Catalytic ketonisation of acetic acid over modified zirconia
1. Effect of alkali-metal cations as promoter

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Abstract

The catalytic ketonisation of acetic acid was studied over fifteen different metal-doped zirconia samples. Among all, the catalytic aspects of alkali-metal cation-promoted zirconia were extensively studied and found most effective for ketonisation of acetic acid. The reactions were performed in a fixed-bed reactor by varying the temperatures, flow rates of reactant and mole percent of alkali on the catalyst. Except Li, all the alkali-metal ions were capable of enhancing the catalytic activity. Complete conversion with high selectivity for acetone was observed in the temperature range of 623–698 K. Among all the alkali-metal-modified zirconia, sodium was the most effective promoter for ketonisation reaction. The observed activity order followed Na > K > Cs > Li. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Zirconia; Ketonisation; Promoter; Acetic acid; Yield and selectivity

1. Introduction

Long since it has been the practice to obtain ketones by the pyrolytic decomposition of metal carboxylates, mostly salts of calcium and thorium [1,2]. Later on attempts are being made to synthesize ketones, directly by the vapor phase ketonisation of carboxylic acids over different solid catalysts [3–5]. As this direct synthesis method is simple, economical and versatile, efforts are being made for further improvements. Oxides of thorium [6–8], cerium [9], manganese [10,11], zirconium [12–14], rare earth metals [15–17] as well as alkaline earth metals [18] and metal oxides supported on pumica, alumina, silica or titania are found to be active catalyst for this reaction. Zirconia is also found active in the ketonisation of aldehydes and esters [19,20].

No systematic work has so far been carried out on the ketonisation of monocarboxylic acid using metal oxide promoted zirconia. The present work deals with the systematic study on the catalytic behavior of alkali-metal-doped zirconia for the vapor phase conversion of acetic acid to acetone which proceeds according to the general equation:

$$2RCOOH = RCOR + H_2O + CO_2 \qquad (1)$$

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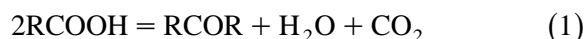
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2. Experimental

2.1. Materials and method

Zirconium hydroxide gel was prepared by adding required volumes of 0.4 M $ZrOCl_2 \cdot 8H_2O$ and 6.7 M NH_4OH solutions simultaneously to an ammoniacal solution at pH = 10.2, under stirring condition. The precipitate obtained was aged for 24 h, filtered, washed with distilled water till free from chloride ion and dried in an oven at 383 K for 12 h. The solid crystalline mass thus obtained was crushed into powders, below 140-mesh (-105 μ) size.

2.2. Precursor for the dopants

The chemicals used as precursors for doping, LiOH, NaOH, KOH, $CsNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3$, $Sm(NO_3)_3$, and $Y(NO_3)_3$, unless otherwise stated are of analytical grade.

2.3. Doped catalysts

The catalysts modified with different metals were prepared by incipient wetness technique in which required volume of 0.1 M aqueous solution of different metal ion was added to the zirconium hydroxide powder. The pasty mass thus obtained was evaporated to dryness on a hot plate, calcined at 723 K for 6 h in a muffled furnace at a heating rate of 5 K min^{-1}.

3. Characterization

3.1. Powder X-ray diffraction

Powder XRD patterns of pure and alkali-metal-doped zirconia were recorded on a Philips powder diffractometer, equipped with a monochromator and mounted on a Philips PW 1710 X-ray generator with Cu $K_{\alpha 1}$ radiation ($\alpha 1 = 1.54056$ Å).

3.2. Determination of textural properties

The specific surface area of the catalysts were determined by adsorbing N_2 at liquid nitrogen temperature according to the BET method using a Quantasorb (Quantachrome USA). Prior to adsorption–desorption studies all the samples were degassed at 423 K and 10^{-4} Torr for 5 h.

