Catalysis Today 179 (2012) 73–77

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of the pretreatment of Fe-silicalite on its activity in the ammoxidation of propane

Roman Bulánek, Kateřina Raabová*, Eva Baďurová

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice 53210, Czech Republic

ARTICLE INFO

Article history:
Received 15 April 2011
Received in revised form 20 June 2011
Accepted 21 June 2011
Available online 29 July 2011

Keywords:
Gas reduction-nitridation
Pretreatment
Fe-silicalite
Ammoxidation
Acrylonitrile
Propane

ABSTRACT

The catalytic performance of Fe-silicalite activated by gas reduction-nitridation (GRN) was studied in the direct ammoxidation of propane with molecular oxygen as the only oxidizing agent. It has been demonstrated that the presence of the reducing agent, propane, is indispensable in order to obtain active catalyst. Relatively mild conditions of the pretreatment, temperature 540 °C, short time of the activation (5 h) and small flow of ammonia with propane resulted in the active and selective catalyst (44% selectivity to acrylonitrile at 25% conversion of propane). Pretreated catalyst reached interesting results also in the term of productivity. Moreover it was found out, that once nitrided catalyst does not deactivate and during the time on stream the selectivity to acrylonitrile does not decline.

1. Introduction

Acrylonitrile (ACN) is a very important intermediate mainly used in acrylic fibers, for the synthesis of acrylonitrile–butadiene–styrene (ABS), styrene–acrylonitrile (SAN) plastics and nitrile–butadiene–rubber (NBR) [1]. Currently more than 90% of ACN is synthesized by the ammoxidation of propylene over Bi–Fe–Ni–Co molybdates, in the process known also as a SOHIO process. Although this process reaches very good results, the selectivity above 85% with 95% conversion of propylene, mainly because of the increasing difference between the prices of propylene and propane and also because of the risk of shortcoming of olefin, there is a great interest to substitute propylene by propane. For this purpose different classes of the catalyst were studied, among them: (i) mixed oxide catalysts with either scheelite (Bi, V, Mo) [2–5] or rutile (V, Al, Sb) [6–10] structure, (ii) supported catalytic systems [11–13], (iii) vanadyl pyrophosphates [14,15], (iv) zeolite materials doped with different metals [16–20] and (v) nitrided materials (VAlON, nickel molybdenum mixed nitrides) [21,22].

Recently, different materials such as zeolites [23–29], mesoporous silicas [30–33] and (silico)-aluminophosphates [34–36] activated by nitridation at high temperatures in the flow of ammonia have been the object of many investigations and publications. It has been proposed and by means of different characterization methods (IR spectroscopy, XPS) [25–27,29] demonstrated that during the nitridation, some of the oxygen atoms from Si–O–Si, Si–O–Al or Al–O–P framework are replaced by nitrogen forming amido, imido groups thus resulting in the material with increased basicity compared to the parent material. It has been also shown that the content of the nitrogen inserted in the catalysts can be controlled by the temperature and the time of the nitridation [24,25,29]. Materials pretreated by the nitridation performed high activity in the basic reactions, for example in Knoevenagel condensation of benzaldehyde [23–26,28] or ethylation of ethylbenzene with ethanol [37] and also in the reactions such as photocatalytic water splitting [38–42], ammoxidation of 3-picoline [43] and as mentioned above in ammoxidation of propane [22]. Formation of acrylonitrile from propane in the reaction catalyzed by the zeolitic materials is, according to the previous research, conditioned by the absence of the strong acid sites [19]. In the literature it has been even demonstrated that increased basicity of the catalyst is favorable for the formation of acrylonitrile in the ammoxidation of propane over metallic oxide catalysts [44]. Considering the enhanced alkalinity of the nitrided catalysts, these materials could be potentially a convenient catalytic system for the direct ammoxidation of propane.

