Hydration of Olefins into Alcohols

N.M. Popova, K. Dosumov

D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry
142 Kunaev Street Almaty, 480100, Kazakhstan

Abstract

Review on hydration of olefins into alcohols is presented. It is shown that mineral acids (H_2SO_4, H_3PO_4), their salts, molybdenum and tungsten heteropolyacids of 12 range and zeolites are used as the catalysts. The reaction proceeds with high selectivity at 1-100 atm pressure and 473-673K through carbonium ion formed via interaction of adsorbed olefin with proton H^+ and then with H_2O yielding alcohol. It is concluded that for gas phase hydration of olefins use of proton substituted zeolites with ratio Si / Al = 7 – 9 and strength of Bronsted centers from – 8.2 to – 5.6, with high heat of adsorption for olefins and low heat of adsorption for water is effective instead of mineral acids on SiO_2.

In oxidative catalysis direct selective oxidation of alkanes to oxygen containing products and their oxidative dehydrogenation into olefins and further conversion of the olefins into valuable products through oxidation and hydration is a priority direction [1,2]. Utilization of monolith porous catalyst in multifunctional rectors for combination of processes is perspective [3]. It is known from the world practice that olefins are the main raw material for synthesis of different organic compounds. Majority of ethylene and propylene obtained through catalytic and steam pyrolysis of ethane, propane and gasoline fractions is used for polymerization (20-50%), production of styrene and its derivatives (20-24%), acrylonitrile (15-20%), ethylene and propylene oxides (12-16%), alcohols (ethanol 8-10%, butanol 10-13%, isopropanol 7-14%) and also ethylenglycol, acetone, acetaldehyde, acetic acid acroleyne, propionic aldehyde, vinyl acetate through oxidation and hydration over heterogeneous catalysts [4-9].

The reaction of hydration of olefins into alcohols is known for a long time and is used in industry. This is the method for ethanol production from ethylene, isopropanol from propylene and isobutanol from mixture of butylenes [5,6]. Concentrated H_2SO_4 is used when the process is carried out in two stages (96-98% H_2SO_4 at 80 ^{0}C, 25 atm through formation and hydrolysis of mono and diethylsulphate) or orthophosphoric acid supported on silica gel is used when the process is carried out in one stage (H_3PO_4/SiO_2 in gas phase) are used as catalysts [5,6]. The degree of ethylene conversion in gas phase is 3.8 4.8% in one run, and selectivity is 95-98.5%. The important condition of the process is ethylene must have concentration 90% and more. Use of circulation system lets to obtain 93-94% ethanol with admixtures of diethyl ether and acetaldehyde. Use of mixture of niobium and phosphoric acids after preheating at 773 K lets to increase yield of ethanol during ethylene hydration [10]. Investigation of gas phase hydration of ethylene over salts $Me(HPO_4)_2 \times nH_2O$ (Me = Ge, Zr, Ti, Sn) at atmospheric pressure in a flow unit at 473 K showed that use of $Sn(HPO_4)_2$ increases considerably the rate of ethanol formation up to 3 mmol/min g as compared to H_3PO_4/ SiO_2 (0.13 mmol/min g) with selectivity 99.9% [11]. The rate of the reaction was proportional to the number of acidic centers in the range $0.8 < H_0 < 1.5$.

The disadvantages of the said syntheses are high consumption of mineral acids, necessity to use special acid proof equipment, loss of phosphoric acid from the support (this reduces the activity) formation of by-products and high expenses for isolation of the products.

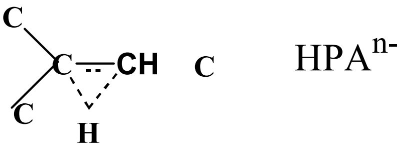
---

*corresponding author. E-mail: orgcat@nursat.kz

Printed in Kazakhstan

Hydration of olefins is a exothermic reaction $CH_2=CHR + H_2O = CH_3(OH)R$ where R = H, CH_3, C_2H_5 and it runs preferably at low temperatures and high pressures. This is the typical reaction that is catalyzed by acids like hydration of acetylene, which is accelerated by iron, copper, mercury, and palladium sulphates [12-14].

Heteropolyacids (HPA) possess higher activity and selectivity than that for mineral acids (H_2SO_4, H_3PO_4, HNO_3). They are used in industry for olefin hydration. The activity depends on the nature of the HPA and the row of activity is as follows: HPW $\cong$ HPMo > HSiW $\cong$ HSiMo > $H_2PMo_{18}O_{62}$ [15]. It was found [16] that proton donor activity of HPA is two times higher than that for mineral acid solutions. This is important since the main stage in the mechanism is strong interaction of protonated olefin.



