 to 650°C and a the third peak starts above 650°C. The first two peaks could be assigned to the reduction of Co₃O₄ to CoO and CoO to metallic cobalt respectively [8]. The very broad tailing nature for the second peak could suggest the reduction of highly heterogeneous CoO species having strong interaction with the support. The third high temperature peak above 700°C is due to reduction of lanthanum carbonate [9]. Analysis of the first peak in figure 3 showed a very clear shift in the maximum of this peak depending on the support calcination conditions. The temperature at which the maxima of this peak is located can be ranked in the following order; 5CML-N₂ ($349^{\circ}C$)> 5CML-Vac $(334^{\circ}C) > 5$ CML-air $(322^{\circ}C)$. This trend clearly shows that calcination of Mg/La support in N₂ facilitate the process to obtain a better catalyst with enhanced metal support interaction.

Representative SEM images are shown in Figure 4. It is clear from these images that all supports are containing Mg/La mixed oxide which is in grain shape morphology as confirmed by EDAX. The amount of Mg/La mixed oxide phase is more in supports calcined under N₂ and vacuum atmospheres compared to air calcined supports. The SEM and EDAX results showed that air calcined supports are giving big bulk form of MgO and La₂O₃. The Mg/La mixed oxide grains are dispersed on these oxides. Sponge like morphology of MgO is observed in ML-Vac support. Hence the support calcined under different atmospheres not only affects the interaction among the catalyst components, but also affect the morphology of the support.



Figure 3: H2 – TPR patterns of cobalt catalysts (a) 5CML-air, (b) 5CML-OH, (c) 5CML-Vac, (d) 5CML-N2



Figure 4: SEM images of Mg/La supports calcined at 450°C under different atmospheres

3.2 Activity Testing

The activity measurements for AD presented in Figure 5.A, clearly shows that 5CML-N2 catalyst is the most active among all catalysts. On the other hand 5CML-OH (prepared by different precipitation procedure) catalyst shows the lowest activity at same reaction conditions. It is clear that the calcination atmosphere of the support greatly influences the final catalytic activity. Studied catalysts are could divided into two groups according to their activity. The first group which has high activity in AD was prepared using supports calcined in non-oxidizing atmosphere (e.g. N₂ or vacuum). The other group of catalysts was prepared by air calcined supports and they exhibited a much lower activity. Thus it could be concluded that support calcination in an oxidizing atmosphere is not beneficial considering the catalyst activity.



Figure 5: (A) Activity results (B) Arrhenius plots for NH3 decomposition over cobalt catalysts

Figure 5.B illustrates the Arrhenius plots and the estimated apparent activation energies of all catalysts. It is clearly seen that the 5CML-OH catalyst had the highest activation energy (95.6kJ/mol). By calcining the support in N2 atmosphere activation energy greatly decreased to 67.1 kJ/mol and correspondingly NH₃ conversion sharply increased up to 90% at 550 °C. Additional investigation is required to clarify the role of calcinations atmosphere on the activity of these catalysts. Nonetheless, it is very clear that higher activity is positively correlated with high surface concentration of Co and high Co support interaction obtained as a result of calcination of the support in non-oxidizing atmosphere.

3. CONCLUSIONS

Performing calcinations of the support in non-oxidizing atmospheres is a vital precondition for preparation of active cobalt supported catalyst for ammonia decomposition. From the XPS results, it was shown that cobalt surface metal concentration was highest for the most active catalysts for which the support was calcined in nitrogen (5CML-N2 catalysts). The TPR measurements also showed strong metal support interaction for this catalyst. From the SEM results the formation of Mg/La mixed oxide increased in 5CML-N2 catalyst. Further work however is required to better understand the effect support calcinations in different atmosphere on the activity of cobalt catalysts. Nonetheless, it is very clear that higher activity is positively correlated with high surface concentration of Co and high Co support interaction brought about by calcination of the support in non-oxidizing atmosphere.

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