In this paper, we report significant improvement of catalytic activity of Fe-silicalite activated by gas reduction-nitridation used for the direct ammoxidation of propane. Fe-silicalite has been already studied [18,19] for this reaction and it was shown that pretreatment plays crucial role in the activation of catalyst. It was

---

* Corresponding author. Tel.: +420 466 037 052; fax: +420 466 037 068.
E-mail address: katerina.raabova@upce.cz (K. Raabová).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.06.030

demonstrated that pretreatment at the high temperature in the water vapor leads to the active catalytic system, especially in the mixture of nitrous oxide and molecular oxygen used as the oxidizing agents. The catalytic activity of steamed sample in the propane ammoxidation in the presence of only oxygen was relatively low. It was hypothesized that the role of N_2O is mainly as the promoter for the activation of propane for the formation of propylene [19] or also that N_2O is responsible for the changing of the oxidation state of active iron sites [18]. Because performing the ammoxidation with nitrous oxide is disadvantageous from the economical point of view we decided to further study other types of Fe-silicalites activation for the ammoxidation reaction only in the presence of molecular oxygen.

2. Experimental

Fe-silicalite catalyst with the concentration of Fe 4300 ppm (Si/Fe = 210) introduced during zeolite synthesis was investigated. Fe-silicalite was prepared by hydrothermal synthesis from mixture in which molar composition was as follows: TEOS:$FeCl_3 \cdot 6H_2O$:NaOH:TPAOH = 0.2:0.002:0.05:0.004. The synthesis was done in the autoclave with stirring at 160 °C for 48 h. The resulting material was calcined in oxygen at 430 °C for 3 h in order to remove the template. The NH_4 form of the zeolite was prepared by ion exchange of the calcined material with 0.5 M solution of NH_4NO_3 at room temperature for 1 week. The set of tests of the direct ammoxidation of propane was carried out on the catalyst, which has been pretreated by GRN for various times, ranging from 1 to 19 h. Each test was carried out as follows: 80 mg of the catalyst has been pretreated in the flow of ammonia and propane for the chosen time. The feed composition was 5 vol.% of ammonia and 5 vol.% of propane in helium, the total flow rate was 100 cm^3/min, at the temperature of 540 °C. After such pretreatment, the sample was calcined in the flow of oxygen/helium mixture (5 vol.% of O_2) for 30 min and subsequently reaction mixture comprising 2.5 vol.% of propane, 5 vol.% of oxygen and 5 vol.% of ammonia in helium with total flow rate 100 cm^3/min was prepared. The reaction was measured at the temperature of 540 °C. Analysis of the products was made in TOS (time-on-stream) of 50 min and higher (in the case of catalytic performance stability of nitrided sample study). Product gases were analyzed online by GC equipped with TCD and FID detectors. Conversion, selectivity and yields were calculated on the basis of the mass balance.

3. Results and discussion

The products of the direct ammoxidation of propane were acrylonitrile (ACN), propylene, acetonitrile (AcCN), carbon oxides and traces of methane, ethane and ethene.

