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GAS-PHASE CONVERSION OF GLYCEROL OVER MIXED METAL OXIDE CATALYSTS

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Introduction

Glycerol is a by-product of biodiesel production. For 1000 kg generated biodiesel about 100 kg of crude glycerol are produced. The increase in biodiesel production results in the accumulation of this cheap and renewable raw material. Therefore it is imperative to find new ways of utilizing raw bio-glycerol that will be beneficial for the environment. Acrolein and hydroxyacetone (acetol) are important basic chemicals that can be used for the synthesis of acrylic monomers, propanediol and numerous fine chemicals. Acrolein and acetol can be synthesized by the catalytic dehydration of glycerol [1]. Therefore, during the last decade, the catalytic conversion of glycerol to acrolein and acetol has gained big scientific and industrial interest. Different acidic catalysts including zeolites and supported solid acids have been proposed as heterogeneous catalysts for the gas-phase dehydration of glycerol [2—5]. The disadvantage of the reported catalytic processes is the formation of a large amount of by-products and the progressive catalyst deactivation. Today, a special interest is focused on the investigation of catalytic systems comprising mixed metal oxides and heteropoly acids, which allow the selective conversion of glycerol and prevented catalyst deactivation [4—6]. However, there is a lack of agreement among various results on the function of different metal oxides on the reactions pathways in the catalytic conversion of glycerol.

The goal of this study was to investigate the catalytic behaviour of alumina phosphates loaded with Cr-, Cu-, Ce-, Fe-, Mn-, Mo-, V- and W-oxides to get more insight into the effect of transition metal oxides on the catalytic performance and to provide a basis for the structure-activity relationships for the dehydration of glycerol. Additionally the aim was to find a catalyst for selective conversion of glycerol to acrolein or acetol and compared their activity with conventionally or analogous acidic catalyst such as Al_2O_3—PO_4.

Experimental

Bifunctional mixed oxide catalysts MO—Al_2O_3—PO_4 was prepared by simultaneous wet impregnation of γ-Al_2O_3 (Acros) with a water solution of H_3PO_4 and the corresponding metal salts. The molar ratio between metal, alumina and phosphate was kept constant, i.e., M : Al = = 1 : 10 and PO_4 : Al = 1 : 12. The following metal salts were used for impregnation: metal nitrates of Cu, Cr, Ce, Fe, Mn, and ammonium metavanadate and ammonium molybdate. The impregnated samples were dried at 110 °C and calcined at 520 °C for 4 h. A catalyst fraction of a grain size between 0.15 und 0.30 mm was used in the catalytic experiments.

Textural properties were determined from the adsorption-desorption isotherms of nitrogen at -196 °C using an ASAP 2010 apparatus (Micromeritics). Acidity of the catalysts was determined by NH_3-TPD, a mass-spectrometer (GSD 301; Pfeiffer) was used for the detection of the desorbing ammonia.

The gas-phase dehydration of glycerol was performed at 280 °C under ambient pressure in a fixed-bed quartz reactor (i.d. 6 mm) using 200 mg of catalyst. A 5 wt% aqueous glycerol solution was introduced into the reactor by a liquid-flow evaporator (Bronkhorst) at a rate of 1.0 g/h and at gas space velocity (GHSV) of 90 h^{-1} (glycerol). The reactions products were condensed in an ice-water trap and collected hourly for GC analysis on a Chrompack 9001 equipped with OPTIMA-WAX-MN capillary column

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(l:30 m, i.d. 0.32 mm) and FID detector. Quantification was carried out in the presence of an internal standard as described in [7].