3.3. FTIR study

The FTIR spectra of pure and alkali-metal-modified zirconia samples were recorded at room temperature on KBr phase using a JASCO FTIR 5300 spectrophotometer in the range 4000 to 400 cm^{-1}. Before making palettes, all the samples were heated at 473 K for 2 h.

3.4. Surface basicity

Surface basicity of the catalysts were determined on the basis of irreversible adsorption of some organic acids, such as Phenol ($pK_a = 9.9$), acrylic acid ($pK_a = 4.2$). In each experiment, 10 ml of freshly prepared solution of phenol–acrylic acid in cyclohexane was pipetted into adsorption bottle containing 0.1 g catalyst. The bottles were shaken for 2 h at constant temperature (298 K) and the concentration of the substrate in solution in equilibrium with the adsorbed substrate was determined spectrophotometrically.

Sorption experiments were developed at the wavelength of maximum adsorption (λ_{max}, nm) and in the concentration range of the adsorbate where the Beer–Lambert law was followed. In each experiment, time needed to achieve equilibrium condition at constant temperature was checked and never found more than 1.5 h. The chemical interaction, adsorbate–catalyst surface was consistent with the Langmuir adsorption isotherm equation,

$$\frac{c}{X} = \frac{1}{bX_m} + \frac{c}{X_m} \tag{2}$$

where c is the concentration of the substrate in solution, in equilibrium with the adsorbed substrate; b is a constant; X is the amount of the adsorbed substrate per gram of the solid and X_m is the monolayer coverage which correspond to the theoretical amount of solute adsorbed by 1 g of solid if all sites are covered.

This method provides both the total concentration of the basic sites and their relative strength by the use of organic acids with different pK_a. All the samples were heated at 473 K for 2 h before carrying the experiment. Similar method was adopted else where [21].

3.5. Ketonisation of acetic acid

Catalytic ketonisation reaction was carried out in a fixed-bed quartz reactor (10 mm, i.d.) on line with gas chromatograph. The reactor was placed inside a programmable tubular furnace (Stanton Red croft, UK) containing 0.5 g of the catalyst. A nitrogen flow, saturated with acetic acid vapor at room temperature was led through the catalyst. Prior to the catalytic test, each of the samples was pretreated under nitrogen flow at 473 K for 2 h. The products were analyzed by on line Gas Chromatograph, (CIC, India) operated on FID mode and using a Porapack Q column. The authenticity of the products were verified by comparing the retention time with the standard sample. At the steady state, percentage yield and selectivity of ketone were calculated from quantitative conversion of the acid.

4. Results and discussion

The X-ray powder diffraction pattern of the samples calcined at 723 K are shown in Fig. 1(a) and (b). The patterns reveal the high crystallinity nature of all the doped and undoped catalysts. Zirconium hydroxide gel prepared with ammonium hydroxide at pH = 10.2, on calcination at 723 K shows predominantly monoclinic phase. However, the same sample when doped

with 0.5 mol% Na leads to predominantly tetragonal phase, whereas samples doped with Li, K, and Cs show little variation in phase transformation from monoclinic to tetragonal. Absence of peak due to alkali-metal oxide, indicates migration of metals from the surface to the zirconia lattice. This type of phenomenon was also observed in case of other matrices [22]. The peaks due to monoclinic phase gradually disappears with increase in sodium content and with 5 mol% Na only tetragonal phase is found in the sample. The increase in sharpness of the peaks with increasing Na content shows better crystallization of the solid.

The BET surface area of all the samples calcined at 723 K are presented in Table 1. The effect of alkali metals on the surface area have been studied over a wide range of solids and are found responsible for the decrease in the specific surface area of catalyst [23,24]. Samples doped with 0.5 mol% of Na, K, and Cs exhibit almost the same surface area as that of pure zirconia, whereas sample doped with 0.5 mol% of Li causes a decrease in specific surface area to nearly half of pure zirconia. This decrease in specific surface area may be attributed to the rearrangement in the original zirconia network thus reducing the porosity of the solid.