The study was focused on investigation of the effect of the special type of activation, gas reduction-nitridation, on the catalytic performance of Fe-silicalite. First studied aspect was the influence of the time of the pretreatment on the catalytic activity. The results are reported in Fig. 1. The time of nitridation of zero hour refers to the activity of the parent catalyst, which was calcined for 1 h in the dry oxygen at 540 °C. The figure shows that the activity of non-nitrided Fe-silicalite is very low; the conversion of propane is lower than 4%. The prevalent product is propylene with the selectivity of 92%, other products being ethene, CO_2 and acetonitrile. No acrylonitrile was detected. It is known from previously published studies that calcination of Fe-silicalites in dry oxygen preserves Fe^{3+} cations in the tetrahedral framework positions, which is connected with presence of Broensted acid sites. This is highly disadvantageous for propane ammoxidation due to decomposition of acrylonitrile to acetonitrile on these acid sites. Already after 1 h of the nitridation of Fe-silicalite, the catalyst exhibits enhanced activity and, especially, converts propylene to acrylonitrile. As the time of the pretreatment of catalyst increases, conversion of propane increases together with selectivity to acrylonitrile. The maximum of selectivity to acrylonitrile is obtained after 5 h of the GRN (44%). Conversion of propane reaches the maximum value after 7 h of the pretreatment (31%) and with additional time of pretreatment does not change because of the total conversion of oxygen. These results indicate that longer times of the nitridation are not convenient for the catalyst, not only because the performance of the catalyst is limited by the total consumption of oxygen, but also because in these conditions the prevalent products are carbon oxides (after 19 h of the nitridation the selectivity to CO_x being 63%) at the expense of ACN. Almost during the whole time of the pretreatment the ratio of acrylonitrile to acetonitrile yield is systematically increasing from 4.6 obtained after 1 h of the pretreatment to 12 reached after 17 h of the pretreatment. In industry, the synthesis of acetonitrile is currently provided only as the by-product of the ammoxidation of propylene. The amount of the produced acetonitrile obtained from this process is more than sufficient to cover the demand for this solvent and thus the excess stock of acetonitrile is disposed. Consequently, there is an interest to maintain the ratio of yield of ACN/AcCN as high as possible. Obtained ratio of ACN/AcCN yield in the ammoxidation of propylene is reported to be about 25 [1]. On the other hand, yield ratios of ACN/AcCN for the catalysts proposed for the direct ammoxidation of propane are in the range from 0.8 to 17. However, the major part of the catalytic systems obtains the ratio lower than 10 [2,8,11,12,18]. From this point of view, our catalyst reaches quite interesting results.

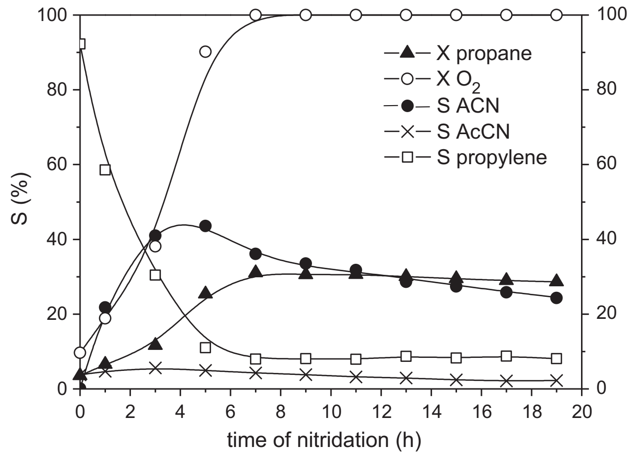

Fig. 1. Effect of the time of the pretreatment on the catalytic activity of Fe-silicalite in the direct ammoxidation of propane. Reaction condition: $T = 540\,°C$, $m_{cat} = 80$ mg, $F = 100\ cm^3/min$, $C_3H_8/NH_3/O_2 = 2.5/5/5$ vol.%, TOS = 50 min.

Redox catalytic activity of Fe-zeolites is usually associated with presence of extra-framework Fe cations, which are generated from ferrosilicate by extraction of iron ions from framework upon treatment at higher temperatures in the presence of a strong ligand as e.g. water. Such treatment leads to materials with substantial catalytic activity, as was reported in the literature [18,19], but their selectivity to ACN was markedly lower than selectivity obtained on our material. Therefore we suppose that catalytic performance of our material is caused by another process carried out on the zeolite surface in the presence of ammonia by nitridation. In the literature different kinds of zeolites, such as zeolite Y, zeolite X, BEA, ZSM-5, IFR, SSZ-13 [23–29,45] were reported to be nitrided only in the high flow of ammonia, in most of the cases for a long time at high temperature (higher than 800 °C). Comparing these methods of pretreatment with our method of the nitridation, it is evident that the big advantages of our activation of the material are the relatively mild conditions, short time of the pretreatment (5 h), small flow of ammonia during the pretreatment (5 cm^3/min) and temperature being only 540 °C. The key parameter which allows performing the activation under such mild conditions is the presence of the reducing agent during the nitridation. This has been already demonstrated by Suehiro et al. [46] and Yamakawa et al. [47] when they studied the nitridation of Al_2O_3 and $Al(OH)_3$ for the synthesis of AlN. They reported, that small amount of the reducing agent, such as propane, allows carrying out the process at lower temperature than the conventionally used one with higher extent of the nitridation [46]. It was suggested that the role of the reducing agent is to accelerate the rate of the nitridation process.

