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Oxidative catalysis on high-temperature ionic melts

Yu S Chekryshkin, T A Rozdyalovskaya, A A Fyodorov, G V Lisichkin

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Abstract. The results of studies of the catalytic oxidation of organic compounds in the presence of molten transition metal salts and oxides are surveyed. The attention is focused on extensive oxidation of halogen-containing compounds. The bibliography includes 197 references.

I. Introduction

Molten salts, in particular, alkali, alkaline earth and rare earth metal halides, carbonates, sulfates, molybdates, tungstates and vanadates, are distinguished by thermal and radiation stability, low volatility, low viscosity, and high electrical and thermal conductivities over a broad temperature range. Owing to these properties, ionic melts are of interest as high-temperature electrolytes,[1,2] energy storage devices and heat carriers,[1–5] and as gas- and dust-trapping liquids.[6–8] Molten electrolytes (metal oxides and salts) are used in coating of metal surfaces[9,10] and in thermal and electrochemical storage cells and fuel cells.[1,2,9,11–13] The present review considers the use of metal oxide and salt melts as catalysts of oxidation of some organic and inorganic compounds and as the media for these reactions.

In recent years, considerable attention has been devoted to the so-called ionic liquids, *i.e.*, salts formed by quaternised nitrogenous heterocycles (or amines) and Lewis acids, which are liquid under normal conditions. The application of these compounds as catalysts for skeletal isomerisation of alkanes and for metathesis, alkylation, disproportionation and oligomerisation of alkenes has been described.[14–25] High catalytic activity of ionic liquids, which is attributable to their high polarity and high acidity, was noted. Thus they induce isomerisation of alkanes at 30 – 70 °C.

Yu S Chekryshkin, **T A Rozdyalovskaya**, **A A Fyodorov** Institute of Technical Chemistry, Urals Branch of the Russian Academy of Sciences, ul. Lenina 13a, 614990 Perm, Russian Federation. Fax (7-3422) 37 82 62, tel. (7-3422) 37 82 88 (Yu S Chekryshkin), (7-3422) 37 82 53 (T A Rozdyalovskaya), (7-3422) 37 82 91 (A A Fyodorov), e-mail: cheminst@mpm.ru
G V Lisichkin Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax (7-495) 236 05 33, tel. (7-495) 939 46 38, e-mail: lisich@petrol.chem.msu.ru

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The salt melts considered in this review are also ionic liquids.† These high-temperature melts are used to carry out reactions that are thermodynamically allowed only at elevated temperatures (cracking, dehydrogenation). In addition, due to the high thermal conductivity, it is expedient to use molten salts in the processes accompanied by pronounced heat evolution or absorption, for example, pyrolysis, partial and extensive (complete) oxidation of organic compounds, coal gasification, and so on.

Molten catalysts (MC) have the following specific features which make them unique.

1. Unlike the conventional heterogeneous catalysts, MC exhibit high performance stability, because the 'liquid – vapour (or gas) phase' interface is constantly renovated during the catalysis.[28–30]

2. High thermal conductivity of ionic melts provides easy solution to the heat supply or withdrawal problem in highly endo(or exo)thermic reactions. The risk of local overheating resulting in the destruction of active sites, which is typical of traditional catalysts, markedly decreases.

3. An important advantage of MC is the simplicity of their preparation. They are usually prepared by simultaneous or consecutive fusion of the components. There is no need to be concerned about optimisation of the surface texture and the surface area, the mechanical strength or the grain-size distribution of the catalyst, *etc*.

4. High electrical conductivity of ionic melts allows one to use electrochemical methods for the monitoring and control of MC composition during the process.

5. The reactions on MC proceed in the absence of water or aqueous solutions; this is very important as regards environment protection (no wash water).

However, molten catalysts are not free from drawbacks, first of all, this is their relatively high corrosion activity and the need to use special reactors.

Despite the fact that the first studies dealt with reactions of organic compounds catalysed by melts were published more than a hundred years ago,[31] these catalysts have not yet found wide use in industry. Apart from the high corrosion activity of the melts, this is due to poor knowledge of their catalytic properties. Currently, melts are used on an industrial scale only for the synthesis of isoalkanes[26,27,32–34] and for chlorination of hydro-

† In particular, isomerisation of alkanes on a molten salt mixture $AlCl_3 – SbCl_3 – KCl$ also proceeds at 30 – 70 °C.[26,27]

carbons[3,12,35–41] and on a pilot scale for coal gasification.[11,12,42–44]

The purpose of this review is to summarise the published data on the characteristic features of processes catalysed by melts.