Investigations have shown that the activity is growing with increase of HPA acidic function, coordination of HPA anion with isobutylene and solubility of isobutylene. Results of I.V.Kozhevnikov et al. are in accordance with the found regularities [17]. They found out that the rate constants for hydration of isobutylene in water solution of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ linearly growth together with Hammet constants values for acid function of HPA.

In paper [18] the action of some HPA of Mo and W of 12 range, mixture of phosphorus oxides and tungsten with H_3PO_4/SiO_2 was compared in ethylene hydration (table 1). It was found that the reaction proceeds with maximum selectivity (92%) over oxide mixture $W_{0,81}P_{0,19}O_x$. This is close to that for standard catalyst (95.7%). Over heteropolyacids supported on silica the selectivity was lower to 60-72%, while conversion in one run was higher than that for other catalysts. Investigation of amorphous mixture of oxides $W_{0,81}P_{0,19}O_x$ using Raman spectroscopy has shown that during treatment with steam Keggin structure $PW_{11}O_{40}^{3-}$ with defects is formed on the surface of the WO_3 (absorption bands at 995 - 997 cm^{-1}). This structure is the active center for ethylene hydration.

For direct hydration of olefins were used ion exchange resins. In paper [19] effect of temperature and pressure on propylene hydration were investigated in autoclave at 443-493K. The catalysts, sulfonatpolysterendivinylbenzene resins, were pretreated with hydrochloric acid. The conversion at 170-200 ^{0}C was 40-60% and selectivity was 96.0-99.1% when water/olefin volume ratio was 10-12 and reagents/resin volume ratio was 1-2. Dependency of the rate from pressure is linear. However, deactivation of the catalyst was noticed because of proton loss, and treatment with H_2SO_4 is needed at high temperature. So, use of ion exchange resins does not solve the problem of stability of acidic catalysts for olefin hydration.

Table 1

Catalytic activities of mixed metal oxides for hydration of ethane, and activity of other solid acidic catalysts* [18]

Catalyst	Ethylene conversion (%)	Selectivity			
		C_2H_5OH	$(C_2H_5)_2O$	CH_3CHO	Hydrocarbons
$W_{0,5}P_{0,5}O_x$	0.71	83.2	9.8	4.3	1.5
$W_{0,81}P_{0,19}O_x$	0.45	92.0	7.7	0.1	0
$W_{0,92}P_{0,08}O_x$	0.26	90.3	6.5	1.0	1.0
$H_3PW_{12}O_{40}/SiO_2$ 52.1% by weight	4.99	60.1	25.1	6.5	8.2
$H_3PW_{12}O_{40}/SiO_2$ 47.5% by weight	1.46	72.3	7.3	15.6	4.7
H_3PO_4/SiO_2 55.9% by weight	1.21	95.7	4.2	0	0

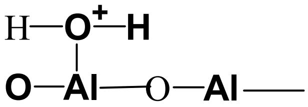
* - Reaction conditions: temperature 473K, pressure 0.6 MPa, SV = 900 h^{-1}, catalyst amount 10 cm^3, feed gas molar ratio $H_2O/C_2H_4 = 0.4$.

In paper Tanabe [4] it is shown that activity of heated sulphates (for example $NiSO_4$) is 50 time higher than that for H_3PO_4/SiO_2 in hydration of ethylene at 493K and pressure 620 mm Hg and H_2O/C_2H_4 ratio = 0.04. The activity of $NiSO_4$ is correlative with concentration of acidic centers with force $1.5 < H_0 < -3.3$. Activity and its relation with concentration of acidic sites with $H_0 < -3$ were found also for other sulphates. When concentration of sites with $H_0 = -3$ is high (more than 0.5 mMol/g) the acidity grows up to –8.2. In this case acetaldehyde and diethyl ether are formed together with alcohol.

Investigation of mechanism of hydration over metal sulphates showed that [4] the reaction proceeds through formation of carbonium ion after interaction of ethylene with H^+, which then reacts with OH formed after dissociation of H_2O to OH and H^+. Proton diffuses from Me^{+2} centers to proton centers of Br∅nsted type. Electronegativity of metal directly affects the rate of ethylene interaction with Me^{+2}.