Results and discussion

Physicochemical characteristics of samples. Table lists the textural properties and acid strengths of all investigated samples. Catalysts loaded with phosphates and different metal oxides clearly show a decrease in the specific surface area and size of the pores in contrast to pure γ-Al_2O_3. The highest loss of surface area was observed for the catalysts impregnated with Mn, Mo and W. These catalysts also exhibited the smallest pores. The loss of surface area can be partially attributed to the sintering of metal oxide particles during calcination on the surface of amorphous alumina. It is confirmed by XRD results showed in fig. 1. In the case of Ce, Fe, V and Mn modified materials, sharp reflections of the corresponding metal oxides are detected in addition to three very broad bands in the range of 35÷ ÷65° = 2θ of amorphous aluminium oxide. The V-APO, Mn-APO, Fe-APO systems show peaks typical for crystallites of the corresponding metal phosphate and metal oxide respectively. This observation stays in agreement with the results of Bautista [8], evidencing the formation of Fe-, V- and Mn- oxides in MO—Al_2O_3—PO_4 compos-
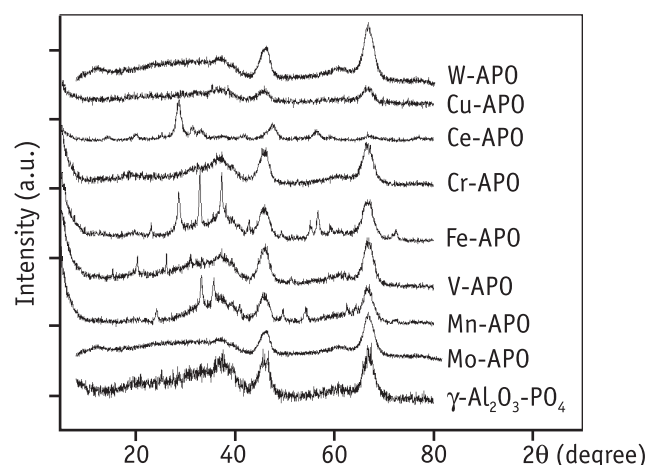

Fig. 1. X-ray diffraction patterns of the various transitions metal oxide supported on phosphated alumina

ites. On the other hand, no peaks associated with crystalline metal oxide phases can be seen in the case of W, Cu and Cr modified samples.

NH_3—TPD-investigations were performed to characterize acidic properties. The surface acidity was expressed as intrinsic acidity (μmol NH_3/m^2) desorbed between 100—600 °C. It can be seen from table, that incorporation of W, Cu and Mo led to an increased acidity. Other metal oxides, i.e., Cr, Mn, V, Ce, and Fe decreased the intrin-

Textural properties, acidities of the fresh and used MO-Al_2O_3-PO_4 catalysts and their catalytic performance for the dehydration of glycerol at 280 °C. Reactions condition GHSV: 90 h^{-1}; Glycerol-Input: 5 % aqueous solution, 1.0 g/h. Selectivity to acrolein and actol are depicted in the Fig. 2

Catalyst	Notation	PD, Å	A_{BET}, m^2/g		IA, μmol/m^2		X^*, %	Selectivity*, %					
			fresh	used	fresh	used		ACA	AAH	AOH	CO$_x$	PhOH	other
γ-Al_2O_3	AO	124	256	78	0.61	0.13	11 (5)	0(0)	2(2)	0(0)	1(0)	3(1)	37(52)
γ-Al_2O–PO_4	APO	115	207	120	1.42	0.72	100(69)	0 (0)	4(3)	1(0)	2 (1	8(7)	20(23)
MnO–Al_2O_3–PO_4	Mo-APO	65	166	151	0.93	1.09	98(90)	3(2)	5(4)	3(5)	5 (4)	9(4)	9(13)
CrO–Al_2O_3–PO_4	Ce-APO	88	185	116	0.90	1.04	70(38)	2(2)	3(6)	2(2)	2(1	4(1)	17(33)
CeO–Al_2O_3–PO_4	Cr-APO	72	211	146	0.94	0.20	100(99)	6(4)	8(11)	2(1)	10(3)	21(13)	28(16)
FeO–Al_2O_3–PO_4	Fe-APO	90	215	187	1.17	1.27	92(50)	3(2)	4(12)	10(15)	9(5)	6(3)	29(27)
VO–Al_2O_3–PO_4	V-APO	80	224	204	1.15	1.75	100(100)	6(4)	8(7)	18(16)	11(14)	9(5)	9(21)
MoO–Al_2O_3–PO_4	Mn-APO	68	163	138	2.26	2.68	100(88)	2(2)	7(6)	1(0)	12(18)	5(3)	14(35)
CuO–Al_2O_3–PO_4	Cu-APO	89	190	163	2.01	1.62	100(96)	3(2)	4(3)	1(1)	3(3)	10(6)	3(12)
WO–Al_2O_3–PO_4	W-APO	70	158	142	2.98	4.60	100/(97)	2(3)	2(3)	1(2)	3(2)	17(6)	2(5)

N o t e s: PD: Average pore diameter measured from the N_2-desorption branch according to the BJH method. IA: Intrinsic acidity measured by NH_3-TPD analysis; ACA: acrylic acid; ACH acetaldehyde; AOH : allyl alcohol; PhOH: phenol.

