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Superbase catalysts from thermally decomposed sodium azide supported on mesoporous γ-alumina

Roxana M. Bota *, Kristof Houthoofd, Piet J. Grobet, Pierre A. Jacobs

K.U. Leuven, Centre for Surface Science and Catalysis, Kasteelpark Arenberg 23, 3001 Leuven, Belgium

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ABSTRACT

Mesoporous γ-alumina because of its homogeneous pore size distribution, represents a good support for alkali metals. Controlled thermal decomposition of impregnated sodium azide on such support yields a superbasic catalyst for the double bond migration of vinylcyclohexane to ethylidene cyclohexane in continuous liquid flow operation. After slurry impregnation of the azide in methanol, ^{23}Na MAS NMR shows the presence of resonance lines corresponding to Na metal particles and sodium oxide on the support. When dry mixing of the catalyst components is done, only supported sodium oxide is found, in association with decreased catalytic activity. It is concluded that both species are necessary components of the superbasic sites required for the isomerization reaction mentioned. In the transesterification of soybean oil with methanol in a batch reactor, the same differences in activity are encountered. The ^{23}Na MAS NMR spectrum of the former catalyst remained unchanged after the transesterification reaction.

1. Introduction

The first successful preparation of mesoporous silica, *viz.* MCM-41 [1,2], was at the basis of a whole pleiade of catalyst supports with high surface area, uniform pore-size distribution in the mesoporous region and high thermostability. Given the potential of traditional γ-alumina as catalyst support in the chemical and petrochemical industries [3], it is not unusual to encounter recent efforts studying the preparation of mesoporous γ-alumina. Materials with specific surface areas up to 800 m^2/g and pore sizes ranging from 2.0 to more than 10 nm have been reported to be characteristic for organized mesoporous aluminas prepared by neutral, anionic and cationic synthesis routes [4].

Although solid base catalysts in general have been received much attention especially due to their advantages for easy separation and recovery, reduced corrosion and environmental acceptance [5], there is still a need to prepare solid superbasic catalysts. Such materials are able to catalyze specific reactions such as double bond shift in olefins such as vinylcyclohexane (VCH), vinylnorbornene and 2,3-dimethyl-1-butene, alkene dimerization and side chain alkylation of alkylaromatics. In particular, strong basic sites with $H_- > 34$ are needed to catalyze such reactions [6]. The reactions are therefore often used to probe the presence of superbasic sites, as they allow *in situ* inspection of the working catalysts, which is often very difficult using physico-chemical techniques.

The double bond isomerization of VCH is considered to be initiated by abstraction of an allylic H by a strongly basic site of the catalyst [7–11]. The allylic H of VCH is attached to a tertiary carbon and is more difficult to abstract in the form of H^+ than the H atoms attached to a secondary or primary carbon atom. Therefore, it is suggested that superbasic sites are required for VCH double bond isomerization (Scheme 1).

There have been attempts to prepare superbasic catalysts by addition of both alkali hydroxides and alkali metals to alumina supports [12]. Such catalysts show high activity and selectivity in the reactions mentioned above to probe superbasicity. Controlled decomposition of sodium azide impregnated in zeolite NaY has been successfully used first to poison the acid sites and then to create strong basic sites in zeolites [6,13–24]. Martens et al. [16–18] have investigated the generation of both metallic particles and ionic alkali clusters in faujasite-type zeolites during controlled thermal decomposition of impregnated sodium azide. The ionic alkali metal clusters were accommodated in the sodalite cages of the faujasite structure, while the neutral metal particles were located in the zeolite large cages. The latter were found to be associated with the development of superbasic sites, able to activate some of the specific substrates mentioned.

Recently, potassium functionalized mesoporous γ-alumina containing impregnated K_2O as active compound, was claimed to act as a solid superbase [24]. Unfortunately, the low activity reported for the isomerization of 1-hexene, does not allow establishing unequivocally the presence of superbasic sites. A

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* Corresponding author.
E-mail address: roxanamelania.bota@biw.kuleuven.be (R.M. Bota).

