Characterization of surface properties of silica alumina by catalytic conversion of methylbutynol

Murad AlSawalha

Organic Materials Division, Industrial Chemistry Center, Royal Scientific Society, P.O. Box: 1438, Al-Jubaiha, Amman 11941 Jordan

Frank Roessner

Industrial Chemistry, Institute of Pure and Applied Chemistry, Carl v. Ossietzky University Oldenburg, D-26111 Oldenburg, Germany

Аннотация

The conversion of methylbutynol (MBOH) over commercially available silica-alumina solids was studied. The formation of 3-methyl-3-butene-2-one (MIPK) was explained in terms of the cooperative action of both Brönsted acidic and co-ordinatively unsaturated surface sites. With increasing silica content the number of defect sites decreases and well ordered silica-alumina is formed

Introduction

The characterization of acid-basic properties of a catalyst is strongly linked with the prediction of both activity and selectivity in many reactions. Numerous physico-chemical methods have been developed to determine the surface properties of oxides. Beside spectroscopic methods like infrared, UV-visible and NMR spectroscopy and thermal methods like calorimetry and thermodesorption [1] catalytic test reactions are the most suitable tools as they are sensitive to the reactive site. The isomerisation of but-1-ene was one of the first proposed test reactions to distinguish between acidic and basic centers taking into account the cis/trans ratio of the but-2-ene formed [2]. The main drawback was, however, that this test reaction is can only be non-ambiguously applied when a single type of the catalytic centers is expected to be present.

The use of alcohols, first of all isopropanol, was proposed by Ai [3]. The acidic sites catalyses the dehydration pathway whereas basic sites form acetone. On the other hand several authors questioned this assumption showing that the formation of acetone is also related to redox properties [4,5].

To keep the advantage of alcohols as reactive probe molecules and to avoid the problem of redox properties 2-methyl-but-2-yne-2-ol (MBOH) has been proposed by Lauron-Pernot et al. [6]. Recently, the state of the art was described in an excellent review [7]. The products formed on different sites of the catalyst as proposed by Lauron-Pernot [6] are given in scheme 1, and it may be seen that, whereas acidic and basics sites of a catalyst are clearly defined amphoteric sites are uncommon. Not many studies have been devoted to the mechanism of formation of 3-methyl-3-butene-2-one (MIPK). As reactive centers either strong acidic sites, e.g. on H-ZSM-5 zeolites [8] , or acid-base pairs on alumina were contradictorily discussed. It is known that alumina, especially in the γ-phase, is catalytically very active in several reactions [9,10]. The catalytic activity of γ-alumina is closely related to certain acid sites which are created by surface hydroxyl groups [11].

During thermal treatment different dehydroxylation processes, accompanied by water desorption take place resulting in additional Lewis acidic sites.

The addition of silica during the synthesis process strongly changes the surface properties of alumina. Applying FTIR spectroscopy, Daniell and Knözinger [12] have been studied the change of surface properties of alumina by silica addition.

They detected several surface species which formation depends on the chemical composition of the amorphous alumosilicate. For such materials with a silica content in the range of 10 – 20 wt.% three types of acidic surface sites were observed: (i) an alumino-silicate phase, (ii) coordinatively unsaturated $Al^{3+}_{(TET)}$ ions exposed on the surface, and (iii) sites with enhanced Brönsted acidity, attributed to bridged OH groups on the exposed alumino-silicate. At higher silica contents the formation of a silica phase covering the alumina crystallites is expected. Furthermore, the morphology of alumina is changed which also should attribute to the acid-base properties of the silica-alumina due to possible formation of different domains of silica and alumina.

Since small changes in the amount of silica added to alumina drastically influences on the surface properties silica-alumina should have a lasting effect on the product distribution in the conversion of MBOH. Additionally, a correlation of the formation of MIPK with the surface properties of silica-alumina should give insight into the nature of the so-called amphoteric sites.