* Selectivity and conversion were analysed for initial 1 h of reaction. Data in parenthesis were analysed for reactions time from 28–30 h.

sic acidity of the catalysts. Our results confirm the general agreement that Lewis acidity, which is predominant for the investigated catalysts, is directly related to Pauling electro negativity [9]. W, Mo and Cu exhibit the highest electro negativity in the row of studied materials; thus, they also show the highest acidity. On the other hand, the lower electro negativities of Fe, Cr, Mn, V and Ce correlate with similar or lower acidities in comparison to the non-modified APO.

Catalytic activity. Catalytic results obtained with the $MO-Al_2O_3-PO_4$ catalysts at 280°C and at constant reactions conditions are listed in table . The major products of the glycerol conversion were acrolein, acetol, acetaldehyde, allyl alcohol, phenol, acrylic acid and CO_x. Products grouped under the label of «other» included propionic acid, acetic acid, acetone and other cyclic products include 3-methylfuran, 2-, 3-dimethyl-furan, C_6-lactone, cyclic acetal derivatives [7]. High amounts of cyclic by-products were observed over Fe-, Mn-, V- and Cr-APO catalysts. These cyclic compounds may be formed by a complex network including the dimerisation of glycerol, aldol-condensation and/or Diels-Alder reaction of acetol, acrolein and acetaldehyde [7, 10]. In most cases, the carbon balance was about 95—98 %. Fig. 2 summarises

Fig. 2. Dependence of the selectivity to acrolein (*a*) and acetol (*b*) on the intrinsic acidity for different catalysts at 1 h and 30 h time on stream at 280 °C

the selectivity to acrolein for TOS 1h and 30h. Pure alumina χ-Al_2O_3 with an acidity of 0.6 µmol NH_3/m^2 can be considered as typical Lewis acid catalyst, showed a low conversion of glycerol (10—15 %) at 280 °C. The APO-catalyst is a typical Brønstedt acid, with a total acidity of 1.42 µmol/m^2, showed a substantial higher conversion as the pure χ-Al_2O_3. The low conversion of glycerol and the low selectivity to acrolein of about 10—12 % over Ce-APO can be attributed to weak acidity and slight basicity [11] of this catalyst. Full conversion and high selectivity towards acrolein of about 45—60 % was obtained for Cu-, Mo- and W-loaded APO catalysts. Over Fe-, Mn- and Cr-APO catalyst the glycerol conversion after 1h TOS are about 70—80 %, indicating the relatively low activity compared to W-, Mo- and Cu-APO catalysts with a high intrinsic acidity of 2.0—2.9 µmol /m^2.

The reaction products obtained over Fe-, Cr-, V- and Ce-APO catalysts were also quite different from those obtained over the strong acidic W-, Mo- and Cu-oxide catalysts. For V-APO and Fe-APO only a low selectivity to acrolein and acetol of ca. 8—12 % were detected. Additionally for V-APO and Fe-APO catalysts the formation of allyl alcohol with a relatively high selectivity of about 10—20 % was observed. Our result with respect to the formation of allyl alcohol is consistent with the data of Jia et al. [5] on a $FeO_x-(Al(H_2PO_4)_3$ catalyst. It was proposed by them, that allyl alcohol can be produced from acrolein via consecutive hydrogen transfer.