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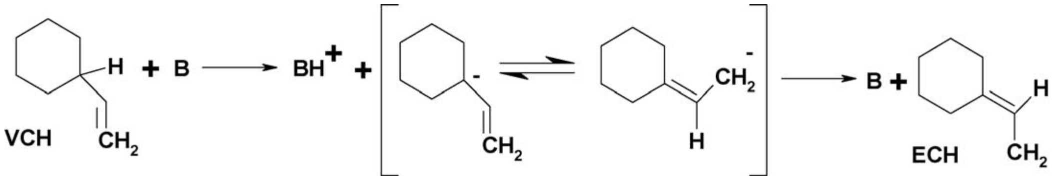
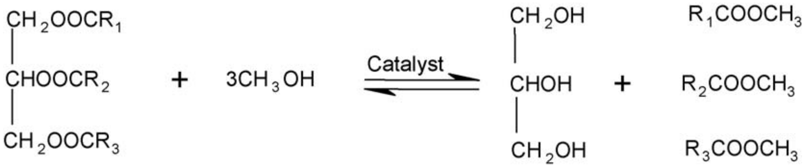


Scheme 1. Mechanism for isomerization of vinylcyclohexane (VCH) to ethylidencyclohexane (ECH) with superbase catalyst B.



Scheme 2. Transesterification reaction of triglycerides with methanol. R_iCOOCH_3 corresponds to the respective methyl fatty acid esters derived from the triglycerides.

solid mixture of dry mesoporous alumina and sodium azide calcined at 400 °C has been shown to have moderate activity in the double bond shift in 2,3-dimethyl-1-butene [25]. Unfortunately no characterization of the sodium metal was provided.

In this paper we report the preparation and catalytic use of thermally decomposed sodium azide-on-mesoporous γ-alumina as a superbasic catalyst in the room temperature double bond migration of VCH, a reaction requiring superbasic catalytic sites to occur [6]. The potential of such catalyst in the transesterification of soybean oil with methanol, a reaction also known as biodiesel synthesis (Scheme 2), was examined as well. It is not implied that this reaction requires the presence of superbasic sites.

2. Experimental

2.1. Catalysts preparation

2.1.1. Synthesis of mesoporous γ-alumina

Mesoporous γ-alumina, denoted as MSU-γ, was prepared according to the method of Zhang et al. [26]. An aqueous mixture of aluminum tributoxide, 2-butanol and the tri-block $(EO)_{19}(PO)_{39}(EO)_{19}$ surfactant, Pluronic P84, was first aged at 65 °C for 8 h, followed by hydrolysis with excess water. The precipitate was aged again at 80 °C for 6 h and then at 100 °C for 24 h. The powder air-dried at 60 °C was then calcined at 350 °C for 3 h and then at 550 °C for 4 h. The powder obtained is denoted as MSU-γ 84.

Nitrogen adsorption isotherms of the mesoporous γ-alumina were measured at 77 K on a TriStar 3000 V6.03A instrument.

2.1.2. Synthesis of supported sodium azide

A methanol slurry of NaN_3 was impregnated on pellets of MSU-γ 84 with a diameter varying between 0.5 and 1 mm. The resulting solid was dried at 60 °C in air and then heated slowly under pure nitrogen at a rate of 1 °C/min till a final temperature of about 370–375 °C was reached. After keeping the solid for 1 h at this temperature, it was cooled down to room temperature and stored under nitrogen. For a typical catalyst, the final Na loading on support was 15 wt.%. This catalyst is denoted as NaN_3/MSU-γ 84.

Alternatively, a solid catalyst denoted as NaN_3/MSU-γ 84DM was prepared by dry mixing under argon atmosphere of air-dry MSU-γ 84 powder with NaN_3, corresponding to a 15 wt.% loading with Na. The two components were ground together in a mortar and the powder obtained compressed and sieved under argon. The pellets with a diameter ranging from 0.5 to 1 mm were activated and stored in the same way as the NaN_3/MSU-γ 84 catalyst. During activation this sample turned from white to black, while bed temperatures up to 550 °C were detected. In parallel a metallic mirror was observed on the glass reactor, corresponding to less than 10% of the Na metal as determined by its dissolution in water and back titration of the basicity. Mirror formation was not observed during activation of the NaN_3/MSU-γ 84 catalyst. When comparing both samples catalytically, it was assured that comparable amounts of sodium were present in the reactor (±5 wt.%).

It should be stressed that during activation of supported azide, in particular around its decomposition point (300–375 °C) much heat has to be removed from the system in order to avoid extreme temperature rise in the catalyst bed (see below). The volume of the vessel should also allow confining the sudden pressure increase due to N_2 release (3 mmol of N_2 per 2 mmol of Na generated). It is of extreme importance to avoid formation of HN_3 (hydrazoic acid) in particular when high amounts of water are present at the moment of azide decomposition. HN_3 might undergo uncontrollable detonations. In our hands the activation of the catalyst was safe, provided the procedures and amounts described are respected. Upscaling should only be attempted by skilled persons.

