

MIPK product (figure 1) which describes the amphoteric sites the used bulk metal oxides (ZrO_2 , TiO_2 , HfO_2)/ Al_2O_3 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 $-196\text{ }^\circ\text{C}$ with the apparatus Quantachrome Autosorb-1. Data acquisition, reduction and calculating were performed by Quantachrome Autosorb software.

2.2 Temperature programmed desorption of ammonia (NH_3 -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.% NH_3 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 $20\text{ }^\circ\text{C}/\text{min}$ from room temperature up to $900\text{ }^\circ\text{C}$ and the amount of releasing compounds was measured with a thermal conductivity detector (TCD). At $900\text{ }^\circ\text{C}$ 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 $900\text{ }^\circ\text{C}$, it was cooled down to $60\text{ }^\circ\text{C}$, which is the temperature at which ammonia adsorption is conducted. In this process, the sample of catalyst is exposed to 5 vol.% NH_3/Ar (Messer-Griesheim) stream ($50\text{ mL}/\text{min}$.) for 30 min at $60\text{ }^\circ\text{C}$ (figure 2).

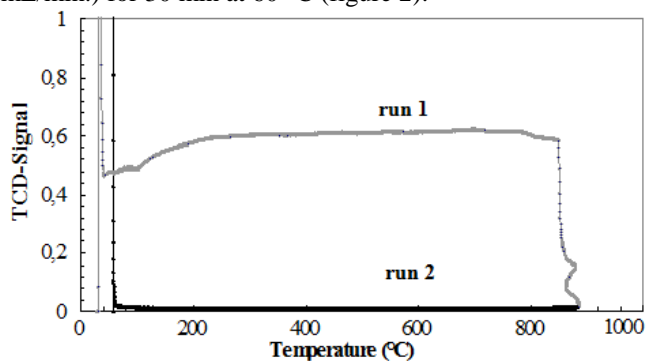


Figure 2: Conditioning of the sample Si/Al (40:60) calcined 3h at $800\text{ }^\circ\text{C}$

3. Materials

3.1 Preparation of zirconium oxides

Zirconium oxide was prepared by calcination of $ZrOCl_2 \cdot 8H_2O$ for 24 h at $500\text{ }^\circ\text{C}$ ($5\text{ K}/\text{min}$). Dehydration occurs stepwise with the formation of the species $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 4H_2O$, $[Zr_4(OH)_8(H_2O)_{12}]Cl_8$ and finally, ZrO_2 .

3.2 Supported metal oxides with alumina by precipitation

The alumina used for synthesis of the supported all samples, calcined 3h at $800\text{ }^\circ\text{C}$ (supplied by Sasol Germany GmbH).

3.2.1 Preparation of Zirconium oxides on Alumina

An amount of 5 g $ZrOCl_2 \cdot 8H_2O$ was dissolved in 100 ml deionized water. The addition of Al_2O_3 to the metal salt solution was performed in the proportion of 95 g. The mixture was heated up to $100\text{ }^\circ\text{C}$ under magnetic stirring. then, the precipitating agent, which is an aqueous NH_3 solution (25 M), was added till the suspension achieved $pH = 7$. After that, the gel was filtered and dried in an oven at $200\text{ }^\circ\text{C}$ ($5\text{ }^\circ\text{C}/\text{min}$.) for 24 h.

3.2.3 Preparation of Titanium oxides on Alumina

The TiO_2/Al_2O_3 samples with a titanium oxide content of 5 % were prepared from 3,7 g titanium chloride ($TiCl_4$) and 35 g Al_2O_3 in 120 ml H_2O . The subsequent preparation procedure was the same as explained in the above point for ZrO_2/Al_2O_3 .

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 HfO_2 were dissolved in each case in 2 ml HNO_3 (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 NH_3 solution (20 M) to $pH = 7$. This process was followed by filtration and drying in an oven at $180\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$.) 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 $800\text{ }^\circ\text{C}$ is $200\text{ }^\circ\text{C}$, this point was observed for TiO_2/Al_2O_3 at a temperature of $217\text{ }^\circ\text{C}$. The maximum of desorbing ammonia for pure alumina (pure alumina synthesized by the Sasol Germany GmbH calcined for 3h at $800\text{ }^\circ\text{C}$ is $200\text{ }^\circ\text{C}$, this point was observed for TiO_2/Al_2O_3 at a temperature of $217\text{ }^\circ\text{C}$.