II. Experimental techniques for the work with molten catalysts

The catalytic processes on molten metal salts and oxides are carried out using special equipment and procedures. Several versions of process implementation involving molten catalysts have been proposed. Most often, MC-catalysed reactions are carried out by bubbling vapour of the feedstock with or without a carrier gas through a melt bed.[35,43,44] Bubble-type reactors are used for this purpose,[45–47] and the contact time of the reaction mixture with the catalyst is controlled by changing the height of the melt bed.[47,48]

In the bubbling of a gas–vapour mixture through a melt, the contact area of the gas–liquid phases and, hence, the degree of feedstock conversion depends on the degree of dispersion of the gas flow. In an ideal case, a gas bubble has a diameter of less than 1 mm, *i.e.*, it is a microreactor with a great surface-to-volume ratio. Therefore, in these systems, the processes that tend to acquire an explosive character when carried out in usual reactors become easily controllable.[49]

A study of thermal properties of a $KPO_3-V_2O_5$ melt has shown[50,51] that oxygen is evolved from the melt in discrete portions. This was attributed to the formation of oxygen microbubbles, which have no time to unite into large particles. The minimum volume of an evolved bubble was calculated to be 5×10^{-5} cm^3. Each bubble acts as a microreactor on the walls of which free radicals are 'quenched' and, hence, chain reactions cannot switch to the explosive mode. Probably, this accounts for the possibility of safe extensive oxidation of phthalic anhydride and nitrobenzene production wastes on the $K_2O-V_2O_5$ melt,[52,53] whereas their combustion in an open flame is accompanied by explosion.

Gas-phase oxidation of *o*-xylene with oxygen bubbled through an eutectic (eut) melt $K_2SO_4-V_2O_5$ (39 mass %) and a melt $K_2S_2O_7-V_2O_5$ (14 mass %) has been reported.[54,55] The experimental data were processed, to determine the bubbling velocity (U), using the equation

$$U=\frac{H}{(H-h)(\pi R^2/Q)}=-\frac{1}{h\pi R^2}\,\frac{\mathrm{d}Q}{\mathrm{d}(1/H)},$$

where H is the effective height of the melt; h is height of the melt at a zero gas velocity; Q is the gas volume flow rate at the melt temperature; R is the radius of the reactor. The resulting velocity was used to determine the residence time of the mixture in the reaction zone.

In the 509–570 °C temperature range for Q = 40 cm^3 s^{-1}, the U value varied from 9 to 18 cm s^{-1}. At 500 °C, the conversion of *o*-xylene in a mixture with oxygen reached 35%–42%. (Note that oxidation of *o*-xylene mixed with nitrogen under the same conditions results in a low conversion of the hydrocarbon, *viz.*, 2.5%–4.5%.) The residence time of the gas–vapour bubbles in the melt zone was ~2 s. It is believed[54,55] that the higher reaction selectivity observed in the melt compared with a solid catalyst having the same composition is due to the isothermal mode of the process, resulting in a decrease in the yields of extensive oxidation products.

The kinetics of reactions on MC is usually studied using a tubular reactor with a melt layer applied onto its internal surface.[56] The residence time is controlled by varying the feed rate of the reaction mixture or the reactor length. The reactor can operate in either continuous or pulse mode.[56,57] Processing of the experimental results obtained with a pulse-type reactor has been described in detail.[58] For reactors operating in the displacement mode, a dependence of the substrate conversion on time was derived using different forms of kinetic equations.

If it is necessary to increase the specific surface area of a molten catalyst, this is applied on a sorbent surface.[59,60] In this case, reactors traditional for heterogeneous catalysis are utilised. The use of supported MC often results in higher yields of the target products with respect to those obtained in the bubbling mode.

The combined reactor and regenerator in which the catalyst reduction and reoxidation stages occur separately appears to be the best version. The ammoxidation process of *m*-xylene using this reactor design has been reported.[61] The reaction mixture enters the reactor at a high rate through a specially designed nozzle and sprays the melt. The reaction proceeds in a vessel filled with finely dispersed drops of the melt. The partially reduced melt flows into a tank from which it moves again into the reactor by means of a gas lift‡ with simultaneous oxidation. The non-consumed hydrocarbons and ammonia are separated from the reaction products and recycled.

The necessity to separate the reactor zones in which the reaction occurs and the catalyst is regenerated is quite common. Thus the oxidative dehydrogenation of ethylbenzene and aliphatic alcohols on the $K_2O-V_2O_5$ melt proceeds more easily than the reaction of vanadium(IV) with oxygen (catalyst regeneration);[46,62] therefore, it is expedient to carry out the oxidation of vanadium(IV) with oxygen at higher temperatures (> 640 °C) and to carry out the oxidation of organic compounds at 500 °C in another reactor zone.