The catalysts were also characterized by means of ^{23}Na MAS NMR spectroscopy. The samples were packed under inert atmosphere in 2.5 mm zirconia rotors and locked. The closed rotors were air-tight as shown by the constant signal intensity over time. The ^{23}Na MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer, at a magnetic field strength of 9.4 T. 1700 scans were accumulated with a recycle delay of 1 s. The spinning frequency of the rotor was 20 kHz. Solid NaCl was used for the calibration of the ^{23}Na chemical shift scale.

2.2. Catalytic tests

2.2.1. Double bond migration of vinylcyclohexane in fixed bed continuous liquid flow reactor

Experiments were carried out at room temperature in a fixed bed continuous liquid flow reactor connected to a syringe pump (Perfusor Compact, B. Braun Melsungen AG type 871482/7) with a bed of 0.5 g of catalyst pellets at a hourly space velocity of 8.4 h^{-1}. The reactor flow sheet is shown in Fig. 1. Separation of substrate and reaction products was done using a GC (HP5890) equipped with a CP-SIL 5CB WCOT Fused Silica column of 50 m, with an internal diameter of 0.32 mm and FID detector at 280 °C. The column temperature was raised from 60 °C at a rate of 2 °C/min till 250 °C.

2.2.2. Transesterification of soybean oil with methanol

The catalytic transesterification of soybean oil with methanol to yield methyl esters of the fatty acids contained in the oil, also known as *biodiesel ex soybean oil* (Scheme 2) was carried out in a

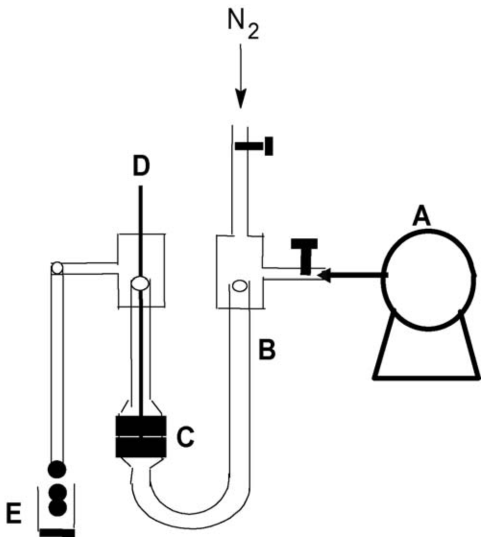


Fig. 1. Flow sheet of the fixed bed continuous liquid flow reactor. (A) Syringe pump; (B) removable glass reactor with (C) catalyst bed; (D) thermocouple; (E) product collection device.

batch reactor equipped with a sampling device at 60 °C with 1 g of catalyst. The reaction was done under nitrogen for 2 h at a stirring rate of 300 rpm. The molar ratio of methanol to soybean oil used was 9:1 and 27:1, respectively.

The analysis of each sample withdrawn from the batch reactor was performed by dissolving 0.1 g into 1 ml of 0.1% n-$C_{17}H_{36}$ in n-hexane solution. The latter was injected into a gas chromatograph (HP 6890) with injection port at 250 °C, equipped with a polar column (BPX-70 SGE) of 60.0 m with an internal diameter of 320 μm and a film thickness of 0.25 μm. Detection was with a FID-detector at 280 °C. The column temperature was held initially at 180 °C for 40 min, heated at a rate of 10 °C/min to 260 °C and held there for 5 minutes. The biodiesel or methyl ester yield, Y, was calculated according to the following formula:

$$Y\,(\%) = \frac{m_{\mathrm{IS}} \times A_{\mathrm{FAMEs}} \times f_{\mathrm{IS}}}{A_{\mathrm{IS}} \times m_{\mathrm{sample}}} \times 100$$

with IS, n-heptadecane (n-$C_{17}H_{36}$) used as a chromatographic internal standard; *f*, the response factor; *A*, the peak area; *m*, the mass (g) of sample or of IS.

3. Results and discussion

3.1. Characterization of support and catalysts

The nitrogen adsorption isotherm measured at 77.3 K for the calcined mesoporous γ-alumina support, MSU-γ 84, is shown in Fig. 2. The data point to successful synthesis of the alumina mesoporous support, with a BET surface area of 298 m^2/g, a pore volume of 0.97 mL/g and an average pore size of 8.8 nm.