In order to find out if the use of the reducing agent is also important for the activation of Fe-silicalite, we decided to carry out the nitridation of parent Fe-silicalite in the absence of propane, under the same reaction conditions as during the previous pretreatment. This test showed that the presence of propane during the nitridation process is indispensable in order to obtain active catalytic system for the reaction. As is shown in Table 1, the performance of the catalyst which was pretreated only in the flow of ammonia for 5 h was very poor, not only that the conversion was low (4%), but also that the selectivity to ACN was less than 3% showing the activity very similar to the sample which was calcined for 1 h at 540 °C in the flow of dry oxygen, as was reported in Fig. 1. Table 1 also reports the “apparent” turn over frequencies reached on these two materials. We prefer rather to use “apparent” TOF, because in this case we are not sure about the exact number of the active centers. TOF expressed in this manner refers to all iron cations presented in the zeolite (but only the part of the iron usually contributes to the activity of the catalyst). The difference in “apparent” TOF of the samples activated by two different methods of nitridation, more than six fold higher “apparent” TOF over the catalyst pretreated by GRN, clearly indicates the high efficiency of nitridation in the presence of the reducing agent.

These preliminary tests led to the decision to further study the ammoxidation of propane over Fe-silicalite, which has been activated by GRN for 5 h. Under these conditions the performance of the catalyst should not be limited by the total consumption of oxidizing agent. Pretreated Fe-silicalite by GRN was further used for the study of the stability of the catalyst during the time on stream and the dependence of the catalytic activity on the reaction temperature.

First the catalytic stability will be discussed. In order to find out if this kind of pretreatment affords the material which does not deactivate during the reaction, we performed the long term test of the ammoxidation of propane studying the changes in the conversion of reactants and distribution of the products. The results are reported in Fig. 2. The reaction was carried out for 5 h, then it was stopped and catalyst was exposed to air after cooling to room temperature overnight. The catalyst was used in the reaction again next day for additional 24 h on the stream. It must be noted that catalyst was calcined in the flow of oxygen/helium mixture (5 vol.% of oxygen) at 540 °C for 30 min before starting the catalytic run. It is clearly seen from Fig. 2 that the catalyst retained its catalytic performance after break of the reaction run. This is a big advantage of this catalytic system in comparison with other nitrided materials, which very often lose nitrogen from framework under air atmosphere [48,49]. The overall changes in the conversion of propane were within the limits of 5% showing that once nitrided Fe-silicalite behaves as a stable material and does not lose any of its catalytic activity. During the 29 h of time on stream and handling in the air, the selectivity to acrylonitrile remained about 44% with the conversion about 20%. Moreover during the whole time on stream the selectivity to acetonitrile was about 6%, thus affording high yield ratio of acrylonitrile to acetonitrile (from 7 to 8).