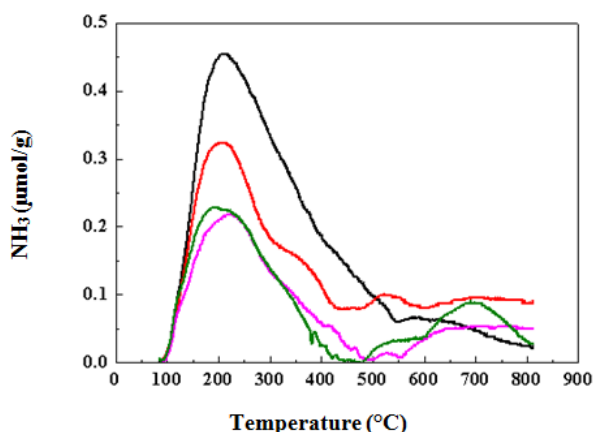


Figure 3: Profiles of temperature programmed desorption of ammonia for different metal oxides/alumina samples

— 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.

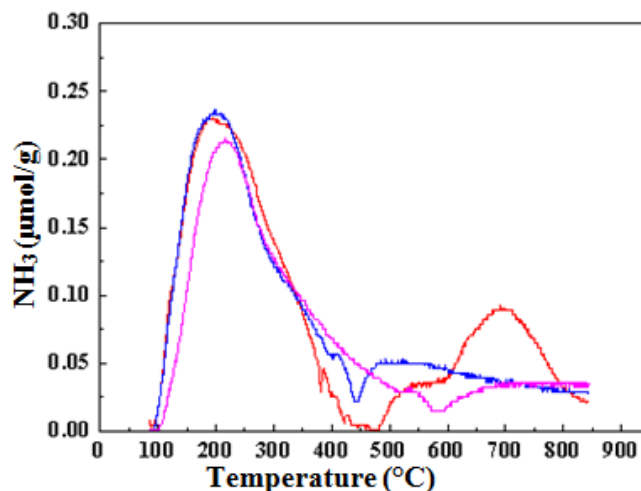


Figure 4: Profiles of temperature programmed desorption of ammonia for hafnium oxides supported on alumina with different ratios (wt.%)

— 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, t=120 min} %		BET surface area m ² /g			X _{MBOH, t=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).

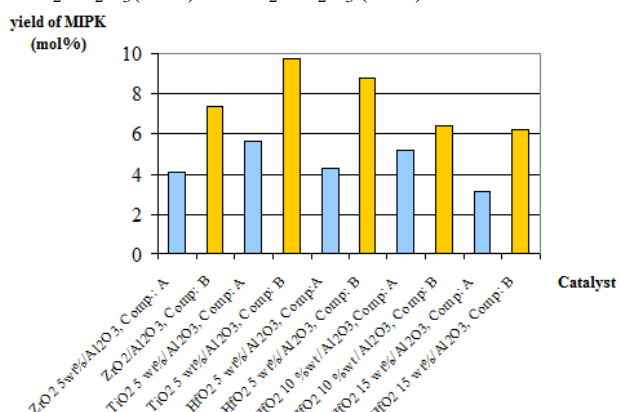


Figure 5: Comparison of the yielded MIPK product after 108 min. time on stream

Generally, it has been reported that the decomposition of H_2O_2 in the presence of metal ions as a homogeneous catalysis is 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 that 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.

References

- [1] H. Lauron-Pernot, F. Luck, J. M. Popa, "A new and simple diagnostic tool for acidic and basic sites of solids," *Journal of Applied Catalysis*, vol. 78, no. 2, pp. 213-225. 1991.
- [2] M. Alsawalha, F. Roessner, "Insight in to the reaction mechanism of the conversion of methylbutynol on silica-alumina", *React. Kinet. Catal. Lett.*, vol. 94, no. 1, pp.63-69, 2008.
- [3] H. Lauron-Pernot, "Evaluation of surface acido-basic properties of inorganic-based solids by model catalytic

alcohol reaction networks", *Cat. Rev.*, vol. 48, pp. 315-361. 2006.

- [4] F. Audry, P. E. Hoggan, J. Saussey, J. C., Lavalley, H. Lauron-Pernot, A. M. Le Govic, "Infrared study and quantum calculations of the conversion of methylbutynol into hydroxymethylbutanone on Zirconia," *Catal.* vol. 168, no. 2, pp. 471- 481, 1997.
- [5] S.Kyeono yun, V. Constantino and T. Pinnavaia, "Synthesis and catalytic properties of silicate- intercalated layered double hydroxides formed by intragallery hydrolysis of tetraethylorthosilicat", *Clay Minerals*, vol. 43, no. 4, pp. 503-510, 1995.
- [6] M. Alsawalha, "Study the Effect of Calcination Temperatures on the Catalytic Properties of Alumina-Silica Catalysts", *International Journal of Research in Engineering and Technology (IJRET)*, Vol. 2, no. 2, , pp. 96-100, 2013.
- [7] R.N. Ram, J.R.P. Gupta and B.B. Prasad, "Studies on some Oxidation reactions a Ru (III) supported catalysts", *Indian J. Chem.*, 17A, pp. 29, 1979.