

Silica Alumina Supported with Metal Oxides: MBOH Catalytic Activities & Effect of Water Addition

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Abstract: At the present research, different samples of Silica alumina doped with different metal oxides such as titanium oxide, hafnium oxide and zirconium oxide characterized by temperature programmed desorption of ammonia, BET measurements and, primarily in the conversion of methylbutynol (MBOH) which is a test reaction for the decisiveness of basic acidic, amphoteric properties of solids. The results showed that acidity of metal oxides supported with alumina take the following order; HfO_2/Al_2O_3 (15:85) < HfO_2/Al_2O_3 (10:90) < HfO_2/Al_2O_3 (5:95) < ZrO_2/Al_2O_3 (5:95) < TiO_2/Al_2O_3 (5:95). Moreover, the effect of water addition to MBOH was considered in this study over different bulk metal oxides supported with silica alumina. Results showed that with the exception of ZrO_2 a clear increase of the MBOH conversion. It was also recorded that the increase in the MBOH conversion can be significantly improved with the samples hafnium oxide doped with alumina, where with HfO_2/Al_2O_3 (10:90) the conversion raised from 40 to 50 % by addition of water.

Keywords: Silica Alumina, Metals oxides, Effect of water addition to MBOH.

1. Introduction

The reactivity of MBOH over solids are shown in figure 1. Lauron Pernot *et al.* [1] have investigated a new test reaction, using methylbutynol (MBOH) that undergoes dehydration to yield 3-methyl-3-buten-1-yne (MBYNE) on acid catalysts such as acidic activated alumina or P_2O_5/SiO_2 and by-products such as 3-hydroxy-3-methyl-2-butanone (HMB). The corresponding dehydrated product 3-methyl-3-buten-2-one (MIPK) was found in the reaction of the MBOH in concentrated sulfuric acid. MBOH test reaction differs from other test reactions by the unique property to give product distribution which is characteristic of entirely acid, basic and amphoteric sites, respectively [1]. This reactivity test using MBOH gives good results in the characterization of acidic and basic properties [2]. Moreover, another technique like temperature programmed desorption of the ammonia method gives a characteristic “fingerprint” of a solid catalyst which can be used to determine the distribution of acid site strength of the surface if ammonia is the sorbed gas, or the distribution of basic sites if carbon dioxide is the sorbed gas. The acidity of aluminosilicates is characterized in terms of Brønsted and Lewis acid sites. Brønsted acid sites are formed by aluminum Atoms connected to silicon by a so-called “bridging hydroxyl” $Al-(OH)-Si$ where the negative charge generated is compensated for by a proton. Lewis acid sites are composed of aluminum with low coordination Or $\equiv Si^+$ ions formed from dehydroxylation in the thermal treatment at $T > 773$ K.