Interestingly, over Ce-APO, Cu-APO and Mn-APO glycerol was after 30 h TOS converted to acetol with a selectivity of 25—40 %, indicating that this metal oxides favor the selective dehydration of primary hydroxyl groups. Fe-, Cr-, Mn- and V-oxides, which are well known as active components in the catalytic oxidation of hydrocarbons showed a full glycerol conversion but only with a selectivity of 10—25 % to acrolein and favored the formation of C_2- and C_3-carboxylic acid, acetaldehyde and CO_x. The last two products can be formed via oxidative C—C-cleavage of hydroxypropionaldehyde, acetol and acrolein or directly from glycerol. Generally, can be concluded, that the conversion of glycerol over Mn-, Fe-, Cr- and V-oxide containing catalysts produced substantial amounts of carboxylic acid, CO_x and unknown products with a total selectivity to the desired product acrolein and acetol of ca. 25—35 %. A formation of phenol with selectivity about 6—10 % was observed for W-, Cu- and Ce-modified catalysts. This phenomenon is obviously associated with the destructive cleavage of hydroxypropionaldehyde to acetaldehyde followed by a trimerization to phenol [12].
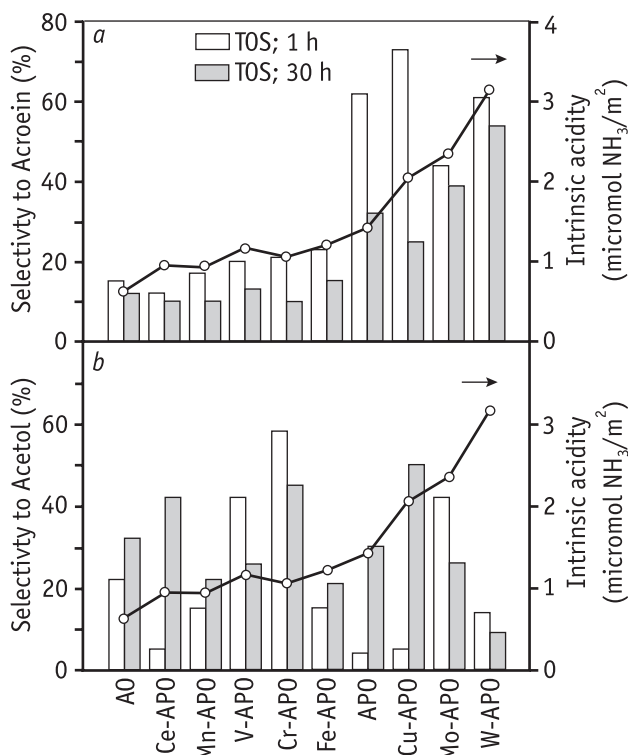
It is well-known that the dehydration of alcohol may proceed via three different mechanisms: E_1, E_2 and E_{1cB}, which differ in the configuration of the transition states [9, 13]. On the other hand, it is accepted, that for the dehydration of alcohols the nature and the amount of acidic and basic sites (Brønstedt or Lewis) play a key role in determining the catalytic performance. We attempted to correlate the selectivity to acrolein and to acetol at low reaction time, after 1 h and after 30 h with the intrinsic acidity determined by TPD for the freshly calcinated catalysts.

The results, given in fig. 2, *a* clearly show that for 1 h und 30 h TOS and at constant reactions conditions the selectivity to acrolein increased with increasing intrinsic acidity, i.e. the selectivity to acrolein correlates with the intrinsic acidity of the catalysts. These results confirm a more general hypothesis about the role of acidity in the selective dehydration of glycerol [2—6]. However, it needs to be mentioned that all $MO—Al_2O_3—PO_4$-catalysts exhibit only centres of weak or moderate acidity, presumably of Lewis type [15]. Chai et al. [3, 14] claimed that the selective conversion of glycerol over acidic catalysts proceeds mostly due to the presence of very strong Brønstedt acidity. This suggestion is opposite to our previous results [7] which showed that APO possesses predominantly weak or moderate acidic centres.

In contrast to acrolein, for acetol no clear correlation between selectivity and intrinsic acidity can be found (see fig. 2, *b*). Selectivities to acetol were detected for all catalysts between 20 and 43 %. Additionally, for Cu-, Cr-, Fe-APO catalysts after 30 h TOS a change/shift in the selectivities from acrolein to acetol was observed. These results can be explained by assuming that during dehydration the changes in the properties of the surfaces caused a possible change in the reaction mechanism. Table lists also the results of glycerol conversion after 1 h and 30 h of TOS. The long-time experiments showed a gradual deactivation of unmodified AO and APO catalysts and a relative constant and full conversion for catalysts modified with transition metal oxides. The initial conversion values (1 h of TOS) show some effect of the intrinsic acidity of the catalysts. The weakly acidic Ce- and Mn- modified catalysts exhibiting the lowest conversion and the strongly acidic W-, Mo- and Cu- modified catalysts show the highest conversion. Moreover, for APO and catalyst loaded with Fe-, Mn-, Cr- and Ce-oxide the conversion decreased more or less with increasing of TOS. The fact that modified APO catalysts have a high and stable activity indicates the role of the transition metal oxide in this catalytic process.