Experimental

Investigated catalysts

For this study different silica-alumina and supplied by Sasol Germany GmbH were studied. The samples differ in ratios of silica to alumina and calcination temperatures. The content of silica in the studied samples was 5, 10, 20, and 40 wt.%. The catalysts were pre-treatment temperatures at T= 550 °C and T=900 °C, respectively, for 3h. Sample names were abbreviated using the prefix Si/Al relating to silica-alumina and a number referring to the content of SiO_2 in wt.% as well as to the calcinations temperature, 550 °C and 900°C, respectively.

For comparison the following zeolites were studied: H-ZSM-5 (Si/Al=45), H-Beta (Si/Al=25) and Y zeolite (Si/Al=5.5) supplied by Sud-Chemie AG, Munich (Germany).

Conditions for methylbutynol conversion

The conversion of methylbutynol was performed in fixed bed reactor. An amount of 0.2 g of the catalyst with a particle size of 200 – 315 μm was used. Adjusting the MBOH flow before evaporation to 0.02 mL/min and using a nitrogen stream of 12 mL/min as carrier gas, a WHSV = 5.2 g_{MBOH} / g_{cat} h was established. A detailed description of the procedures is given elsewhere [13]. The products were analysed on-line on a HP 8090 Series II gas chromatograph with a 60 m Optima Wax capillary column. Conversion, yield and selectivities are given in % and mol%, respectively, and were calculated on the basis of peak areas of the chromatogram considering the response factors of all compounds. Reference substances were obtained from Fluka (MBOH, 99 %, Prenal, 99%,), Aldrich (MBYNE, 98 %, HMB 99%), Acros (acetone 99 %) and Messer-Griesheim (acetylene, 99 %). MIPK was synthesised by acid catalysed dehydration of HMB.

Temperature programmed desorption of ammonia

Silica-aluminas were characterized by temperature programmed desorption of ammonia (TPAD) carried out on an apparatus constructed from Raczek Analyse Technic GmbH, Hannover (Germany). The samples were conditioned at 550°C in helium flow. Afterwards, a mixture of 10% NH3/He was passed over the sample at T=60°C. The physisorbed ammonia was removed by flushing with helium at T=120°C for 2 h. The chemisorbed ammonia was removed by passing helium over the sample as the sample was heated up to T=550°C with a linear heating rate of 10°C/min

Results and discussion

Catalytic activity of silica –alumina in the conversion of methylbutynol

Figure 1 shows the dependence of the conversion on the time on stream at T=120°C. It is evident that the activity increases with an increase in the silica content up to 96 %, which is close to the thermodynamic equilibrium.
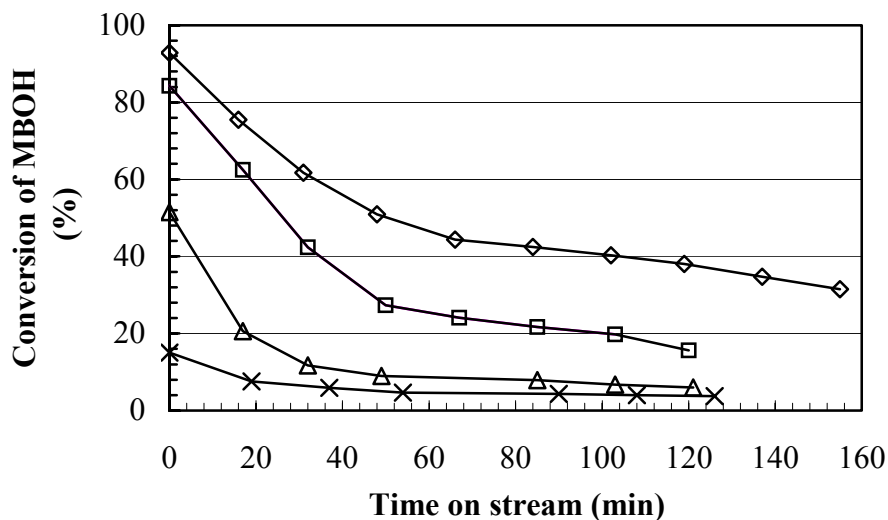