Fig. 2 represents the FTIR spectra of the alkali-metal-doped and undoped zirconia. The band at 3418 cm^{-1} and 1633 cm^{-1} are due to the OH stretching and bending vibrations, respectively. The characteristic peaks for pure zirconia, in the range 400–900 cm^{-1} are attributed to monoclinic phase. This also supports the earlier report [25]. A broad band possessed by 5 mol% sodium doped zirconia in this range indicates a phase transformation from monoclinic to tetragonal. Similar type of change is also observed by Kitajima [26]. This phenomenon is also supported by XRD. IR spectroscopic study of alkali-metal carbonates shows that the intense bands observed in the range 1300–1500 cm^{-1} are due to metal carbonates [27]. IR bands for sample b, f, and g in the same range are not prominent and the haziness in the
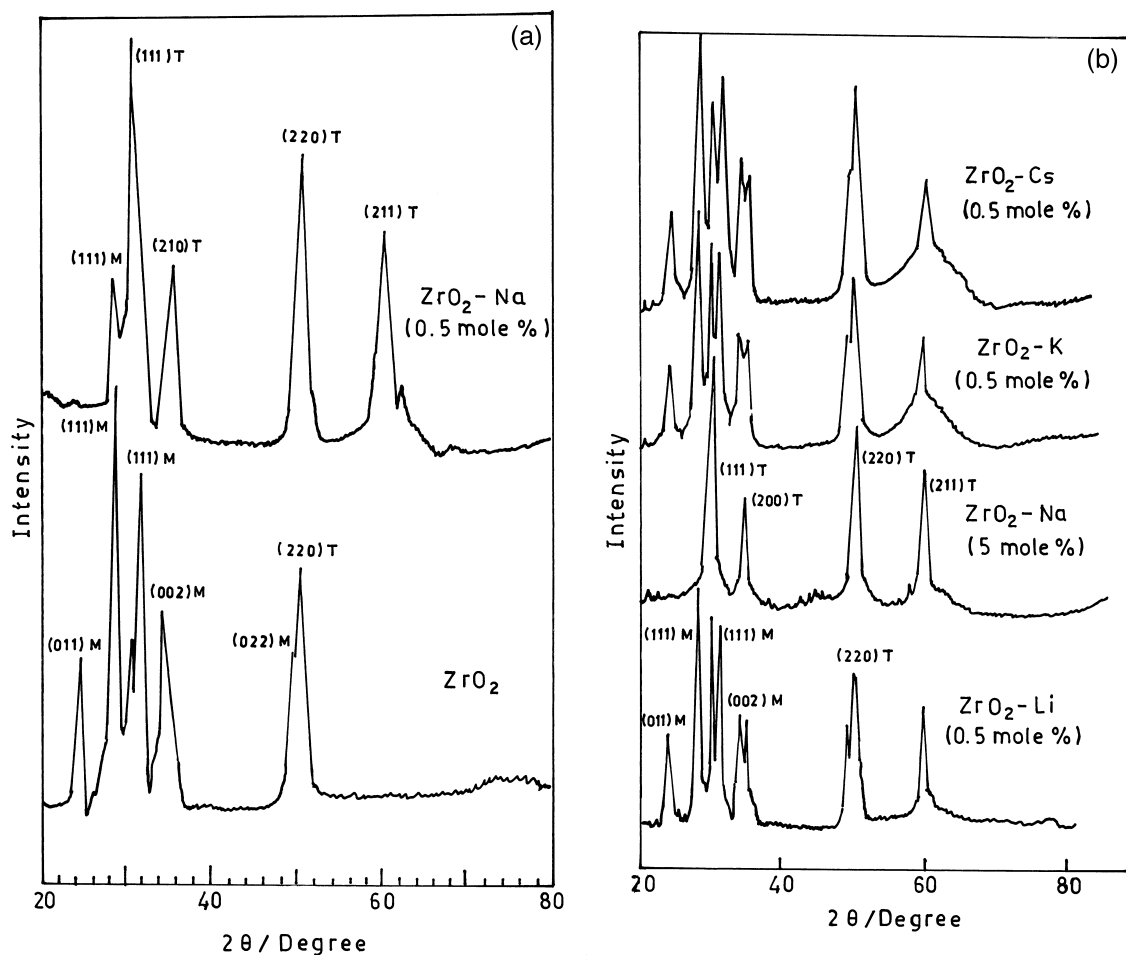
Fig. 1. XRD patterns of pure and alkali-metal-doped zirconia calcined at 723 K.