Mixture of noble metals Rh-Ir supported on active charcoal was used for olefin hydration [20]. Maximum formation of isopropanol (96.3% by mass) was obtained in a flow unit at 673 K, P = 1.6 MPa and flow rate 100-150 h^{-1} over Rh-Ir (1:1)/C when propylene conversion was 8.4%. Reduction of the temperature to 573 increases the rate of propylene conversion to 39.1% but reduces alcohol formation to 72.8% by mass because of acetone formation (25.4% by mass).

Use of different zeolites (H_v, H-mordenite, HZSM-5) that possess high surface acidity ($H_0 \leq -8.2$) is more perspective for olefin hydration in gas phase because they are more thermally stable as compared to that for mineral acids [21]. Exchange of H^+ to different metals does not reduce the acidity and after heat treatment at 773-873K BAC are mainly formed.



$$\begin{array}{l} H{-}O^{+}{-}H \\ \quad\; | \\ O{-}Al{-}O{-}Al{-} \end{array}$$

Data on olefin hydration over different zeolites by Minachev with co-authors are being published since 1976 [22-28]. Investigation was carried out in a flow unit at 473-673 K and pressure up to 20 MPa. It was shown that over zeolite catalyst with SiO_2/Al_2O_3 = 3-4 optimum temperature of the process is 473 K and optimum pressure is 60 atm [22] (figure 1 and 2). Conversion depends on the nature of the olefin: 9.6% for ethylene, 18.2% for propylene and 18.0% for butylenes i.e. growing with increase of reaction activity of the olefin [23]. Introduction of chromium instead of H increases the yield of alcohols and productivity up to 0.09 g per hour per cm^3. This productivity is close to that for industrial phosphorus acid catalyst. The increase of temperature up to 538 K and pressure up to 15 MPa increases conversion up to the equilibrium one (25%, figure 1,2)

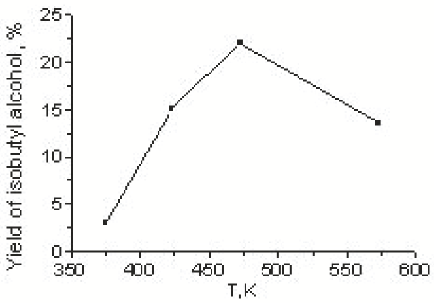


Fig.1. Dependency of isobutyl alcohol yield from hydration temperature at P=120 atm, H_2O: isobutylene = 6:1 [18]

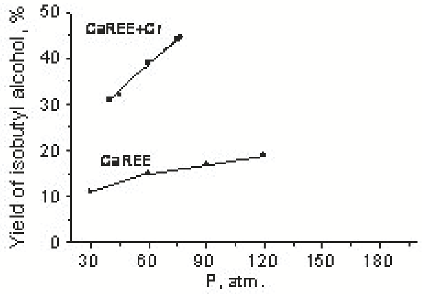


Fig.2. Effect of pressure to hydration isobutylene over CAREE-zeolite at 473. H_2O isobutylene = 6:1 [18]

Use of zeolites with high content of silica with 5% Cr_2O_3 additives (does not included in CVK zeolite structure, SiO_2/Al_2O_3 = 70 – 90) and dealuminated faujasite increases the activity [24] and stability of the catalysts [27]. Introduction of chromium reduces formation of coke and aromatic compounds that are usual for zeolites with high content of silica [23-25] (figure 3,4,5). It was shown that the hydration proceeds through carbonium ion mechanism [26] via addition of proton to adsorbed olefin and further interaction of the latter with water producing alcohol. Active catalysts were stable for 380 hours and possessed low energy of bonding of H_2O - zeolite (T_{max} desorption 323 K, T_{end} = 433 K). Other zeolites Y held water up to 500 K. From the above said data one can make some conclusions on selection of zeolites promoted with oxides for olefin hydration. Cations introduced into zeolites affect heat of olefin adsorption, for example, ethylene, which determines initial rate of hydration (figure 6) [4]. In [29] for the first time ethylene hydration at atmospheric pressure over proton exchanged zeolite catalysts (ZSM-5, mordenite, ferrierite) was shown. H substituted HZSM-5 with SiO_2/Al_2O_3 ratio 16.3 was the best in the row: HZSM-5 > H ferrierite > H mordenite. Conversion of ethylene into ethanol was 1.4% at 493 K over this catalyst.

Valuable factor that affects activity of zeolites is temperature of heat treatment that determines acidity of the catalysts. It could be determined with NH_3 thermodesorption method.