Fig.1. Conversion of MBOH over different Si/Al (550), reaction temperature 120 °C, ✕ Si/Al 5, △ Si/Al 10, □ Si/Al 20, ◇ Si/Al 40

Furthermore, all catalysts undergo a rapid deactivation during the initial period up to 60 min. The higher the silica content the higher the drop in activity. Increasing the reaction temperature to T=180 °C (Figure 2) two effects can be distinguished: (i) the catalysts with the a silica content of 30 and 40 wt.%, respectively, do not deactivate and (ii) the initial conversion of the low silica materials increases up to 70 and 80 %, respectively. However, their activity declines with time on stream.
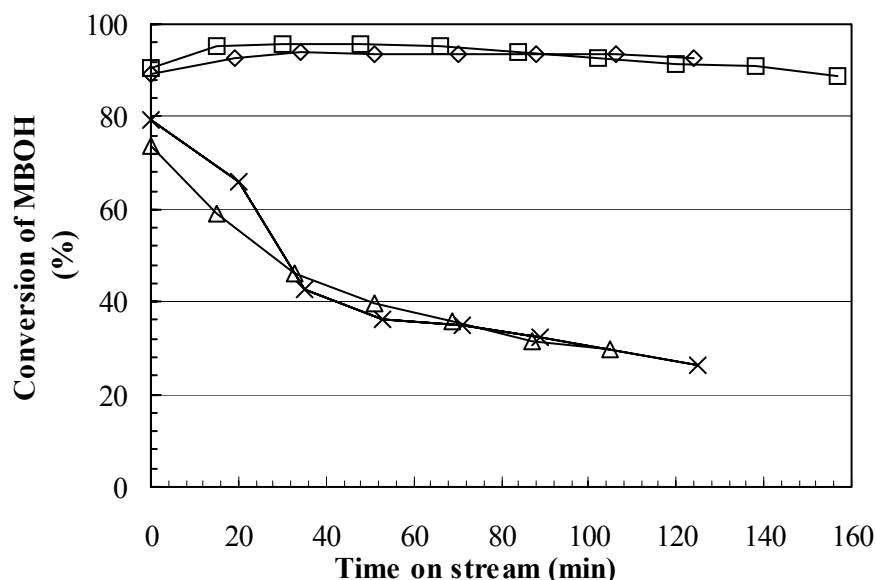

Fig. 2. Conversion of MBOH over different Si/Al (550) at reaction temperature 180 °C. ✕ Si/Al 5, △ Si/Al 10, □ Si/Al 20, ◇ Si/Al 40

The behaviour could be explained in term of reaction inhibition both by product and methylbutynol. Especially the formed water could be strongly adsorbed on the active sites blocking
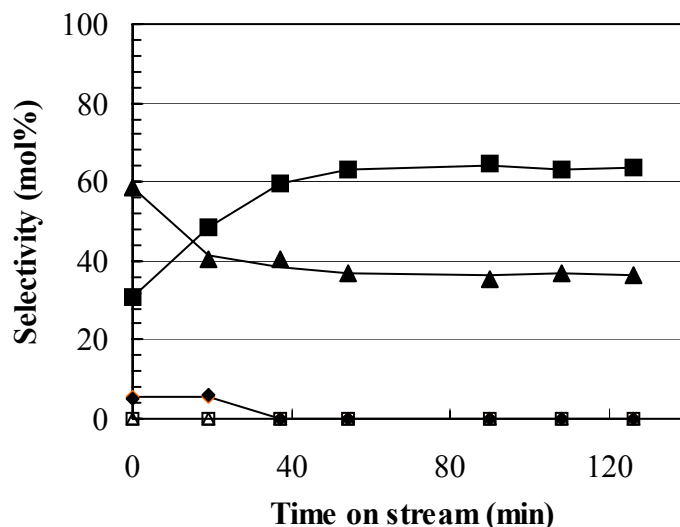
the access of MBOH. At higher temperature (T=180°C) the desorption is preferred and the access of MBOH is improved which results in a higher, constant activity. Catalysts which contain less silica have a lower number of acid but their strength is higher according to the model of Knözinger [9]. Therefore, the interaction with water is stronger, even at higher temperature, which finally results also in product inhibition. MBYNE and Prenal were detected as products. Both are formed via the acid pathway (scheme 1). Figures 3 and 4 depict the selectivities over Si/Al 5 (550) at reaction temperatures of 120°C and 180 C, respectively.