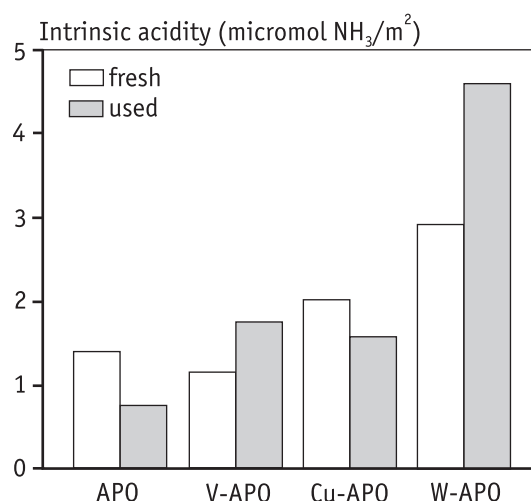In order to clarify the role of acidity and of transition metal oxide components in the glycerol conversion on

Fig. 3. Comparison of the intrinsic acidity of freshly calcined catalysts (fresh) and after reaction with glycerol at 280 °C for 3 h of TOS (used)

long-term stability and product distribution detailed investigations using XRD, TPR and XPS were presented in detail in [15]. In this paper we report about changes of surface area, acidic properties and the amount of coke deposition due to dehydration of glycerol using N_2-physisorption, NH_3-TPD and elemental analysis. Fig. 3 compares the intrinsic acidity of unmodified APO and of Cu-, V- and W-APO catalysts before and after dehydration of glycerol at 280 °C.

In the case of APO a strong decrease of ca. 60 % in intrinsic acidity was observed after 30 h of TOS. A slight decrease in acidity (~ 18 %) was also detected for Cu-APO. In contrast, the acidity of W- and V-modified APO catalysts increased for about 20—38 %. It can be summarised that all spent $MO-Al_2O_3PO_4$ catalysts showed a change in the form of NH_3-TPD profiles, i.e. the formation of new strong acidic centres with a desorption maximum at about 450—480 °C [15]. Generally, an increase in the catalyst acidity (between 5 und 30 %) was detected. A renewed calcination of the spent catalysts with air at 500°C for 4—6 h led to disappearance of the formed strong acid sites and the initial catalytic acidity and selectivity were completely restored and the crystallinity and the textural properties were also restored. This suggests that the observed new acid sites formed in the course of the reaction are of organic nature.

Finally TPO investigations were carried out for the spent catalyst after 30 h TOS at 280 °C. The relative amount of coke deposits are shown in Fig. 4. The Ce-APO catalyst with lower intrinsic acidity clearly exhibited the highest coke formation comparable to unmodified
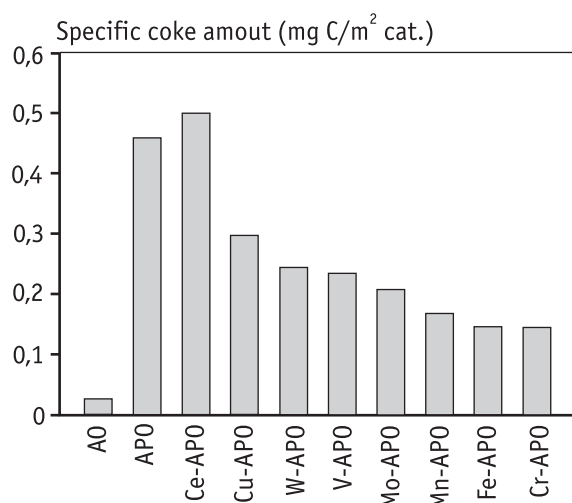
Specific coke amout (mg C/m² cat.)