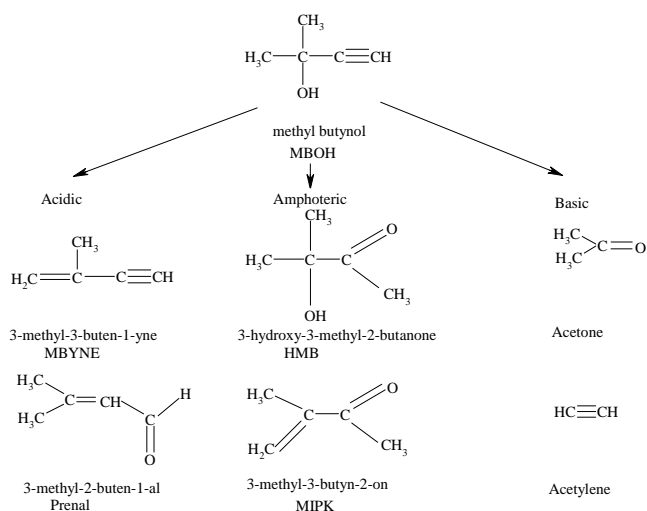


Figure 1: Overall reactivity of MBOH

One can speculate in accordance with the literature that generally the strength of the Brønsted sites increases with increasing silicon content [3]. The acid, amphoteric and basic catalysts, respectively, show a very suitable reaction by producing different products for each reaction pathway, namely 3-methyl-3-buten-1-yne (MBYNE) or 3-methyl-2-buten-1-al (Prenal) at acid sites and acetone together with acetylene at basic sites. Consequently, the conversion of methylbutynol is suited to classify catalysts according their acid-base properties [2] - [6]. The present work pertains to the study of metal oxides supported with alumina and, to find the correlation between TPD of NH_3 and catalytic test reaction of MBOH conversion. Moreover, this paper focused on investigating the effect of water addition on the MBOH conversions after 120 min. time on stream, also on the surface areas after the reaction. The correlation between the conversion and the surface areas for bulk metal oxides (ZrO_2 , TiO_2 , HfO_2)/ Al_2O_3 catalysts before and after the addition of water to MBOH was considered and, on the selectivities of

MIPK product (figure 1) which describes the amphoteric sites the used bulk metal oxides (ZrO₂, TiO₂, HfO₂)/Al₂O₃ catalysts.

2. Experimental

The experimental apparatus and conditions for MBOH conversion was set up as described at the literature [5].

2.1 BET surface area

The surface area of samples was characterized by the BET method, performing adsorption of nitrogen at -196 °C with the apparatus Quantachrome Autosorb-1. Data acquisition, reduction and calculating were performed by Quantachrome Autosorb software.

2.2 Temperature programmed desorption of ammonia (NH₃-TPD)

Alumina-silicas were characterized by temperature programmed desorption of ammonia with an apparatus constructed from Raczek analyze technic GmbH, Hannover. The apparatus consists of an adjustable oven to heat the sample, gas supplies for helium and a mixture of 5 vol.% NH₃ in argon (Messer-Griesheim) and a thermal conductivity detector for gas analysis. Figure 2 presents the conditioning diagram of a silica alumina catalyst. For a typical experiment 0.5 g of fresh catalyst was placed within a U-tube in the oven. During the first run, the sample was heated under He stream at a rate of 20 °C/min from room temperature up to 900 °C and the amount of releasing compounds was measured with a thermal conductivity detector (TCD). At 900 °C no more compound desorbed from the surface of the sample and the TCD-signal drastically decreases to zero. If one reproduces this procedure for the same catalyst (run II), no signal is detected anymore, which means that the surface of the sample is free from adsorbed compounds after high temperature treatment.

After heating the sample up to 900 °C, it was cooled down to 60 °C, which is the temperature at which ammonia adsorption is conducted. In this process, the sample of catalyst is exposed to 5 vol.% NH₃/Ar (Messer-Griesheim) stream (50 mL/min.) for 30 min at 60 °C (figure 2).

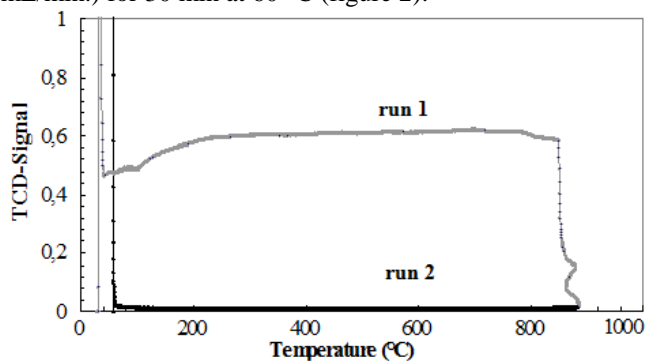


Figure 2: Conditioning of the sample Si/Al (40:60) calcined 3h at 800 °C

3. Materials

3.1 Preparation of zirconium oxides

Zirconium oxide was prepared by calcination of ZrOCl₂*8 H₂O for 24 h at 500 °C (5 K/min). Dehydration occurs stepwise with the formation of the species [Zr₄(OH)₈(H₂O)₁₆]Cl₈*12 H₂O, [Zr₄(OH)₈(H₂O)₁₆] Cl₈*4 H₂O, [Zr₄(OH)₈(H₂O)₁₂] Cl₈ and finally, ZrO₂.