Scheme 1. Reaction pathways of conversion of methylbutynol on different surface sites

MBYNE and MIPK are the main products after 120 min time on stream (t.o.s.). At a reaction temperature of 120 °C the selectivity of MIPK increases from 30 mol% in the initial period of the reaction to 60 mol% within 40 min on stream. In general, a high Si/Al ratio causes a lower electron density on the surface oxygen species, thus the protons will be more loosely bonded to these oxygen species and therefore the acid strength increases. Another explanation for the strong acidity at high ratios of SiO_2 is that weak bonds between alcohol oxygen and the structure aluminium cations are formed. Therefore, the electron pair acceptance strength of these cations increases, hence acidity increases [8].

Fig.3. Selectivity of the products over Si/Al 5 (550), reaction temperature 120 °C. ◇ Acetylene, ◆ Acetone, ▲ MBYNE, △ Prenal, ■ MIPK, □ HMB
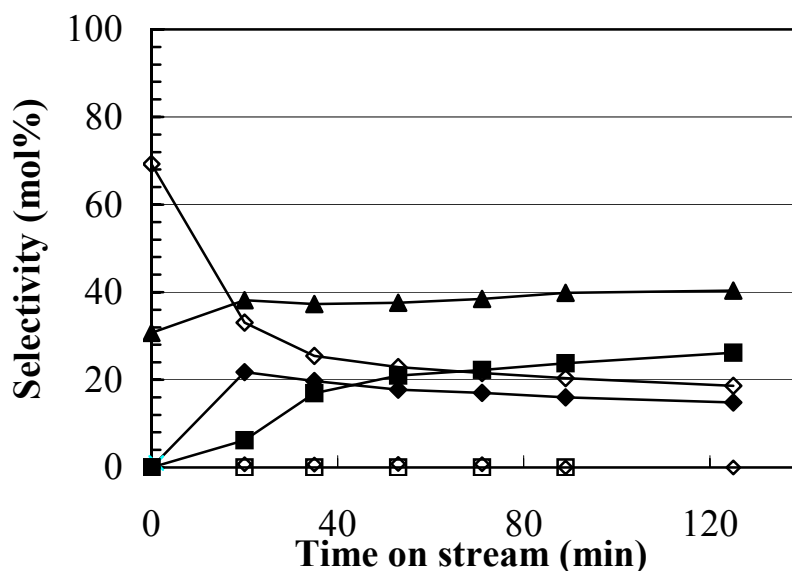

Fig. 4. Selectivity of the products over Si/Al 5 (550), reaction temperature 180 °C. ◇ Acetylene, ◆ Acetone, ▲ MBYNE, △ Prenal, ■ MIPK, □ HMB

Other products like acetone are only observed at the initial period of the reaction up to 20 min t.o.s., i.e. basic centers are deactivated immediately at the beginning of the reaction.

The increase of the reaction temperature from T=120 °C to T=180°C results in half as high selectivity of the products MBYNE and MIPK (see figure 3 and 4). This effect is accompanied by the appearance of acetylene and acetone with selectivity of about 25 mol%.

Acetone and acetylene are the products, which are formed at basic sites (see scheme 1). It is noteworthy that the ratio acetylene to acetone over studied samples was slightly higher than the expected stoichiometric value of one. This effect could be explained in term of aldol condensation of acetone resulting in high molecular condensation products which cannot desorb at the applied conditions.

The mechanism of the transformation from methylbutynol to the main products 3-methyl-3-buten-1-yne (MBYNE) and 3-methyl-3-butene-2-one (MIPK) can be explained by scheme 2 and 3. The acidic hydroxyl groups form a transition state in which the alcoholic oxygen is attacked by

the acidic hydrogen of the surface. After elimination of water the acid site is restored, accompanied by the desorption of MBYNE.