Fig. 4. Relative amount of coke deposited on used catalysts after dehydration of glycerol at 280 °C for 10 h TOS

APO, while the coke depositions over the other transition metal-oxide modified catalysts was lower. The higher coke deposition over Ce-APO can be explained also by the slight basicity [9, 11] of Ce-oxides or Ce-phosphates which favour based-catalyzed oligomerization of glycerol to heavy carbonaceous compounds (coke precursors). The large differences in the amounts of coke deposition for the other MO-Al₂O₃-PO₄ catalysts appear to correlate with the acidity of the fresh catalysts.

The loss of specific surface areas of the fresh and spent catalysts was biggest for the alumina precursor, APO and Ce-APO. The other metal containing catalysts exhibit much smaller decreases in the BET area. The amount of deposited coke correlates with the loss of the specific surface areas of the studied catalysts (see table).

The above discussion contains no information on the dependence of a mechanism of the formation of acrolein and acetol on the nature of the acidic sites, since the NH₃—TPD-analysis cannot distinguish between Brønstedt and Lewis acidity. Generally, for the dehydration of different alcohols it has been suggested [9, 13] that the elimination of water via a secondary OH-group is a fast reaction and proceeds at Brønstedt and Lewis acid sites. Contrary the elimination of water via the primary OH-group proceeds only with the participation of Lewis acid sites and possess essentially higher activation energy [16]. Possible reactions involving primary and secondary hydroxyl groups in the dehydration of glycerol are proposed by many authors, which result in a parallel formation of two enol intermediates [2—6]. The enols would undergo rapid rearrangement to 3-hydroxypropionaldehyde and hydroxyaceton (acetol). It

was assumed that the catalytic dehydration of glycerol to acetol proceeds on Lewis acid sites and also on Brønsted basic sites. Therefore, the mechanism of acetol formation is still a matter of controversy. Recently Kinage et al. [17] reported that Na-oxide supported on CeO₂, Al₂O₃ and ZrO₂ having predominantly basic sites which favor the formation of acetol. Additionally was supposed that the formation of acetol can also be associated with Brønstedt acid sites. It is supposed that on acidic sites the dehydration of glycerol leads first to 2-propene-1,2-diol followed by its rearrangement to acetol. Over basic sites it is assumed that initially a dehydrogenation of glycerol leads to glyceraldehydes followed by dehydration to 2-hydroxy-2-propenal and their further hydrogenation to acetol. Chiu et al. [18] and Sato et al. [11, 19] communicated that copper-chromites and alumina supported Cu-oxide catalyzed the dehydration of glycerol to acetol with a selectivity above 40—75 % at 250—300 °C. According to [11, 18, 19], the formation of acetol in presence of Cr-, Cu- und Ce-oxides may proceed via radical reaction pathways with a change in the oxidation states of transition metal oxides.

Conclusions

Bifunctional transition metal oxide containing Al₂O₃-PO₄ catalysts showed different activity and stability in the gas phase dehydration of glycerol at constant reaction conditions. To summarize, W-APO was the best catalyst for a maximum acrolein selectivity of about 52—58 %. Best performances in terms of selectivity to acetol (35—50 %) were obtained for Cu-APO, Cr-APO and Mn-APO catalysts. Only in the case of the formation of acrolein a correlation between acidity and selectivity could be found. For Fe-, Cr-, Mn- and V-oxide containing Al₂O₃-PO₄ the formation of phenol, allylalcohol, acetic acid, acrylic acid, acetaldehyde and CO$_x$ with a selectivity between 1 und 20 % were observed.

The results show that the presence of transition metal oxides on phosphated alumina with acidic properties is promising to catalyze specific reaction pathways of the dehydration of glycerol leading to acrolein and/or hydroxyacetone. The presented results show the importance of acidity and redox properties of the catalysts on the conversion of glycerol and the product distribution. It can be concluded that acidity is a prerequisite for an initial high conversion, while the presence of the redox component influences the long-term stability and the product distribution. This property could be important from the standpoint of potential applications.

References

1. *Zheng Y., Chen X., Shen Y.* // Chem. Rev. 2008. Vol. 108. P. 5253.