3.2 Supported metal oxides with alumina by precipitation

The alumina used for synthesis of the supported all samples, calcined 3h at 800 °C (supplied by Sasol Germany GmbH).

3.2.1 Preparation of Zirconium oxides on Alumina

An amount of 5 g ZrOCl₂*8 H₂O was dissolved in 100 ml deionized water. The addition of Al₂O₃ to the metal salt solution was performed in the proportion of 95 g. The mixture was heated up to 100 °C under magnetic stirring. then, the precipitating agent, which is an aqueous NH₃ solution (25 M), was added till the suspension achieved pH = 7. After that, the gel was filtered and dried in an oven at 200°C (5 °C/min.) for 24 h.

3.2.3 Preparation of Titanium oxides on Alumina

The TiO₂/Al₂O₃ samples with a titanium oxide content of 5 % were prepared from 3,7 g titanium chloride (TiCl₄) and 35 g Al₂O₃ in 120 ml H₂O. The subsequent preparation procedure was the same as explained in the above point for ZrO₂/Al₂O₃.

3.2.4 Preparation of Hafnium oxide on Alumina

Different ratios of hafnium oxide (5, 10, and 15 wt. %) were loaded on alumina. For this, 3 g HfO₂ were dissolved in each case in 2 ml HNO₃ (3 mole %) and 100 ml deionized water was added. The solution was heated for about 12 minutes under continuous mixing to solve the metal salt. After cooling to room temperature that amount of alumina 45 g was added which was necessary to achieve a hafnium oxide content of 4, 10 or 15 wt. %. The obtained slurry was neutralized by aqueous NH₃ solution (20 M) to pH = 7. This process was followed by filtration and drying in an oven at 180 °C (10 °C/min.) for 24 h. The catalysts were marked with the numeric value indicating the loaded weight percentage of hafnium oxide in the sample (4, 10 and, 15 wt.%).

4. Results and Discussion

Figure 3, presents ammonia TPD for three different metal oxides supported on alumina: zirconium oxide, hafnium oxide and titanium oxide. The adsorption of ammonia for the three samples studied varies in reaching the maximum. The maximum of desorbing ammonia for pure alumina (pure alumina synthesized by the Sasol Germany GmbH calcined for 3h at 800 °C is 200 °C, this point was observed for TiO₂/Al₂O₃ at a temperature of 217°C. The maximum of desorbing ammonia for pure alumina (pure alumina synthesized by the Sasol Germany GmbH calcined for 3h at 800 °C is 200 °C, this point was observed for TiO₂/Al₂O₃ at a temperature of 217°C.

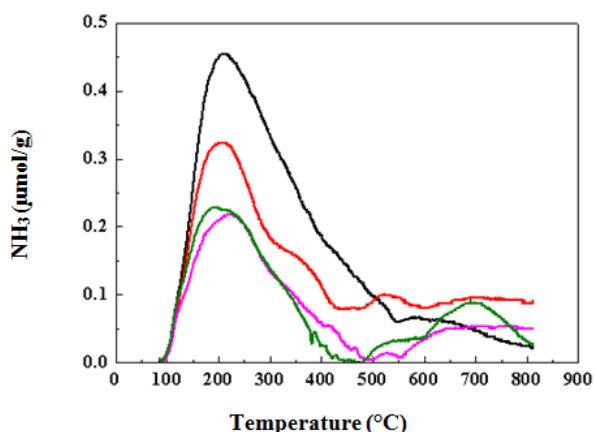


Figure 3: Profiles of temperature programmed desorption of ammonia for different metal oxides/alumina samples

— Pure alumina — TiO₂ — HfO₂ — ZrO₂

A similar asymmetric but lower peak was found in the same sample of TiO₂/Al₂O₃ at a higher temperature of 580 °C exhibiting strong acidic centers. The maximum in the NH₃-TPD spectra for ZrO₂/Al₂O₃ was obtained at 200 °C, while in the case of HfO₂ sample, it is possible to distinguish two highest peaks. The first one is detected at a temperature of 230 °C and the maximum of the second one is centered at 700 °C and is also high but less intensive than that observed at lower temperature. This temperature significantly shows strong acidic centers. The sample was measured to calculate their capacity of desorbing ammonia (table 1) and, the results of TiO₂/Al₂O₃ were found higher than the ones of the other samples, which contained ZrO₂/Al₂O₃ or HfO₂/Al₂O₃.