Transition state

3-methyl-3-buten-1-yne
(MBYNE)
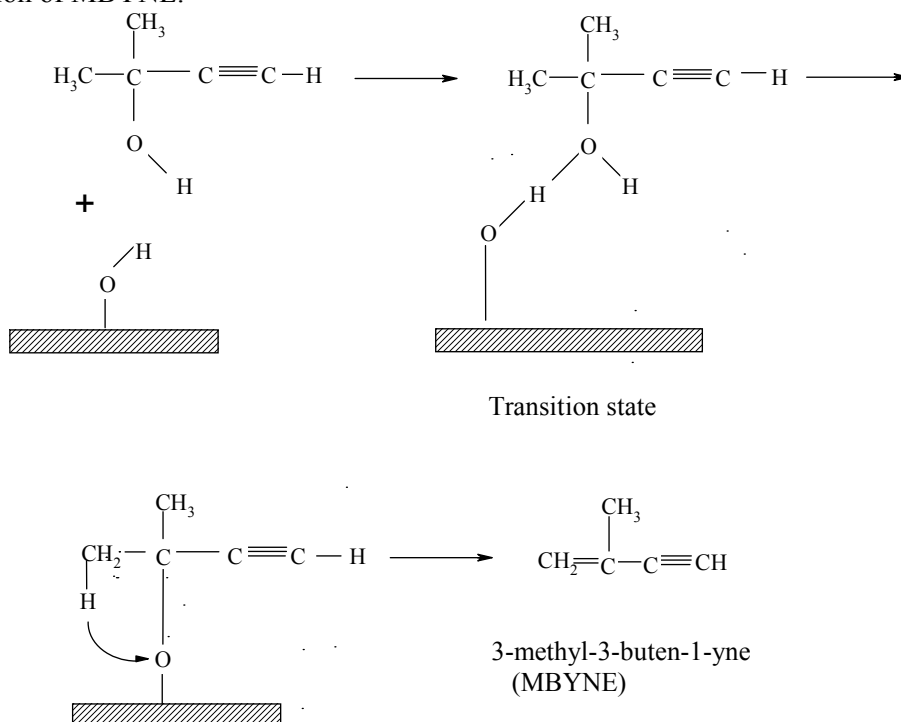
Scheme 2. Reaction scheme for the formation of MBYNE

Aramendia et al. [14] suggested that hydration of MBYNE leads to formation of MIPK. Hereby, the formed water is added to the triple bond and the enol is rapidly transformed into the carbonyl.
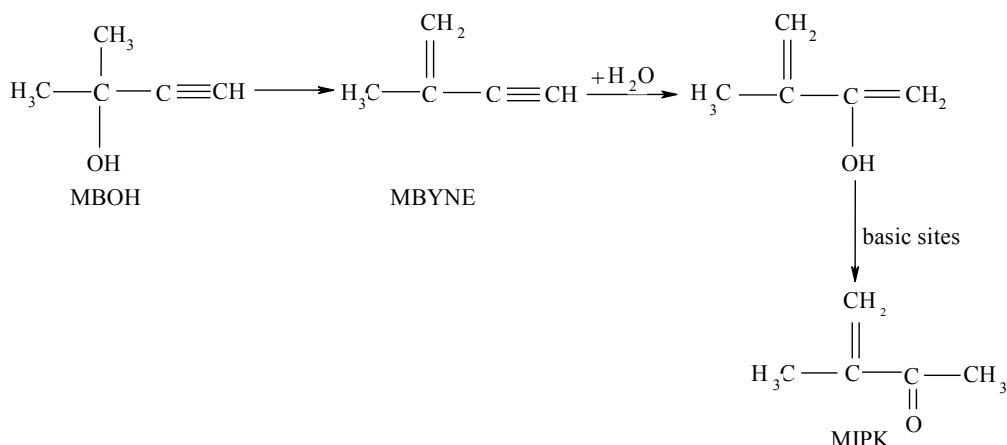
Scheme 3. Reaction scheme for the formation of MIPK according to Armendia et. al [14]