spectra may probably be due to the adsorbed carbon dioxide. The vibrational features observed in the range 1340–1456 cm^{-1} for samples d and e may be due to carbonate of the metals formed by the chemical interaction of carbon dioxide with the hydroxyl groups or absorbed water over the solid surface. From the spectra of c, d, and e, it is clear that increase in sodium contain increases the prominence of the peaks in the range 1340–1456 cm^{-1} and with ZrO$_2$–Na (5.0 mol%) a sharp peak at 1456 cm^{-1} is observed.

The surface basicity values (X_m) of the representative catalysts are given in Table 1. In every case the absorption of organic acid is in consistent with the Langmuir adsorption isotherm (Eq. (2)). From the plot of c/X vs. c, we calculated the values of X_m, i.e., saturation coverage of the solute for a particular adsorbate. Since the absorption depends upon the pK_a values of the organic acids, thus by definition X_m values for phenol absorption measure strong basic sites, whereas the X_m values for acrylic acid measure the total basicity of the catalyst. For a particular solid, the weak basic sites are measured from the difference of X_m of acrylic acid and phenol absorption. The basicity thus measured with different organic acids (phenol,

Table 1
Physico-chemical properties of alkali-metal-ion-doped zirconia calcined at 723 K

Active phase	Alkali-metal (mol%)	Phase	S_{BET}	Basic sites	
				Phenol ($\mu mol\ g^{-1}$)	Acrylic acid ($\mu mol\ g^{-1}$)
ZrO_2	0.0	M+T	56	39	78
ZrO_2–Li	0.5	M+T	25	9	80
ZrO_2–Na	0.25	T+M	45	–	–
ZrO_2–Na	0.5	T	58	14	51
ZrO_2–Na	5.0	T	52	–	–
ZrO_2–K	0.5	M+T	59	36	82
ZrO_2–Cs	0.5	M+T	56	34	77

T = Tetragonal; M = Monoclinic.

acrylic acid) shows that the catalysts are moderately basic. Except for Na, there is little difference between the X_m values of pure and alkali-
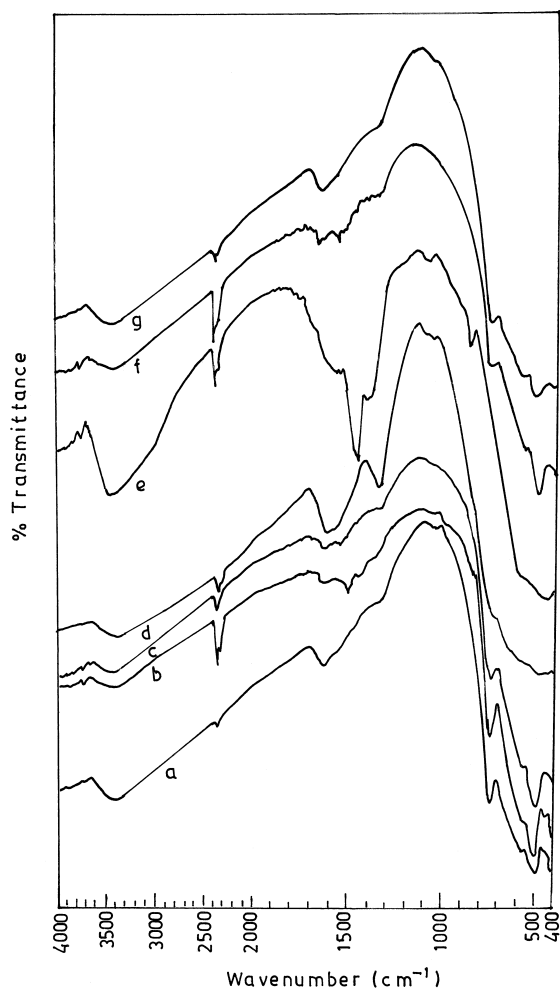
metal cation promoted zirconia. However, sodium promoted sample responds to an appreciable variation in the basic strength which may be due to the carbonate groups formed on the surface. The carbonate groups may block the basic sites and hinder the interaction of incoming acid molecules with the sites nearer to the carbonate groups.