The sodium species present in the catalysts after thermal activation were determined with solid state ^{23}Na NMR. Several sodium species can be present in such catalysts, namely metallic sodium particles, ionic sodium clusters as observed in zeolite NaY, sodium oxide, and residual sodium azide. Metallic sodium particles are known to give a signal between 900 and 1200 ppm. In particular, large metallic sodium particles yield a signal around 1125 ppm, corresponding to the Knight shift of sodium metal [27]. On the other hand, sodium oxide gives a broad signal around −10 ppm, while residual sodium azide shows a easily distinguishable very sharp signal at −11 ppm.

From Fig. 3 it follows that the ^{23}Na MAS NMR spectrum of the NaN_3/MSU-γ 84 catalyst shows next to the presence of sodium oxide (−10 ppm), a high amount of metallic sodium with $\delta = 1132$ ppm, while for the NaN_3/MSU-γ 84DM catalyst, only one resonance line at −10 ppm is observed, that can be attributed to sodium oxide particles. Metallic species or residual sodium azide with sharp resonance line at −11 ppm, were not detected on the latter catalyst obtained by dry mixing of the components.

The presence of only sodium oxide particles on the activated NaN_3/MSU-γ 84DM catalyst can be correlated to the presence of residual moisture from the mesoporous support, which is still present when the sodium azide starts to decompose. Moreover, due to the exotherm generated by azide decomposition, the residual surface hydroxyls will be dehydroxylated, yielding more water.

The same air-dry catalyst support impregnated with methanol slurry of the azide will contain much less water, while most of the methanol will be released before azide decomposition. As the azide decomposition occurs also in a more controlled way with a much less pronounced exotherm, the presence of lower amounts of sodium oxide and significant amounts of sodium metal are not unexpected. It cannot be decided whether both species are discrete entities or should be visualized as sodium metal particles partially oxidized at their external surface rim. It can be anticipated that the latter configuration should exhibit higher basic strength compared

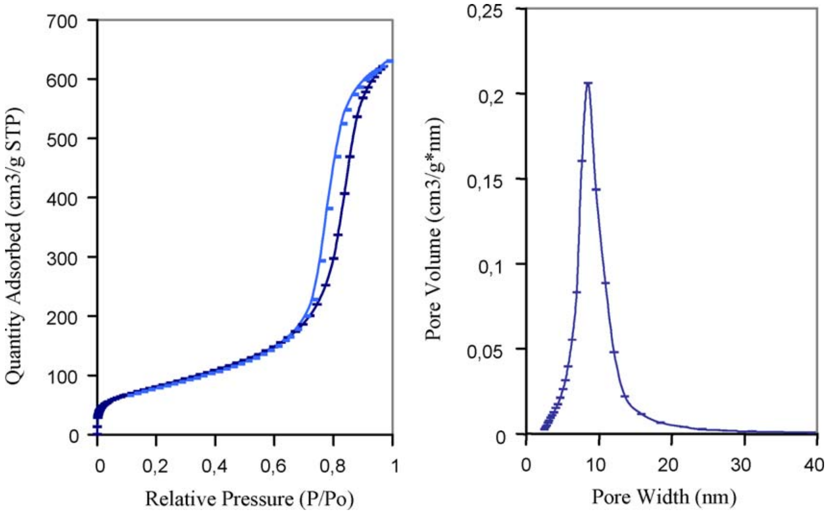


Fig. 2. Nitrogen adsorption isotherms (left) and BJH pore-size distribution (right) for calcined MSU-γ 84.

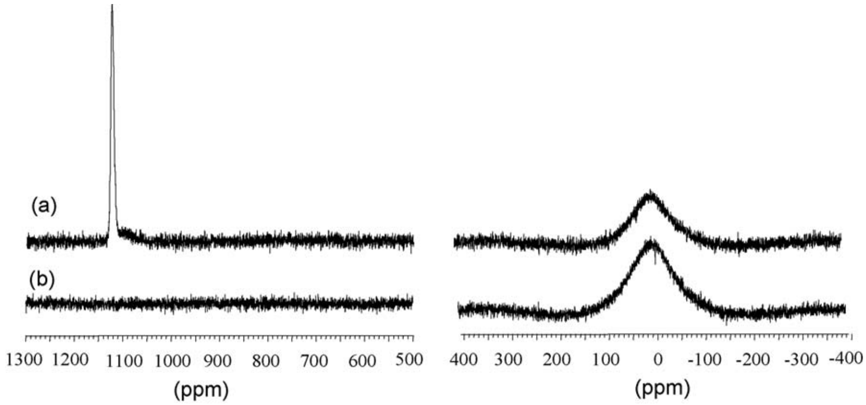


Fig. 3. ^{23}Na MAS NMR spectrum of (a) NaN_3/MSU-γ 84 (top spectra) and (b) NaN_3/MSU-γ 84DM catalysts (bottom spectra), activated up to 375 °C.

to that of bulk sodium oxide by electron donation from the subsurface metal to the O ions of the surface oxide.