Temperature programmed desorption of ammonia

In table 1, the results of the TPAD measurements are compiled. The desorption maxima of the relatively broad desorption profiles were observed in the range of 280-450°C. As expected the amount of desorbed ammonia depends on the Si/Al ratio of the catalyst. The increase of amount of SiO_2 leads to an increase in the amount of chemisorbed ammonia, independent on the calcinations

temperature. This can be discussed in terms of formation of brigded hydroxyl groups which has Brönsted acidic properties. Although the determination of the acidity distribution was not in the focus of the present study, one can speculate in accordance with the literature that generally the strength of the Brönsted sites increases with increasing silicon content [12]. According to literature Brönsted acid sites are required for the formation of MIPK [14]. Therefore, with respect to table 1 an increase in MIPK formation should be expected with increasing Si/Al ratio.

Table 1. Comparison of the amount of adsorbed ammonia in dependence on the calcination temperature

| Sample | Calcination Conditions | | | |
| | 550 °C, 3 h | | 900 °C, 3h | |
	Adsorbed NH$_3$ (μmol/g)	Al content (wt.%)	Adsorbed NH$_3$ (μmol/g)	Al content (wt.%)
alumina	107	100	260	100
Si/Al 5	288	95.2	120	95.2
Si/Al 10	289	89.9	214	89.9
Si/Al 20	289	80.4	223	80.8
Si/Al 40	332	61.3	234	60.8

Influence of GHSV on the formation of MIPK

The dependency of the selectivity of MIPK on the conversion of MBOH was investigated applying different amounts of catalyst. From figure 5 it is obviously, that the lower the conversion the higher the selectivity to MIPK. This fact is a strong indication for the assumption that MIPK seems to be a primary product of MBOH conversion.
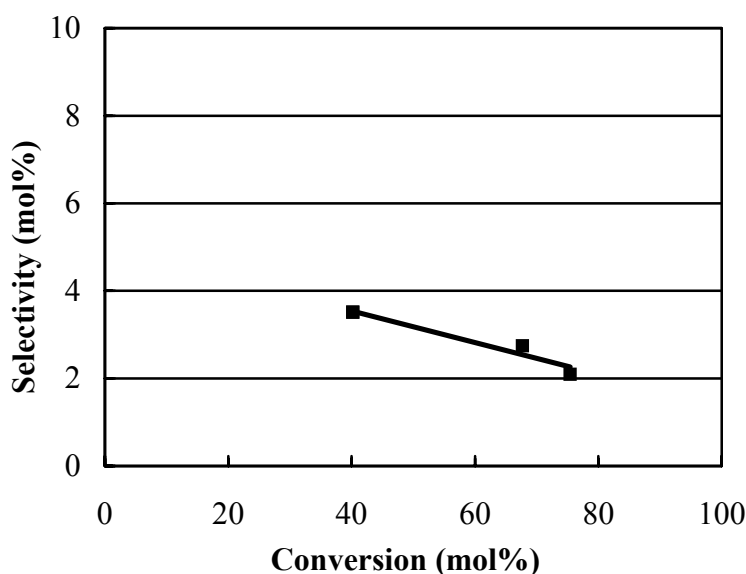

Fig. 5. Selectivity of MIPK over different amount of Si/Al 5 (550), reaction temperature 120 °C, t.o.s. = 20 min

Effect of water on the conversion of MBOH

As mentioned above Aramendia et.al. [14] proposed that the formation of MIPK is the result of addition of water, which is produced by dehydration of MBOH, to MBYNE (Scheme 3). Their conclusions are based on the studied influence of addition of water to MBOH converted on ZrO$_2$. Consequently, the increase of the partial pressure in the gas phase should influence on the selectivity of MIPK formation. To proof this hypothesis a mixture of 95 vol% MBOH and 5vol%

water was passed over silica alumina with different Si/Al ratio. No influence of added water both on conversion and selectivity of MIPK formation was observed.