In order to increase yield of ethanol at low pressure of 1-5 atmospheres it was proposed to use porous 40% zeolite pipe (length = 6 cm, outer diameter = 12, internal diameter = 6 mm filled with granulated (16-32 mm) zeolite catalyst from outside H^+ZSM-5 (SiO_2/Al_2O_3 = 20) preheated to 673 for 2 hours (figure 7) [26]. In the case when porous tube with ZSM-5 powder was used at 463-473 K the following mixture was produced C_2H_5OH : C_2H_4 : H_2O = 48.5 : 47.7 : 3.7. The yield of ethanol was growing with the increase of pressure steeper than that for catalyst granules (figure 8) because the catalyst serves as a sieve at the same time.

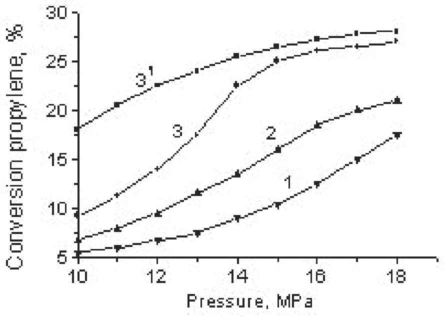


Fig.3. Dependency of propylene conversion from the temperature and pressure [19] over CrNC catalyst, 1 - 513, 2 - 513, 3^1 - 538 K. (3^1 – thermodynamic data).

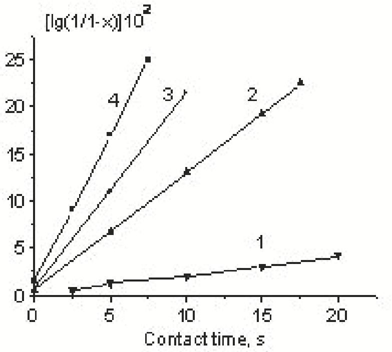


Fig.4. Dependency between lg (1/1-x) and contact time in propylene hydration over CrHC at 756 (1), 786 (2), 811 (3), 826 R (4) [19].

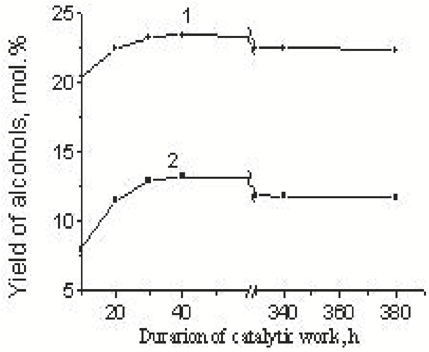


Fig.5. Stability of CrHC catalyst in hydration of propylene (1) and ethylene (2) [19].

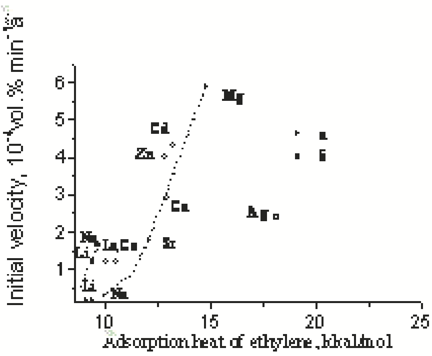


Fig.6 Dependency initial reaction on rate in ethylene hydration at 493 K (a) and 573 K (b) from heat of adsorption on in ion exchange forms of zeolite A [3].