2. *Tsukuda E., Sato S.* et al. // Catal. Commun. 2007. Vol. 8. P. 1349.

3. *Chai S.H., Wang H.P.* et al. // Green Chem. 2007. Vol. 9. P. 1130.

4. *Atia H., Armbruster U., Martin A.* // J. Catal. 2008. Vol. 258. P. 71.

5. *Jia C.J., Liu Y., Schmidt W., Schueth F.* // J. Catal. 2010. Vol. 269. P. 71.

6. *Ulgen A., Hoelderich W.* // Catal. Lett. 2009. Vol. 31. P. 122.

7. *Suprun W., Lutecki M., Haber T., Papp H.* // J. Molec. Catal. A. 2009. Vol. 309. P. 71.

8. *Bautista F.M., Campelo J.M.* et al. // Appl. Catal. A. 2003. Vol. 243. P. 93.

9. *Tanabe K., Misono M., Ono Y., Hattori H.* // Stud. Surf. Sci. Catal. 1989. Vol. 51. P. 5.

10. *Wang F., Dubois J.L., Ueda W.* // J. Catal. 2009. Vol. 268. P. 260.

11. *Sato S., Takahashi R., Kobune M., Gotoh H.* // Appl. Catal. A. 2009. Vol. 356. P. 57.

12. *Miller I.J., Saunders E.R.* // Fuel. 1987. Vol. 66. P. 130.

13. *Diez V.K., Apestequila C.R., Di Cosiomo J.I.* // J. Catal. 2003. Vol. 215. P. 220.

14. *Chai S.H., Wang H.P., Liang, Y., Xu B-Q.* // J. Catal. 2007. Vol. 250. P. 342.

15. *Suprun W., Gläser R., Papp H.* // DGMK-Conference «Conversion of Biomass». Gelsenkirchen, Germany. 10—12 Mai, 2010. P. 307.

16. *Jani M.J., Macht J., Iglesia E., Neurock M.* // J. Phys. Chem. C. 2009. Vol. 113. P. 1872.

17. *Kinage A.K., Upare P.P.* et al. // Catal. Comun. 2010. Vol. 11. P. 620.

18. *Liu S.Y., Zhou* et al. // ChemSusChem. 2008. Vol. 1. P. 578.

19. *Sato S., Akiyama M.* et al. // Appl. Cat. A. 2008. Vol. 347. P. 186.

ГАЗОФАЗНАЯ КОНВЕРСИЯ ГЛИЦЕРИНА НА СМЕШАННЫХ МЕТАЛЛ-ОКСИДНЫХ КАТАЛИЗАТОРАХ
(Краткое содержание)

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Глицерин является побочным продуктом при производстве биодизельного топлива (на 1 т биодизельного топлива образуется около 110 кг сырого глицерина). При мировом производстве биодизельного топлива 10—12 млн т в год накапливаются излишки сырого дешевого глицерина. Для утилизации сырца — водного раствора глицерина в ценные химические продукты предлагается множество технологических решений среди которых, например, реакции дегидратации, представляющие интерес для промышленного получения акролеина и гидрокисацетона. Для газофазной дегидратации глицерина предложен ряд гетерогенных кислотных контактов. Однако катализаторы на основе цеолитов и твердых бренстедовых кислот подвергаются быстрой дезактивации и обладают недостаточной стабильностью в присутствии водяного пара. В данной работе син-

тезирован и охарактеризован ряд алюмо-фосфатных катализаторов на основе оксидов металлов (Ce, Cu, Fe, Mn, Mo, V и W), нанесенных на χ-Al$_2$O$_3$ и дотированных PO$_4$. При этом соотношение M:Al = = 1/10 и PO$_4$: Al выдержано постоянным (1 : 10 и 1 : : 12). Катализаторы охарактеризованы методом низкотемпературной адсорбции азота, XRD- и NH$_3$-TPD-анализа.

Каталитическая активность контактов исследована в процессе газофазной дегидратации водного раствора глицерина в проточном реакторе при 280 °C при постоянных реакционных условиях. Установлено, что активность катализаторов в конверсии глицерина и селективность образования продуктов зависит от их общей кислотности и типа оксида металла переменной валентности. Наилучшей селективностью к образованию акролеина об-