3.2. *Catalytic performance of sodium azide supported on mesoporous γ-alumina for the double bond migration of vinylcyclohexane*

As illustrated in Figs. 4 and 5, the catalytic activity of the sodium azide-on-mesoporous γ-alumina catalysts for the VCH isomerization depends on the preparation method. The NaN_3/MSU-γ 84 catalyst shows the highest activity and stability for comparable amounts of Na in the reactor. The conversion of VCH decreases only slowly over time from almost 100 to 80%, while in case of the NaN_3/MSU-γ 84DM catalyst the conversion decline of VCH is faster from almost 70 to 38%. The selectivity for ECH remained above 95% in both cases. The difference in initial activity should be assigned to the different nature of the active site, *viz.* oxide ions of sodium oxide in surface oxidized Na metal particles or in bulk sodium oxide (see above). Though this picture is to a certain degree speculative, it is in line with current views on superbasicity of Na-on-support catalysts [6,8,25].

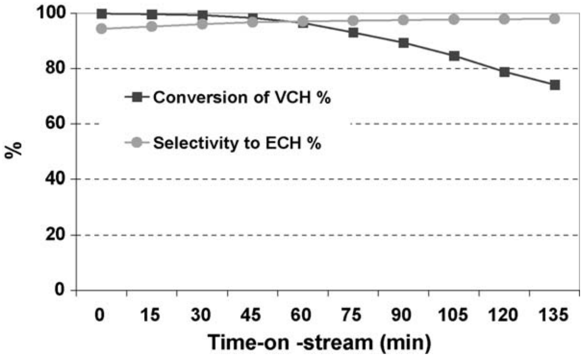


Fig. 4. Room temperature catalytic activity with a NaN_3/MSU-γ 84 catalyst.

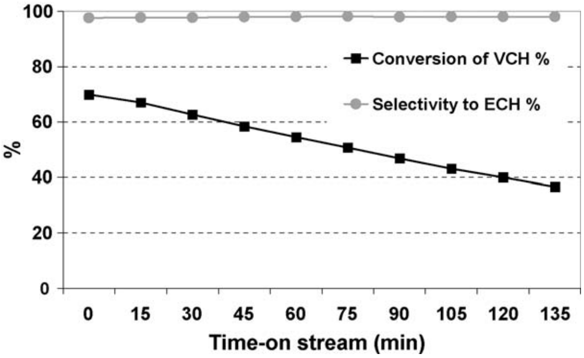


Fig. 5. Room temperature catalytic activity with a NaN_3/MSU-γ 84DM catalyst.

^{23}Na MAS NMR on a fresh and used NaN_3/MSU-γ 84 catalyst shows a decrease of the Na metal particles (1132 ppm) and a parallel increase in the sodium oxide species (−10 ppm). The deactivation of the catalyst can therefore be associated with this transformation, *viz.* the deeper oxidation of surface oxidized sodium metal particles and is an *a posteriori* confirmation of our interpretation of the NMR lines. The slight deactivation of this catalyst is due to the presence of impurities in the feed, *viz.* water, oxygen and carbon dioxide. Indeed, when ultrapure VCH is used obtained by thorough de-aeration and drying, the catalyst stability is extended significantly (results not shown).

Dry mixing of the catalyst components followed by thermal activation, as in NaN3/MSU-γ 84DM, invariably shows after thermal activation the appearance of sodium mirrors at the reactor outlet. The extent of Na loss is below 10% and cannot be responsible alone for the decreased activity. The enhanced deactivation is for a major part due to sintering of the supported sodium oxide particles as it occurs even with pure feeds (results not shown).