The catalyst regeneration (saturation with oxygen in the case of oxidation) can be performed during gas lift transportation of the melt.[63] The melt is first saturated with oxygen and then excess oxygen is removed in the separation zone until a specified partial pressure is attained. To increase the selectivity of oxidation of organic compounds[64] and prevent the formation of explosive mixtures, it is necessary to eliminate the contact of the hydrocarbon feedstock and reaction products with oxygen. This allows one to carry out simultaneously two processes with opposite signs of thermal effect (an endothermic process in one zone and an exothermic process in the other zone) and thus to balance the heat flows. For example, such reactor has been used for the production of synthesis gas by oxidation of lower alkanes (C_1-C_4) in a flow of molten metal oxides.[65] The proper oxidation was carried out in one reactor zone, while in the other zone, the oxidation products were reformed. This endothermic process yielded synthesis gas virtually free from nitrogen. The partially reduced melt was routed into the regeneration zone for oxidation with atmospheric oxygen.

A special reactor has been developed for the processing of solid urban waste by fusion in a slag melt under conditions of air bubbling. In this reactor, solid waste particles of different sizes are captured by melt drops, get into the high-temperature region (1250 °C) and burn. This process for urban waste destruction has already been tested on an industrial scale.[66–68]

Non-friable bulk materials are processed using tanks filled with a molten catalyst.[69,70] The possibility of using molten catalysts for extensive oxidation of organic polymers containing a metal cord with subsequent recovery of the metal from wastes formed in the manufacture and applications of various reinforced polymeric and rubber articles has been demonstrated.[71]

III. Characteristic features of reactions proceeding on melts

Owing to the high thermal conductivity of inorganic melts, the heat supply to the reactor in the case of endothermic reactions (hydrocarbon pyrolysis and cracking) and the heat withdrawal from the reaction zone in the case of oxidation (especially,

‡ Gas lift is a device for lifting a liquid by the energy contained in the compressed gas that is mixed with this liquid.

extensive oxidation) of organic compounds are easier for the reactions with MC. This allows one to intensify the processes.

The by-products (tars and coke) formed during high-temperature reactions are either collected on the melt surface (and, hence, they can easily be removed mechanically from the reaction zone) or distributed throughout the bulk of the melt without the formation of a continuous crust [30, 72] (this facilitates their removal by oxygen bubbling, *i.e.*, burning out [30]). The addition of glass-forming metal oxides (boron oxide [29] or metal oxides that increase coke wettability [73]) favours the uniform distribution of coke throughout the melt. High rate of oxidation of soot was attributed [74] to good wettability of soot in the presence of the V_2O_5 melt.

Since metal oxides and inorganic salts exist as melts over a broad temperature range and have a high thermal conductivity, the temperature in the reactor can be quickly changed and finely controlled, which is important for catalytic reactions carried out under non-steady-state conditions.[75] The perturbations introduced into a heterogeneous catalytic system (the changes in the reactant concentration, temperature and electrode potential) are controlled more easily when the reaction is carried out on the melts rather than on solid catalysts for which the surface structure is poorly reproducible.

High diffusion coefficients of oxygen in melts, in particular, $10^{-7}-10^{-5}$ cm^2 s^{-1} (Refs 75 and 76), determine high rate of structure relaxations and allow one to study fast steps of a heterogeneous catalytic process. Structural changes in a molten catalyst can be induced and detected by various methods, including electrochemical ones. In this case, the reaction products are simultaneously detected, which is important to gain information on the process mechanism.[77, 78] This possibility was demonstrated for the first time in a study of SO_2 oxidation mechanism under non-steady-state conditions on a $K_2S_2O_7-V_2O_5$ melt.[75, 76]

The relatively high oxidation temperatures of organic compounds on MC do not prevent investigation of the kinetic effects, namely, the isotope (KIE) and compensation effects. For example, for the oxidative dehydrogenation of *para*-substituted and deuterated ethylbenzene on the $KVO_3-V_2O_5$ eutectic melt, primary KIE and inverse secondary KIE were observed and the $\log k$ *vs.* σ_R^0 dependence was established.[56, 79] It was concluded that oxidative dehydrogenation of ethylbenzene derivatives is a multistep process. At a temperature of up to 550 °C, the oxidation involves sorbed oxygen and follows an associative (concerted) mechanism, which switches to the stepwise oxidation–reduction mechanism at higher temperatures. The first step is the reaction of V_2O_5 as the MC component with the aromatic system of the benzene ring. Presumably, the reaction is facilitated by the replacement of hydrogen atoms in the benzene ring by deuterium. This leads to an increase in the equilibrium concentration of the initially formed π-complex, which is then converted into styrene, and to an increase in the dehydrogenation rate (inverse secondary KIE). The replacement of hydrogen atoms at α-carbon in ethylbenzene by deuterium results in a twofold decrease in the rate constant for ethylbenzene dehydrogenation (or a 25% decrease per deuterium atom). This relatively high (in view of the fact that the rate constants were determined at 540–600 °C) primary KIE value indicates that the hydrogen atom is rather remote from the carbon atom in the transition state.