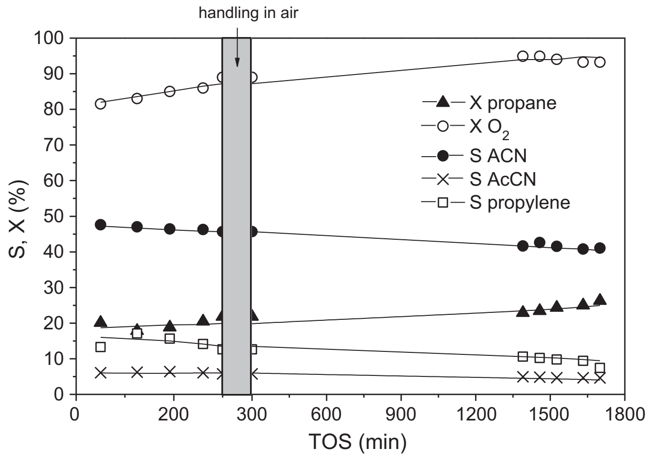

Fig. 2. Stability of the catalytic performance of 5 h nitrided catalyst during the time on stream. Reaction condition: $T = 540\,°C$, $m_{cat} = 80$ mg, $F = 100\,cm^3/min$, $C_3H_8/NH_3/O_2 = 2.5/5/5$ vol.%.

Fig. 3 shows propane conversion and product selectivities as a function of reaction temperature, which is one of the key parameters that influence the catalytic activity. Considering the difficult activation of alkanes, it is obvious that reaction temperature of the ammoxidation of propane has to be higher than the temperature of the ammoxidation of propylene. From Fig. 3 it is evident that temperatures below 480 °C are not sufficient to activate propane. In these conditions the conversions of propane are very low and the primary product is propylene. With increasing temperature, the conversion of propane monotonically increases. Selectivity to ACN reaches the maximum values at 520 °C and decreases with increasing temperature because of the formation of carbon oxides. This study also shows, that at very low conversion of propane, the primary product is propylene which subsequently, as the temperature increases, forms acrylonitrile and carbon oxides. This is in accordance with the hypothesis, that the first step of the ammoxidation of propane is the formation of propylene [50].

Although Fe-silicalite activated by GRN did not provide very high conversion of propane compared to other catalysts studied for this reaction, the advantage of using this material pretreated by GRN for the direct ammoxidation of propane can be demonstrated by expressing the activity of the catalyst by means of productivity. Table 2 reports different catalysts studied for the ammoxidation of propane and the obtained productivities. As can be seen from the reported table, Fe-silicalite activated by GRN reaches very good results compared to other studied catalytic systems.

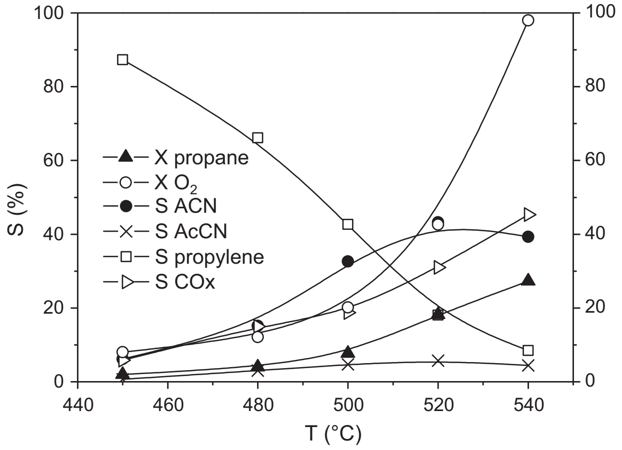

Fig. 3. Effect of the reaction temperature on the catalytic activity of 5 h nitrided catalyst. Reaction condition: $m_{cat} = 80$ mg, $F = 100\,cm^3/min$, $C_3H_8/NH_3/O_2 = 2.5/5/5$ vol.%, TOS = 50 min.

Table 1
Comparison of the catalytic activity of Fe-silicalite activated by nitridation and gas reduction-nitridation at 540 °C for 5 h. Reaction condition: $m_{cat} = 80$ mg, $T = 540$ °C, $F = 100$ cm^3/min, $C_3H_8/NH_3/O_2 = 2.5/5/5$ vol.%, TOS = 50 min.