3.3. *Catalytic performance of sodium azide supported on mesoporous γ-alumina for the transesterification of soybean oil with methanol*

The NaN_3/MSU-γ 84 and NaN_3/MSU-γ 84DM catalysts were also tested in transesterification of soybean oil with methanol in a batch reactor at 60 °C which represent mild reaction conditions. As shown in Fig. 6, the NaN_3/MSU-γ 84 shows again higher activity than NaN_3/MSU-γ 84DM. After 2 h the biodiesel yield was 60 and

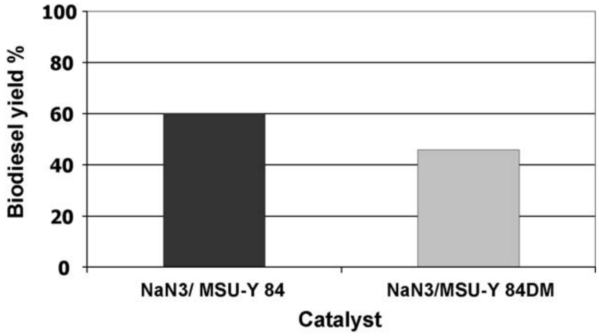


Fig. 6. Activity of NaN_3/MSU-γ 84 and NaN_3/MSU-γ 84DM catalysts in transesterification of soybean oil with methanol. Reaction conditions: 60 °C; 300 rpm; 1 g catalyst; reaction time, 2 h; MeOH: soybean oil molar ratio of 9:1, batch reactor.

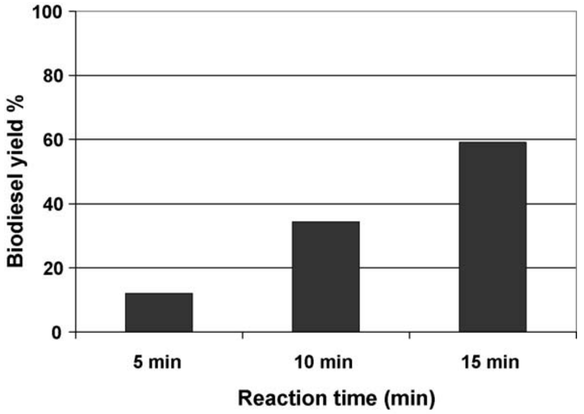


Fig. 7. Biodiesel yield obtained with NaN_3/MSU-γ 84 using a methanol/soybean oil molar ratio of 27. Reaction conditions: 60 °C; 300 rpm; 1 g catalyst; reaction time, 15 min, batch reactor.

45% in case of the NaN_3/MSU-γ 84 and NaN_3/MSU-γ 84DM catalyst, respectively.

The stoichiometric ratio of the transesterification reaction requires three moles of alcohol for one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. It is known that enhanced molar ratios yield higher ester yields [28,29]. For the NaN_3/MSU-γ 84 catalyst it was found (Fig. 7) with high methanol/oil ratios that the reaction is extremely rapid as after 15 min already the thermodynamic equilibrium of about 60% is reached. The ^{23}Na MAS NMR of the used catalyst shows a spectrum that is identical to that of the starting catalyst shown in Fig. 3(a). Thus it seems that the superbasic sites evidenced by the presence of the Na metal and Na oxide lines are not affected by this reaction medium.

4. Conclusion

A sodium azide methanol slurry supported on mesoporous alumina was decomposed in a controlled way, yielding NMR resonance lines that could be assigned to Na metal and Na oxide species. This solid showed superbasicity as evidenced by its capability to catalyze the double bond shift in vinylcyclohexane. The minor deactivation of this catalyst in time using a continuous liquid flow reactor could be attributed to feed impurities. The NMR lines are assumed to correspond to sodium metal particles containing oxide at the external rim. This is confirmed by the slight decrease of the Na metal line and the corresponding slight increase of the sodium oxide line during subsequent runs with unpurified VCH.

When dry sodium azide was grinded in presence of mesoporous γ-alumina and subsequently thermally activated, only Na oxide species were present on the support, next to Na mirror formation (less than 10% of Na) on the glass walls of the vessel. This was ascribed to the presence of some residual water at the temperature of azide decomposition and/or the interaction of sodium metal particles with water from surface OH dehydroxylation. This solid was significantly less active in the double shift catalysis of VCH, probably due to the lack of superbasic sites stemming from the combined action of supported sodium metal and sodium oxide. It deactivated significantly assumed to be due to sintering of the supported sodium oxide.

In the transesterification of soybean oil with methanol the first catalyst showed very high biodiesel yields in mild conditions, while the ^{23}Na MAS NMR picture of the catalyst remained virtually unchanged after reaction. The second catalyst devoid of superbasic sites showed less activity.

Acknowledgements

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