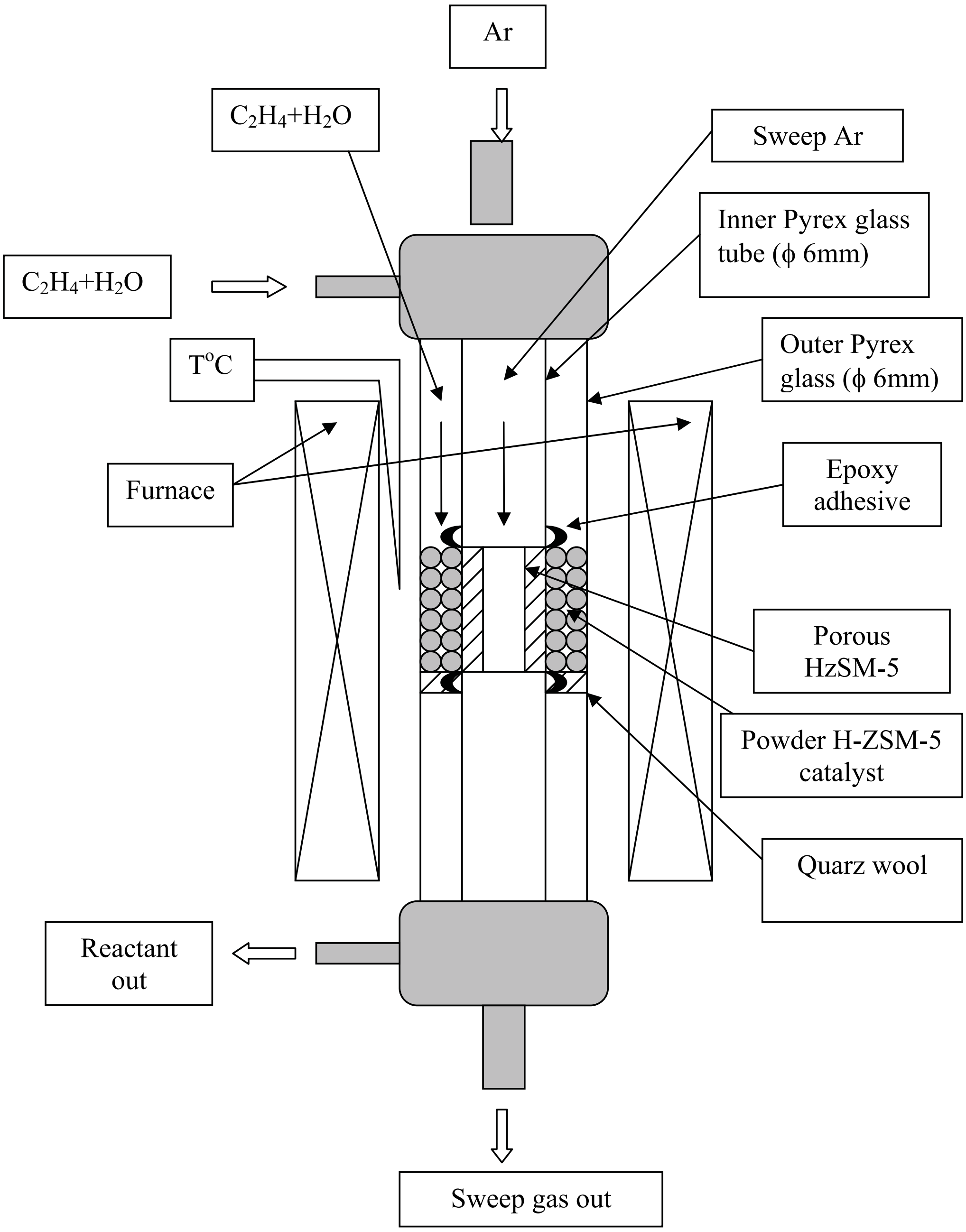


Fig. 7. Schematic view of the reactor [26]

In paper [31] hydration of n-butenes was investigated on powder proton substituted zeolites having different structure and alumina content at 423 K, H_2O : olefin ratio = 1 in steel autoclave at 44-100 atm. It was shown that maximum yield of alcohol is declining in the row H-mordenite (5.9-7.07%) > HZSM-5 (5.73%) > offerite (3.29%). Over H-mordenite composition of products and alcohol yield depends on atomic ratio Si/Al (figure 9, 10) [31] and reaches the maximum at the ratio = 7 – 9. When the ratio Si/Al is more than 10 conversion of butenes and selectivity is lower because of dimerization into dimethylhexane.

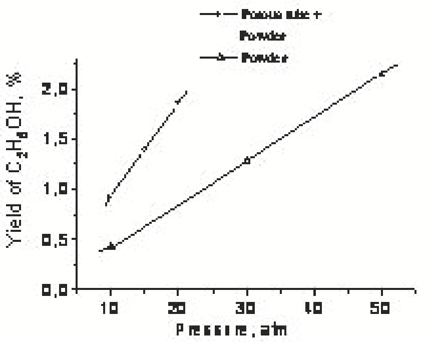


Fig. 8. Yield of ethyl alcohol as a function of reaction pressure W/F = 18,8 g of catalyst xh/mol, sweep Ar, 1 atm; feed gas C_2H_4/H_2O = 1 [26].

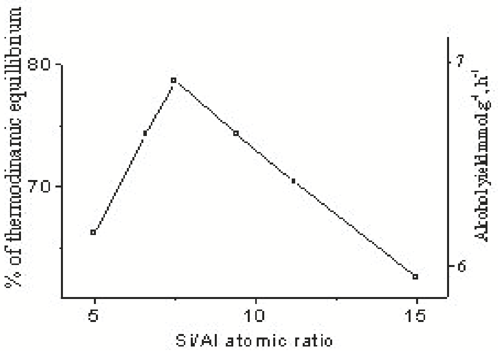


Fig 10. Effect of the Si/Al atomic on alcohol yields over mordenite [27].