Pretreatment of Fe-silicalite	Conversion (%)	Selectivity (%)			Y ACN/AcCN	TOF (h^{-1})
	propane	ACN	propylene	AcCN		
GRN	25.4	43.6	11	5	8.8	289
Nitridation	4.1	2.8	86	2.6	1.1	44

Table 2
Catalytic activity of the different materials studied for the direct ammoxidation of propane.

Catalyst	T (°C)	Activation	$W/F_{(propane)}$ (kg·h/mol)	Ox. agent	X C_3H_8 (%)	S ACN (%)	P (mol/kg·h)	Ref.
Fe-silicalite HT	550	30 vol.% H_2O in N_2 (30 ml/min), 873 K, 5 h	0.006	$N_2O + O_2$	42	25	17.5	[18]
Fe-silicalite HT	550	30 vol.% H_2O in N_2 (30 ml/min), 873 K, 5 h	0.006	O_2	16	30	8	[18]
Fe-silicalite GRN	540	5 vol.% C_3H_8 + 5 vol.% NH_3 in He (100 ml/min), 813 K, 5 h	0.012	O_2	25	44	9.3	This work
GaZSM5	500	Calcination, N_2, 723 K; air, 823 K	0.16	O_2	48	40	1.2	[17]
VAlON	500	30 l/h NH_3, 773 K, 5 h	0.008	O_2	59	50	36.9	[22]
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}O_n/SiO_2$	420	Calcination, inert gas, 773–873 K, 1–3 h	0.37	O_2	91	56	1.5	[51]
VOx/SbOx/Al_2O_3	440	Calcination, 673 K, 4 h	0.038	O_2	70	30	5.5	[52]
CaBiMoO	490	Calcination, air, 793 K, 6 h	0.012	O_2	15	63	4	[2]

Our study shows that activation of Fe-silicalite by gas reduction-nitridation leads to the active and selective material for the direct ammoxidation of propane by molecular oxygen. The enhanced activity of the material can be explained by the chemical/structural changes of the Fe-silicalite upon the nitridation. This pretreatment can (i) lead to the extraction of iron from the framework into extra-framework position, (ii) lead to formation of extra-framework Fe species with different degree of oligomeration than classical hydrothermal pretreatment in water vapor, (iii) cause formation of different type of extra-framework Fe complexes (e.g. oxinitridic species FeO_xN_y or nitridic species FeN_x) by interaction of ammonia with Fe species and (iv) change the acid–base properties of support by the substitution of framework oxygen by various nitrogen species in the zeolite framework, leading to the formation of amido, imido groups and increasing the basicity of this material compared to the parent one. Osipova and Sokolovskii [44] demonstrated on the series of metallic oxide systems that increasing basicity of the catalyst is favorable for the formation of acrylonitrile in the ammoxidation of propane. In addition, we cannot exclude that the nitrogen incorporated in the zeolite framework is directly involved in the formation of acrylonitrile. The results obtained from our study compared to other hydrothermally pretreated Fe-silicalite used for the ammoxidation of propane [18,19] clearly indicates that the enhanced activity of our Fe-silicalite cannot be ascribed only to the generation of extra-framework iron species. The detailed characterization of parent, nitrided and used catalysts by multi-spectroscopical approach is necessary for understanding of the principle of the changes in the Fe-silicalite catalyst during the gas reduction-nitridation treatment and possible role of the N-containing surface species in the reaction mechanism of propane ammoxidation. The characterization of our materials is now under study and should be the object of the prepared publication.

4. Conclusion

Fe-silicalite prepared by hydrothermal synthesis was activated by the gas reduction-nitridation at 540 °C for 5 h in the flow of ammonia and propane and subsequently studied in the direct ammoxidation of propane. It was found out that gas reduction-nitridation, compared to the nitridation without the reducing agent, is an efficient method for the catalyst activation. Nitrided Fe-silicalite catalyst exhibited stable catalytic performance during the long time on stream (29 h). Relatively high TOF and productivity were reached over this catalytic system showing the enhanced activity of nitrided Fe-silicalite compared to other catalysts proposed for the direct ammoxidation of propane.