This experimental fact clearly demonstrates that water, being present in the gas phase, is not involved into the reaction. Otherwise, the added water should influence the adsorption-desorption equilibrium, and consequently, the MIPK formation should be changed. Therefore, the formation of MIPK should be the result of an intra-molecular rearrangement.

Formation of MIPK over silica alumina

From data given in table 2 it is evident that the exclusive presence of strong acidic sites, as present in zeolites or silica-alumina Si/Al 40 (550), is insufficient to explain the formation of MIPK. According to Knözinger at al. [9] addition of small amounts of silica to alumina results in drastic changes of the alumina surface. One should distinguish between two types of centers existing on the surface: (i) isolated acidic surface site, (ii) acidic center with coordinatively unsaturated surface center in the vicinity.

The adsorption of MBOH on isolated acidic centers results in dehydration to MBYNE (scheme 3, path A). Therefore, both a high degree of conversion and high selectivity to MBYNE were observed for materials with well-ordered structures, e.g. zeolites and silica-alumina Si/Al 40 (Table 2). Furthermore, the formation of MBYNE correlates with the increase of number of acidic centers on silica-aluminas as determined by TPAD.

Table 2. Conversion of MBOH and selectivity over different types of zeolites and different silica alumina (550) at reaction temperature 120 °C after t=90 min

Catalyst	Si/Al ratio	X_{MBOH}	C_2H_2 (mol%)	C_3H_6O (mol%)	MBYNE (mol%)	Prenal (mol%)	MIPK (mol%)
H-ZM5	45	46.9	0.0	0.0	90.4	9.6	0.0
H-Beta	25	9.6	0.0	0.0	95.8	4.2	0.0
Y	5.5	4.9	0.0	0.0	95.5	4.5	0.0
Si/Al 5	5	4.3	0.0	0.0	35.4	0.0	60.3
Si/Al 10	10	7.9	0.0	0.0	65.0	0.0	35.1
Si/Al 20	20	21.7	0.0	0.0	21.2	0.0	2.2
Si/Al 40	40	40.3	0.0	0.0	99.3	0.7	0.0

The adsorption of MBOH on coordinatively unsaturated surface centers, which are probably vacancies, should result in a polarization of the triple bond. The next step (scheme 3, path B) is the addition of an acidic proton of the adjacent Brönsted acidic site to the negatively polarized sp-hybridised carbon atom and formation of intermediate carbenium which rearranges exclusively by a methyl shift. Finally, the scission of OH bond and restoration of surface hydroxyl groups leads to MIPK formation.

Such type of centers exists only in disturbed structures. Usually, their number is low and, consequently, their overall catalytic activity is lower compared to isolated acidic sites..

It was observed that Si/Al 5 and Si/Al 10 permit both pathways presented in scheme 4 route; (A) to MBYNE and (B) to MIPK , while Si/Al 20 and Si/Al 40 favor only route (A) because MIPK is not observed. Taking into account the model of Knözinger [9], one can suggest that the further addition of silica health the structural defects, which detailed structure is unknown yet, i.e. the number of coordinatively unsaturated sites decreases and, consequently, the formation of MIPK is suppressed. This speculation is in agreement with the catalytic results (see table 2).
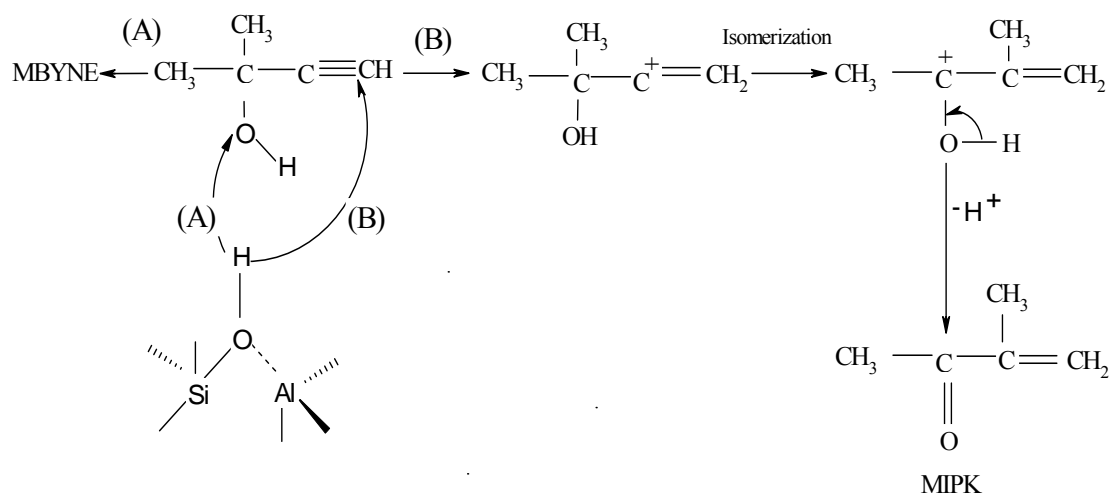
Scheme 4. Proposed reaction scheme for the formation of MIPK on coordinatively unsaturated surface sites