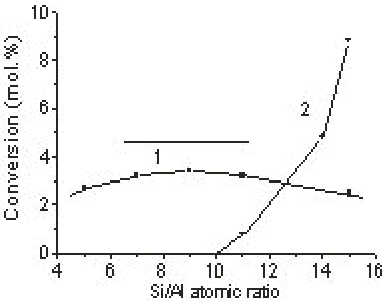


Fig. 9. Hydration (1) and dimerization (2) activity of mordenite as a function of the Si/Al atomic ratio (1 – sec butyl alcohol, 2 – C_8H_{16}). The Line shows the alcohol thermodynamic-cally limited conversion [27].

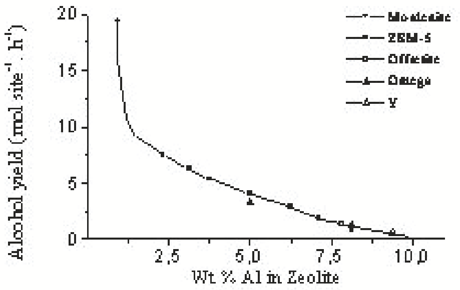


Fig.11. Correlation between hydration on activity per protonic site and aluminum content in the various zeolites [27].

The yield of alcohol is declining considerably together with increase of aluminium content in different zeolites (figure 11). From figure 11 one can see that the rate of olefin hydration is related directly to quantity of [H] i.e. is determined by the force of the acidic centers. Existence of such direct correlation between H_0 and reaction rate was known earlier for hydration of olefins in H_2SO_4, or HPA solutions. In paper [27] it was shown with H_2O sorption that zeolites with high silica content are hydrophobic strong acids in water not only because of high acidity, but because of high surface activity towards organic indicators as compared to that for water. Zeolites with high silica content (Si/Al > 9.2) possess strong acidic centers ($-8.2 < H_0 < -5.6$), and for zeolites with Si/Al < 3.5 and 3.7 < Si/Al < 6.9 possess weak acidic centers ($H_0 > +1.5$), and for mordenite $H_0 > -3$.

So, one can conclude that for zeolites and mineral acids activity in hydration is a function of acidity of proton centers. To obtain more active catalysts it is necessary to maintain Si/Al ratio at 7-9 and strength of acidic centers between –8.2 and –5.6.

Introduction of some cations instead of H^+ provides positive effect because this increases heat of ethylene adsorption. Tanabe [4] and Minachev [22] point out to positive effect of Cd, Zn, Cr, Ca, REE.

Elements of the I group decrease zeolite activity, but introduction of Cr, REE, Ca in zeolites with high module leads to increase of activity and stability of the catalysts, and reduction of coke formation. If increase of heat of ethylene adsorption increases the rate of hydration [4], then energy of water adsorption, in contrary, should be minimum (T_{des} = 383 K).

Patent search of data on olefin hydration on heterogeneous catalysts showed that in early works (1972-1980) H_3PO_4 supported on SiO_2 and alumosilicates were used, later on TiO_2, and ZrO_2 [32]. Zeolites (erionite, mordenite, ferrierite) with SiO_2/Al_2O_3 = 20-500 when are used in the process contain in their composition Ca, Cr, AEE, REE. In some patents were described use of heteropolyacids Mo, W, V, oxides of tungsten, chromium, nickel, copper, manganese, copper sulphates and other metals. Most often the reaction was carried out in flow units, sometimes in autoclaves. In flow units after separation of water alcohol solutions mixture of olefins with alkanes was recycled after concentration on zeolites [33]. In some patents a cascade of rectors was used [34].