Figure 4, presents NH₃-TPD of hafnium oxide supported on alumina with different ratios. The experiment should prove the hypothesis that, when the higher the alumina content in the sample, the higher is the amount of desorbed ammonia. Looking at the desorption of ammonia from the samples with different HfO₂/Al₂O₃ ratios, the highest point for all samples is reached at 200 °C.

Table 1: Comparison of total concentrations of acidic sites and specific surface area for different pure rare earth metal oxides and oxides supported on alumina

*Fresh sample	*BET m ² /g	*Fresh sample	Acidity amount in temp. range 100 °C – 400 °C (µmol/g)	Acidity amount in temp. range 500 °C – 800 °C (µmol/g)	Al ₂ O ₃ content wt. %	*BET m ² /g
Pure Al ₂ O ₃	197	-	260	-	100	-
TiO ₂	4.96	TiO ₂ /Al ₂ O ₃	237.0	72.2	96.0	125.6
ZrO ₂	8.25	ZrO ₂ /Al ₂ O ₃	166.6	60.3	95.0	106.3
HfO ₂	9.47	HfO ₂ /Al ₂ O ₃	173.1	50.2	95	100.4
-	-	HfO ₂ /Al ₂ O ₃	142.1	30.2	90	122.6
-	-	HfO ₂ /Al ₂ O ₃	120.6	21.4	85	120.4

* Surface area measured before the reaction.

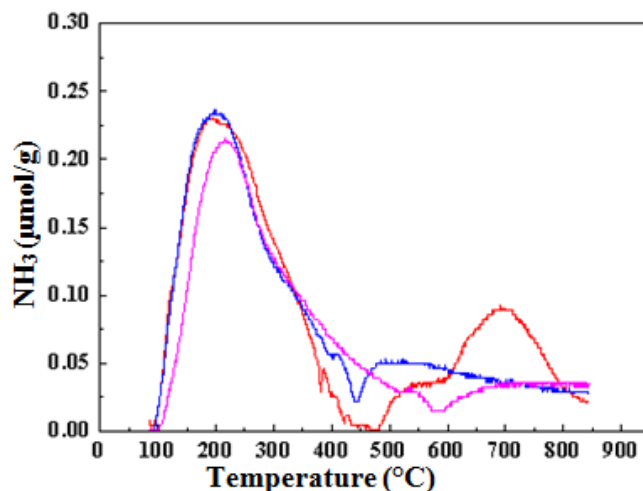


Figure 4: Profiles of temperature programmed desorption of ammonia for hafnium oxides supported on alumina with different ratios (wt.%)

— HfO₂/Al₂O₃ (5:95) wt.%, — HfO₂/Al₂O₃ (10:90) wt.%
 — HfO₂/Al₂O₃ (15:85) wt. %

The sample containing 5 wt. % of hafnium oxide shows two high peaks at higher temperature, whereas the second peak has its maximum around 700 °C, indicating strong acid sites. A straight correlation between the concentration of the acidic sites and the content of alumina in the catalyst can be proved by the data presented in table 1. Because of the strong desorption of ammonia from the raw material used in the synthesis of the samples (pure alumina calcined 3h at 900 °C synthesized by Sasol GmbH) the results of NH₃-TPD for metal oxides supported on alumina are divided into two groups as shown in table 10. The first group shows the desorbed ammonia in the temperature range between 100 °C and 500 °C which could be effected by alumina content. The second group presents the dissolved ammonia, which could describe the acidity of the metal oxide and not of the alumina and that is in range temperatures between 500 °C and 800 °C.