Ketonisation of acetic acid over alkali-metal cation promoted zirconia and pure zirconia are manifested in Fig. 3. From the reaction profile it is evident that unpromoted and 0.5 mol% alkali-metal cation promoted zirconia exhibits negligible activity below 573 K. Beyond this temperature Li and Na followed a sigmoidal path, whereas the observed conversion profiles are linear for unpromoted, K and Cs promoted zirconia regardless of the gas hourly space velocity.

Catalytic conversion of unpromoted and different mol% of sodium promoted catalyst are highlighted in Fig. 4. This shows that the activ-
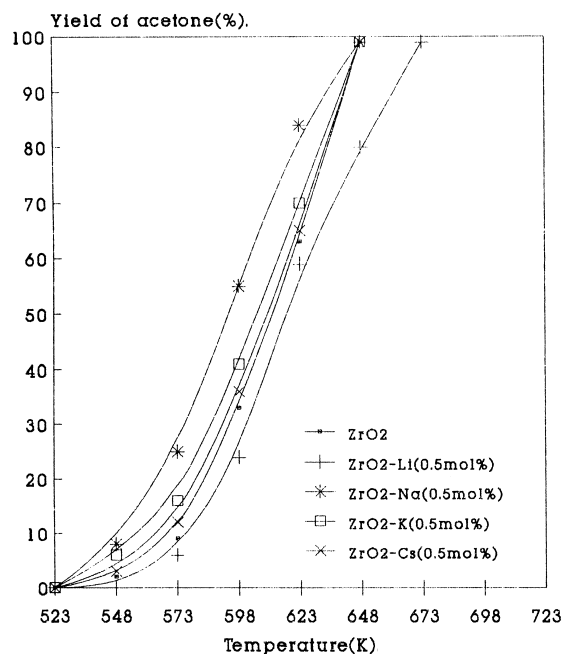

Fig. 2. FTIR spectra of pure and alkali-metal-doped zirconia.

Fig. 3. Influence of active phase upon catalytic activity of alkali-metal-doped zirconia in ketonisation of acetic acid; GHSV = 160 ml g^{-1} min^{-1}.

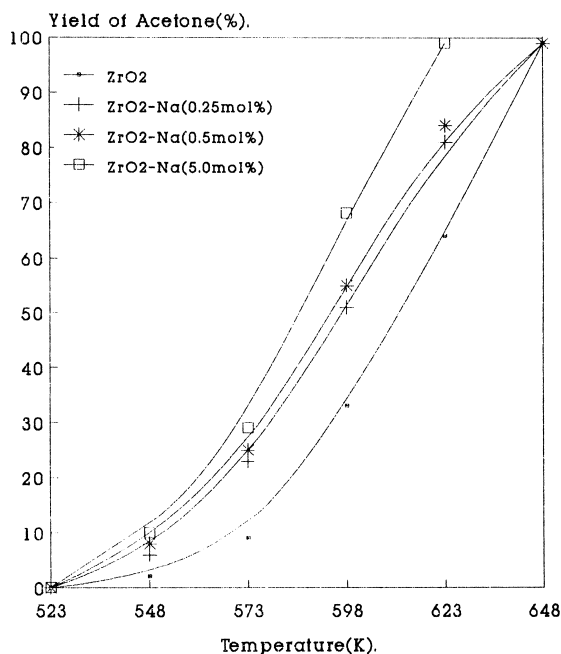Fig. 4. Influence of sodium contain on zirconia in ketonisation of acetic acid; GHSV = 160 ml g^{-1} min^{-1}.