Analysis of patents on olefin hydration in flow units lets to conclude that zeolites preliminary heated to 773-873 K in N_2, He atmosphere with SiO_2/Al_2O_3 ratio from 10-12 to 50 are mainly used as the catalysts. Hydration of ethylene, propylene, butenes is carried out at 5-100 atm and H_2O/olefin = 1-5. Flow rate of liquid olefin through the catalyst was 0.5-10 h^{-1}. At 438-623 K (temperature is higher when number of C atoms in olefin is more) conversion of olefins was 3.5-9.6% for ethylene, 17.3-18.2% for propylene. The conversion grew up to 35% when natural ferrierite or ZSM-5 with TiO_2 and ZrO_2 additives was used [35]. Conversion of butylene was 9% and that for isobutylene was 18%. Yields of alcohols were from 10 to 39.6%. In works carried out by Minachev and co-workers it is shown that zeolitechrom catalyst, in which Cr is not included in the zeolite lattice, is stable for 380 hours. Selectivity of olefin hydration over zeolites is high and is in the range from 98.4-100%. In some works industrial mixture propane-propylene, propane-isobutylene was used for hydration. The obtained mixture of isopropyl and tret-butyl alcohols is used as additive for gasoline to increase octane number [33-38].

Conclusion

General conclusion is as follows. For olefin hydration under pressure high silica and H-substituted zeolites with certain strength of acidic centers ($-8.2 > H_0 > -5.6$) are more effective. Relationship between the number of the said active sites and rate of hydration was found out. Using the results one may suppose that optimum catalyst should possess weak adsorption of H_2O and strong adsorption of olefin. Unfortunately there are little data on long use of zeolite catalysts for hydration in industry. Also, there are little information on the nature and bond energy of olefins, H_2O and oxygen on the surface of the catalysts. There are no data (except [30] on use of zeolite catalysts supported on porous blocks. The role of supported and incorporated in zeolite elements in hydration mechanism is not clear. Tanabe showed [39] that some mixed oxides (ZnO-ZrO, CdO-Fe_2O_3, ThO_2-V_2O_5, TiO_2-CeO_2 etc.) could catalyze hydration of propylene. However, acidic properties of the said oxides are not investigated. In future, it is important to develop zeolite catalysts not only for ethylene hydration, but also for hydration of propane-propylene (30-40% propylene) and butane-butylene (15-40% butylene) fractions from oil processing units in order to produce from the obtained alcohols acetone, acetaldehyde, methylethylketone, ethylene oxide and different ethers. Alcohols are in great demand (tens of thousand tons) for industrial complex “Karbid” and “Polypropylene” (Atyrau) in Kazakhstan.

In order to optimize composition of substituted zeolites and to increase their stability and selectivity in olefin hydration it is necessary to investigate their acidic properties using adsorption of NH_3 and other compounds and bonding energy of reactants with the surface using TPD, TPR, TPO and to develop methods to support them on porous ceramic blocks and metal blocks to reduce catalyst consumption and to increase catalyst productivity.

Input of oxygen in the gas mixture can lets to combine processes of hydration and oxidation of olefins over the same catalysts or their mixture into corresponding aldehydes, acids, ketons.

It is known that homogeneous and heterogeneous catalysts on the basis of KCl-CuCl, $PdCl_2$ and $CuCl_2$ and supported on wide porous zeolites (faujasite) are used in industry as catalyst for oxidation of olefins, oxidation of propylene into acetone and acrolein, ethylene into acetaldehyde in the presence of water (olefin : H_2O : air = 1 : 2 : 5) [40,41]. Acetone is produced during propylene oxidation over modified Fe and Ru bentonite [42]. Acrylic acid is produced via oxidation of propylene over Sn and Mn oxides supported on porcelain [43] and acetic acid is produced over Sn-Mo-Fe catalysts [44].