Conclusions

This work focused on the mechanism of the formation of MIPK in the conversion of methylbutynol on silica alumina with different Si/Al ratio. The dependence of MIPK selectivity on the degree of conversion and the inert behaviour of added water let us suggest that MIPK is a primary product of MBOH conversion. A reaction mechanism is proposed which avoids the formation of "free" water on the surface. Depending on the structure of the surface structure in silica-alumina samples, MBOH can be converted on single acidic sites to MBYNE by dehydration. Structural defects or a different ratio of tetrahedrally to octahedrally coordinated aluminium can form co-ordinatively unsaturated sites. The cooperative action of this Lewis acidic and of Brönsted sites is proposed to be catalytically active centers in the formation of MIPK by activation of the triple bond. The presence of this type of surface centres strongly depends on the Si/Al ratio; the higher the alumina content the higher selectivity to MIPK formation.

The amount of desorbed ammonia, determined by TPAD, correlated with the yield of MBYNE, formed by dehydration. This underlines that the formation of MBYNE proceeds on isolated Brönsted acidic sites.

Acknowledgement

References

1. H. Hattori, *Chem. Rev.*, **95**, 537 (1995).

2. H. Pines, W.M. Stalick, *Base catalyzed Reactios of Hydrocarbons and Related Compounds*, Academic Press, New York, 1997.

3. M. Ai, *J. Catal.*, **40**, 318 (1975).

4. C. Lahousse, J. Bachelier, J-C. Lavally, H. Lauron-Pernot, A.-M. Le Govic, J. Catal., **87,** 329 (1994).

5.Corma, V. Fornes, F. Rey, J. Catal., **148,** 205 (1994).

6.H. Laurent-Pernot, Luck, F. Popa, J. M. *Appl. Catal.,* **78,** 213 (1991).

7.H. Laurent-Pernot, *Catalyis Reviews*, **48**, 315 (2006).

8.M. Huang, S. Kaliaguine, *Catal. Lett.,* **18,** 373 (**1993**).

9. H. Knözinger, H. Ratnasamy, P. *Catal. Rev.-Sci. Eng.*, **24,** 31 (1978).

10. R.K Oberlander, In : B.E Leach (ED), *Applied industrial Catalysis*, Vol. 3, Chapter 4 Academic Press, New York, **,** (1984).

11. J. B. Peri,. *J. Phys. Chem.*, **1**, 69, 220 (1956).

12. W. Daniell, H. Knözinger, *Appl. Catal. A: General.,* **196,** 247 (2000)

13. P. Kuśtrowski, L. Chmielarz, E. Bożek, M. Sawalha, F. Roessner, *Adv.. Mater.,* **39,** 263 (2004).

14. M. Armendia, A. Borau,V. Jimenez, C. Marinas, J.M. Porras, A.Urbano, F. *J. Catal.,* **161**, 829 (1996).