ity increases with increasing sodium content from 0.25 to 5.0 mol% in the samples. Contrary to the 0.5 mol% sodium promoted zirconia, a linear conversion profile is seen for ZrO_2–Na (5.0 mol%) sample regardless of reactant space velocity. In the case of 20 wt.% CeO_2–SiO_2, similar type of observation was also observed [4].

With alkali-metal cation promoted zirconia, most frequently observed products in the ketonisation of acetic acid are acetone, carbon dioxide and water (Eq. (1)). Zirconium dioxide, being moderately basic showed an appreciable activity towards ketonisation. Yekerson [18] and Yekerson et al. [28] investigated some oxidic system in detail and proposed two different path through which acetic acid interact with the solid to give acetone. These were: (i) the formation of bulk acetates and their decomposition to acetone, and (ii) surface interaction. The former path is generally followed by oxides of low lattice energy, whereas the later preferentially occurs with solids of high lattice energy. Zirconia, being an oxide of high lattice energy thus might be allowing surface interaction. Modification of zirconia with alkali-metal cations except Li improves its catalytic activity and selectivity. This decrease in the activity in case of Li doped sample may be due to the drastic decrease in surface area of the catalyst. Among the other samples, sodium promoted zirconia was most active and selective. The conversion over 5.0 mol% of sodium doped zirconia was almost 99% at 623 K with selectivity greater than 94%. The above observations may be explained on the basis of formation of surface carbonate groups which also supports the earlier report [29]. However, the activity of the samples con-

Table 2
Catalytic activity of different metal ion doped zirconia for ketonisation of acetic acid

Active phase	Yield of acetone (%)						
	548 K	573 K	598 K	623 K	648 K	673 K	698 K
ZrO_2	2	12	33	63	99	–	–
ZrO_2–Mg (0.5 mol%)	3	13	25	51	78	93	–
ZrO_2–Ca (0.5 mol%)	–	5	22	53	82	99	–
ZrO_2–Sr (0.5 mol%)	–	3	13	39	76	99	–
ZrO_2–Ba (0.5 mol%)	–	5	20	49	85	99	–
ZrO_2–Fe (0.5 mol%)	5	15	39	74	99	–	–
ZrO_2–Co (0.5 mol%)	7	23	60	93	99	–	–
ZrO_2–Ni (0.5 mol%)	5	23	55	90	99	–	–
ZrO_2–Cu (0.5 mol%)	5	19	51	87	99	–	–
ZrO_2–Ce (0.5 mol%)	3	21	38	52	80	99	–
ZrO_2–Sm (0.5 mol%)	4	21	51	90	99	–	–
ZrO_2–Y (0.5 mol%)	7	21	48	60	72	88	99

taining K and Cs are higher than pure zirconia but less than the sodium promoted samples. This reveals that not only carbonate but also the alkali-metal cation played certain roles in modifying the surface of the catalyst and thus increasing the catalytic activity of zirconia. The observed activity order is as follows: Na > K > C > ZrO_2 > Li.