References

1. Kustov L.M., Ross. Chem.Zh. 16: № 1, (1997), 5.

2. Dossumov K., Tungatarova S.A., Massalimova B.K., Kuzembay K.K. MoCrGa catalyst of selective oxidation of oil gas into ketons, aldehydes and alcogols//XVIII Mendeleev congress in the general and inorganic chemistry, Moscow., Russia. 3, 253 p. (2007)
3. Dzisko M.T. Prospects for development of heterogeneous catalytic processes, Abstract of XIV International conference on chemical reactors. Tomsk, 14 IC SB, Novosibirsk, (1998).
4. Tanabe K. Catalysts and catalytic processes. M. Mir, (1993), 172 p.
5. Valakin V.P., Production of synthetic ethanol. M., Chimia, (1976).
6. Brunstein B.A., Klimenko V.L., Cyrkin E.B. Production of alcohols from oil and gas raw materials. Leningrad, Nedra (1964), 198 p.
7. Agaguseynova M.M., Abdullayeva G.N. Oxygenated Complexes of Transition Metals in Alkene Oxidation Reaction//Materials of Azerbaijan-Russian Symposium with international participation "Catalysis for solving the problems of petrochemistry and oil refining". September 28-30, 2010. Baku, Azerbaijan.PP-1. P.123-124
8. A. Magauov. Oil & Gas of Kazakhstan, 4-5, 2010. P.127
9. Innov. Patent RK # 21794, 2009, C07C 49/08
10. Okazaki S, Kurimata M., Jizuka T., Tanabe K., Bull. Chem. Soc, Japan, 60: 37, (1987).
11. Jsobe A., Yabyuchi Y., Jwasa N., Fakezawa N., Appl. Catalysis A: Gener. 194-195: 395 (2000).
12. Dorfman Y.A., Investigation of catalytic acetylene hydration in electrochemical system Ph.D. Thesis, ICN AS KazSSR, Almaty, (1966), 17 p.
13. Nogerbekov B.Y. Investigation of acetylene hydration in the presence of homogeneous catalysts based on copper complexes, Ph.D. Thesis, ICN AS KazSSR, Almaty, (1970), 21 p.
14. Segizbaeva S. Catalytic acetylene hydration in the presence of palladium and iron salts, Ph.D.Thesis. Almaty KazGU (1970), 18 p.
15. Aoshima A., Yamamtsu S., Yamaguchi T, Nippon Kagaku Kaishi 976 (1987).
16. Kozhevnikov I.V., Khankhasaeva S.T., Kulikov S.M. Kinet. Katal 29: 76, (1998).
17. Kozhevnikov I.V., Khankhasaeva S.T., Kulikov S.M., Кинет, катал. 30:50, (1989).
18. Ushikubo T., Kurashige M. and al., Catal Lett., 69:83 (2000).
19. Kaiser J.K., Beuther H., Mooree L.D. at al., J. GEC. Product Research and Development, 296, (1962).
20. Zakumbaeva G.D., Shapovalova L.B. Eurasian Chem. Tech.J., 2: 11 (2000).
21. Isakov Y.I. Neftekhimia, 38 : (6), 404. (1998)
22. Minachev C.M., Mortikov E.S. Masloboev A.A. et al. Neftekhimia, 16: (б): 846, (1976).
23. Tsydulevsky A.M., Novikova L.A., Kondratiev V.A. Neftekhimia, 19: (5): 771,(1979).
24. Tolkacheva L.N., Novikova L.A., Plakhotnik V.A., et al. Neftekhimia, 23 : (б): 803, (1983).
25. Tolkacheva L.N., Afanasiev B.A., Novikova L.A., et al. Neftekhimia, 26 : (5), (1987).
26. Tolkacheva L.N., Dmitriev R.V., Afanasiev B.A., et al. Neftekhimia, 25 : (5), 646, (1986).
27. Tolkacheva L.N., Novikova L.A., Mikheikin N.D., et al. Neftekhimia, 25: (5), 610, 1985).
28. Novikova L.A., Tolkacheva L.N., Plakhotnik V.A., et al. Neftekhimia 23 : (1), 72, (1983).
29. Iwamoto N., Tayima M., Kagawa Sn., J. Catal. (101): 195, (1986).
30. Ishihara T., Matsuo J., Ito M. and al., Ind. Eng. Chem. Res. 36 : 4427, (1997).
31. Francois Fayula, Rafael Jbarra and al., J. Catal. 88 : 60, (1984).
32. EP 798040A1, 1997, C07C 29/04.
33. US Patent # 5488185, 1996, C01C 29/04.
34. US Patent # 4956506, 1990, C07C 41/05.
35. US Patent # 5144084, 1992, C07C 31/10.
36. UK Patent # 2145415, 1985, C07C 29/04.
37. UK Patent # 2147290, 1985, C07C 29/04.
38. US Patent # S484013, 1984, C07C 29/04.
39. Tanabe K. Solid acids and bases. Mir, M. (1973), p.87,132.
40. Skibida N.P., Sakharov A.M., Emmanuel O.N. Totals of science and technology. Ser. Kinetika I Kataliz M., VINITI, 1986, vol.15, p.110.
41. Minachev K.M., Usachev M.Y., Rodin A.P. et al. Neftekhimia, 19:5,751,(1979).
42. Lenarda M. et al., J. Mol. Cat., 92 : (2), 201, (1994).
43. Adzhamov K.Y., Kasymov F.B., Alkhazov T.G. In: Mechanisms of Catalytic Reactions, III USSR Conference. Novosibirsk, IC SB RAS 1982, p.66.
44. Alkhazov T.G., Adzhamov K.Y., Bagiev V.A. Neftekhimia, 19 : (5),757, 1979.

Received 2 iune 2009.