Acknowledgements

A financial support of the Grant Agency of the Czech Republic under the project No. 203/08/H032 and Ministry of Education of Czech Republic under projects Nos. MSM 0021627501 and LC 512 are highly acknowledged.

References

[1] S.D. Jackson, J.S.J. Hargreaves, Metal Oxide Catalysis , Wiley-VCH, Weinheim, 2009.
[2] J.S. Kim, S.I. Woo, Appl. Catal. A 110 (1994) 173.
[3] T. Ushikubo, K. Oshima, A. Kayou, M. Vaarkamp, M. Hatano, J. Catal. 169 (1997) 394.
[4] M. Vaarkamp, T. Ushikubo, Appl. Catal. A 174 (1998) 99.
[5] K. Asakura, K. Nakatani, T. Kubota, Y. Iwasawa, J. Catal. 194 (2000) 309.
[6] G. Centi, R.K. Grasselli, E. Patane, F. Trifiro, Stud. Surf. Sci. Catal. 55 (1990) 515.
[7] M. Bowker, C.R. Bicknell, P. Kerwin, Appl. Catal. A 136 (1996) 205.
[8] J. Nilsson, A.R. Landa-Cánovas, S. Hansen, A. Andersson, J. Catal. 186 (1999) 442.
[9] G. Centi, S. Perathoner, Appl. Catal. A 124 (1995) 317.
[10] A. Wickman, L.R. Wallenberg, A. Andersson, J. Catal. 194 (2000) 153.