Doping with alkaline earth metals rather deactivate the catalyst towards ketonisation (cf. Table 2). Only about 80% conversion is observed in those cases at 698 K. Blackening of the samples at the end of the reaction confirms cock formation. This indicates that acetone formation might be taking place by some other route which favoured cocking. Transition metals are observed as good promoters for zirconia, but rapid deactivation makes them less useful for ketonisation. A remarkable increase in the activity is observed with Sm doped zirconia, whereas cerium and yttrium doping reduces the efficiency of the catalyst.
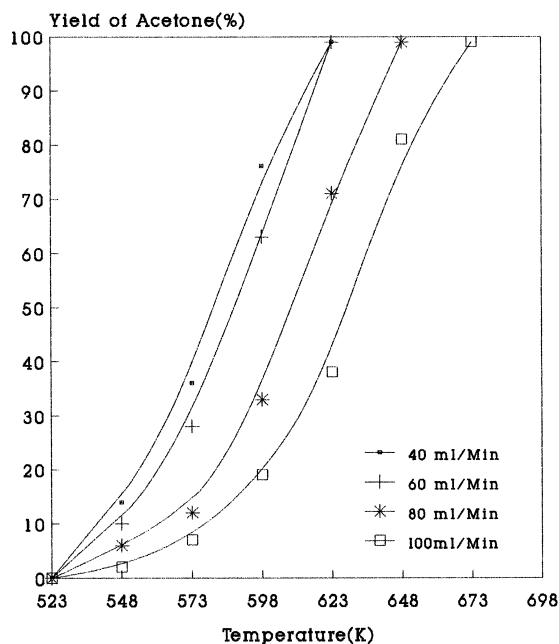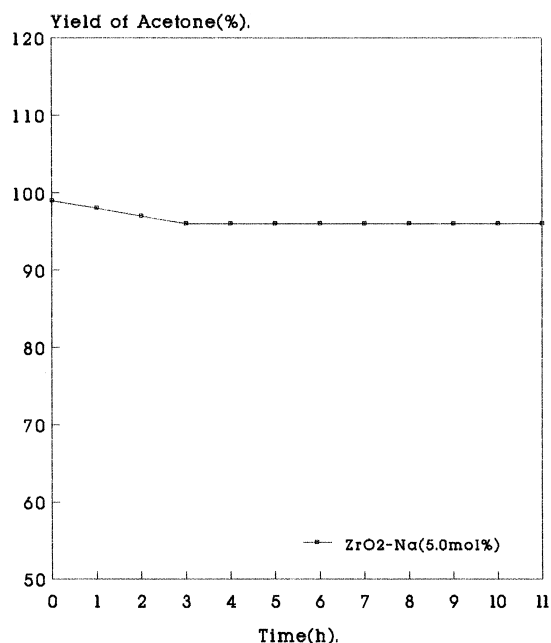

Fig. 6. Yield of ketone in time-on-stream experiment over ZrO_2–Na (5.0 mol%) at 623 K, GHSV = 160 ml g^{-1} min^{-1}.

With the linear increase in gas hourly space velocity (GHSV), significant drop in acetone yield is observed in the temperature range 548–648 K and also shifts the temperature of maximum conversion to higher values (cf. Fig. 5). This effect may be attributed to the variation in proportion of active sites to reactant concentration.

Time on stream reactivity of ZrO_2–Na (5.0 mol%) is depicted in Fig. 6. A slight decrease in activity is observed during the first 4 h of reaction at 623 K; thereafter, it remains nearly constant.

5. Conclusions

For ketonisation of acetic acid, alkali-metals promoted zirconia are found most active as compared to other metal ions doped zirconia samples studied. Acetone is the main product over pure as well as alkali-metal-modified zirconia. Zirconium dioxide, being a high lattice energy solid, prefers surface interaction with the

Fig. 5. Catalytic activity of ZrO_2–Na (5.0 mol%) on ketonisation of acetic acid at various GHSV.

acid for ketonisation. Sodium stabilizes tetragonal phase of zirconia and improves its catalytic activity and selectivity. Alkali metals, specifically sodium probably favours the formation of surface carbonate groups and also modifies the bulk of the zirconia. Both the modifications are responsible for acetonisation of acetic acid. The observed activity order follows: Na > K > Cs > ZrO_2 > Li.

Acknowledgements

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