4.1. Effect of water addition to MBOH

Table 2 depicts the conversions after 120 min. time on stream, surface areas after the reaction and the correlation between the conversion and the surface areas for bulk metal oxides (ZrO₂, TiO₂, HfO₂)/Al₂O₃ catalysts before and after the addition of water to MBOH. With the exception of ZrO₂ a clear increase of the MBOH conversion is observed when water is added. The increase in the MBOH conversion can be significantly improved with the samples hafnium oxide doped with alumina, where with HfO₂/Al₂O₃ (10:90) the conversion raised from 40 to 50 % by addition of water.

Table 2: Conversion and surface area of used samples of the synthesized solids

Sample (wt.%)	X _{MBOH, 1.0 s=120 min} %		BET surface area m ² /g			X _{MBOH, 1.0 s=120 min} /BET	
	After water addition	Before water addition	As-synthesized	BET _A	BET _B	X _A /BET _A	X _B /BET _B
ZrO ₂ /Al ₂ O ₃ (4:96)	23.7	27.6	108	110	108	0.2	0.3
TiO ₂ /Al ₂ O ₃ (4:96)	21.8	48.4	129	114	97	0.2	0.5
HfO ₂ /Al ₂ O ₃ (4:96)	22.7	48.3	122	110	101	0.2	0.5
HfO ₂ /Al ₂ O ₃ (4:96)	42.0	48.6	130	125	109	0.3	0.4
HfO ₂ /Al ₂ O ₃ (15:85)	31.1	45.0	135	122	108	0.3	0.4

On the other hand, increasing the content of hafnium oxide in the catalyst causes a decrease in the MIPK product.

The comparison shown in figure 5 between the samples $\text{HfO}_2/\text{Al}_2\text{O}_3$ (5:95 wt.%) and sample $\text{HfO}_2/\text{Al}_2\text{O}_3$ (15:85 wt.%). This can be explained because increasing the fraction of hafnium oxide in the catalyst decreases also the acidic canters (OH) of alumina, which is needed to attack the triple bond of methyl butynol. Moreover, NH_3 -TPD (high desorption peak of ammonia), and the results presented in table 1 shows that the acidity of metal oxides supported on alumina takes the following sequence:

$\text{HfO}_2/\text{Al}_2\text{O}_3$ (15:85) < $\text{HfO}_2/\text{Al}_2\text{O}_3$ (10:90) < $\text{HfO}_2/\text{Al}_2\text{O}_3$ (5:95) < $\text{ZrO}_2/\text{Al}_2\text{O}_3$ (5:95) < $\text{TiO}_2/\text{Al}_2\text{O}_3$ (5:95).

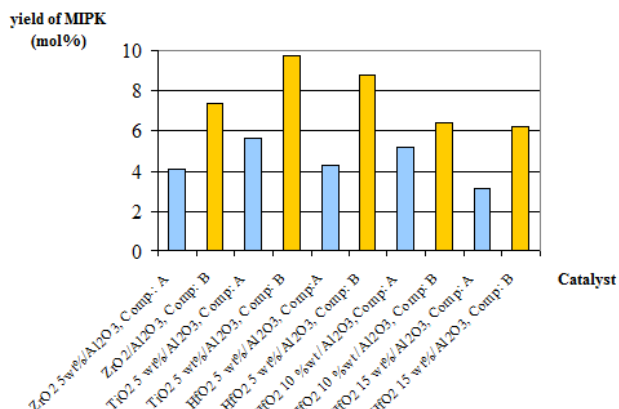


Figure 5: Comparison of the yielded MIPK product after 108 min. time on stream

Generally, it has been reported that the decomposition of H_2O_2 in the presence of metal ions as a homogeneous catalysts slow, but that it is relatively fast when these ions are used along with a small amount of alumina or beryllium oxide [7].

5. Conclusion

It was found a straight correlation between the concentration of the acidic sites and the content of alumina in the catalyst and this can be proved by the data presented in table 1. On the other hand, increasing the content of hafnium oxide in the catalyst causes a reduction in the amphoteric sites (MIPK product). It was also observed and concluded hat when water is added to MBOH, the growth in the MBOH conversion can be significantly improved with the samples hafnium oxide doped with alumina, where with $\text{HfO}_2/\text{Al}_2\text{O}_3$ (10:90) the conversion raised from 40 to 50 %, by addition of water.

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