[11] H. Golinska, E. Rojas, R. López-Medina, V. Calvino-Casilda, M. Ziolek, M.A. Bañares, M.O. Guerrero-Perez, Appl. Catal. A 380 (2010) 95.
[12] M.A. Soria, S. Delsarte, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A 325 (2007) 296.
[13] M.O. Guerrero-Perez, J.S. Chang, D.Y. Hong, J.M. Lee, M.A. Bañares, Catal. Lett. 125 (2008) 192.
[14] G. Centi, T. Tosarelli, F. Trifiro, J. Catal. 142 (1993) 70.
[15] G. Centi, S. Perathoner, J. Catal. 142 (1993) 84.
[16] S.B. Derouane-Abd Hamid, G. Centi, P. Pal, E.G. Derouane, Top. Catal. 15 (2001) 161.
[17] S.B. Derouane-Abd Hamid, P. Pal, H. He, E.G. Derouane, Catal. Today 64 (2001) 129.
[18] J. Perez-Ramirez, N. Blangenois, P. Cruiz, Catal. Lett. 104 (2005) 163.
[19] R. Bulanek, F. Castek, Top. Catal. 45 (2007) 233.
[20] R. Bulanek, K. Raabova, G. Kosova-Kucerova, L. Capek, Stud. Surf. Sci. Catal. 174 (2008) 1151.
[21] H. Zhang, Z. Zhao, C. Xu, A. Duan, Chem. Lett. 35 (2006) 36.
[22] M. Florea, R. Prada-Silvy, P. Grange, Catal. Lett. 87 (2003) 63.
[23] C. Zhang, Z. Xu, K. Wan, Q. Liu, Appl. Catal. A 258 (2004) 55.
[24] T. Hasegawa, C.K. Krishnan, M. Ogura, Micropor. Mesopor. Mater. 132 (2010) 290.
[25] K. Narasimharao, M. Hartmann, H.H. Thiel, S. Ernst, Micropor. Mesopor. Mater. 90 (2006) 377.
[26] G. Wu, X. Wang, Y. Yang, L. Li, G. Wang, N. Guan, Micropor. Mesopor. Mater. 127 (2010) 25.
[27] H. Li, Q. Lei, X. Zhang, J. Suo, ChemCatChem 3 (2011) 143.
[28] S. Ernst, M. Hartmann, S. Sauerbeck, T. Bongers, Appl. Catal. A 200 (2000) 117.
[29] M. Srasra, G. Poncelet, P. Grange, S. Delsarte, Stud. Surf. Sci. Catal. 158B (2005) 1811.
[30] F. Hayashi, K. Ishizu, M. Iwamoto, Eur. J. Inorg. Chem. 2010 (2010) 2235.
[31] G. Wu, S. Jiang, L. Li, F. Zhang, Y. Yang, N. Guan, M. Mihaylov, H. Knözinger, Micropor. Mesopor. Mater. 135 (2010) 2.
[32] N. Chino, T. Okubo, Micropor. Mesopor. Mater. 87 (2005) 15.
[33] Y. Xia, R. Mokaya, Angew. Chem. Int. Ed. 42 (2003) 2639.
[34] P. Grange, P. Bastians, R. Conanec, R. Marchand, Y. Laurent, Appl. Catal. A 114 (1994) 191.
[35] A. Massinon, J.A. Odriozola, P. Bastians, R. Conanec, R. Marchand, Y. Laurent, P. Grange, Appl. Catal. A 137 (1996) 9.
[36] J. Xiong, Y. Ding, H. Zhu, L. Yan, X. Liu, L. Lin, J. Phys. Chem. B 107 (2003) 1366.
[37] X. Guan, N. Li, G. Wu, J. Chen, F. Zhang, N. Guan, J. Mol. Catal. A 248 (2006) 220.
[38] R. Abe, M. Higashi, K. Domen, J. Am. Chem. Soc. 132 (2010) 11828.
[39] Y. Lee, K. Teramura, M. Hara, K. Domen, Chem. Mater. 19 (2007) 2120.
[40] M. Higashi, R. Abe, T. Takata, K. Domen, Chem. Mater. 21 (2009) 1543.
[41] H. Chen, W. Wen, Q. Wang, J.C. Hanson, J.T. Muckerman, E. Fujita, A.I. Frenkel, J.A. Rodriguez, J. Phys. Chem. C 113 (2009) 3650.
[42] Y. Lee, H. Terashima, Y. Shimodaira, K. Teramura, M. Hara, H. Kobayashi, K. Domen, M. Yashima, J. Phys. Chem. C 111 (2007) 1042.
[43] C. Janke, M. Schneider, U. Bentrup, J. Radnik, A. Martin, G. Scholz, A. Brückner, J. Catal. 277 (2011) 196.
[44] Z.G. Osipova, V.D. Sokolovskii, Kinet. Katal. 20 (1979) 420.
[45] L. Regli, S. Bordiga, C. Busco, C. Prestipino, P. Ugliengo, A. Zecchina, C. Lamberti, J. Am. Chem. Soc. 129 (2007) 12131.
[46] T. Suehiro, J. Tatami, T. Meguro, S. Matsuo, K. Komeya, J. Eur. Ceram. Soc. 22 (2002) 521.
[47] T. Yamakawa, J. Tatami, T. Wakihara, K. Komeya, T. Meguro, J. Eur. Ceram. Soc. 26 (2006) 2413.
[48] P.W. Lednor, R. de Ruiter, Inorganic and Metal-Containing Polymeric Materials , Plenum Press, New York, 1990.
[49] P. Krawiec, S. Kastel, Top. Catal. 52 (2009) 1549.
[50] G. Centi, R.K. Grasselli, F. Trifiro, Catal. Today 13 (1992) 661.
[51] U.S. patent no. 6,143,916 (2000), assigned to Asahi Kasei Kogyo Kaisha, Japan.
[52] M.O. Guerrero-Perez, M.A. Bañares, Catal. Today 142 (2009) 152.