This assumption is supported by the dependence of the rate constants for oxidative dehydrogenation of *para*-substituted ethylbenzenes on the σ_R^0 Hammett constants of the substituents R.[56] The equation for this dependence at 600 °C has the form

$$\log k = -0.187 \pm 0.016 + (1.345 \pm 0.120)\,\sigma_R^0$$

$(r = 0.9907, s = 0.0173)$,

where r and s are correlation parameters.

The dependence of $\log k$ on σ_R^0 shows that in the transition state the substituent is involved in resonance interaction with the aromatic system. The polarity of the transition state is also confirmed by high reaction constant ($\rho = 1.345$ at 600 °C), which suggests a radical mechanism of the process. On the basis of elemental and powder X-ray diffraction analyses of solidified catalyst samples taken before and after the reaction, it was concluded that the reaction follows a stepwise mechanism, which switches to a concerted mechanism at temperatures below 550 °C.[80]

A study of the oxidation kinetics of ethanol on K–V–M oxide catalysts containing various metal oxides (about 300 compositions) over a broad temperature range (573–873 K, below and above the melting points of the systems) has revealed [81, 82] a kinetic compensation effect, *i.e.*, parallel variation of the activation energies (E_a) and pre-exponential factors (A) in the Arrhenius equation. This effect is expressed by the relation

$$\log A = cE_a + d = E_a/2.3RT_s + \log k_s,$$

where c and d are constants, T_s and k_s are isokinetic parameters.

Different dependences of $\log A$ on E_a for oxidative dehydrogenation of ethanol to acetaldehyde, extensive oxidation of ethanol to CO_2 and dehydration of ethanol to ethylene indicate that these processes occur on different active sites of the catalyst.[82, 83] The aggregation state of the oxide composition does not influence the pattern of isokinetic dependence.

IV. Relationship between the catalytic reactions proceeding on solid and molten catalysts

Molten catalysts can be used as models to search for new catalytic systems, to establish correlations between the catalyst composition and activity and to study the catalysed reaction mechanisms. The surface of melts has a more uniform composition than that of solid-phase catalysts, which have surface defects and structural and chemical inhomogeneities.[51, 84, 85]

The features elucidated in the studies of properties and action of MC can be used when preparing solid catalysts. However, one should take into account the correspondence of the conditions of application of molten and solid catalysts, for example, coincidence of the temperature range. A large number of salt and oxide systems with melting points ranging from room temperature to 900 °C are available.[86] This makes it possible to select melt compositions with melting points below the temperatures used to carry out most of petroleum refining and petrochemistry processes such as pyrolysis and cracking of petroleum hydrocarbons, oxidation of alcohols and alkylaromatic hydrocarbons and production of monomers.

Analysis of the published data shows that the principles of selection of the chemical composition of molten and solid catalysts do not differ much. For example, the chemical composition (in particular, the content of vanadium with the oxidation state +4 in the $KVO_3-V_2O_5$ melt) was found to correlate with specific oxygen desorption from the melt and its catalytic activity with respect to ethanol oxidation.[85, 87] It is noteworthy that the relationship between the nature of the transition metal oxide added to the $K_3V_5O_{14}$ melt and the catalyst activity in the oxidation of ethanol (Fig. 1) is similar to the relationship established [88] for solid catalysts.

In the oxide catalysts with a more complex chemical composition, the dependence of the catalytic activity on the composition is more complicated. Thus for the oxidation of ethanol, the curve for the activity of the $K_3V_5O_{14}-MoO_3$ melt *vs.* the content of MoO_3 has three maxima for MoO_3 concentrations of 13.3 mol %, 20.5 mol % and 34 mol % (*i.e.*, for molar ratios $K_3V_5O_{14}:MoO_3 = 2:1$, 1:1 and 1:2, respectively).[85, 87] However, the curve for solid catalysts having a simpler composition, $V_2O_5-MoO_3$, has only one maximum at a MoO_3 content of about 30 mol %. The lack of other maxima on the catalytic activity curve can be attributed to the formation, on the surface of catalyst grains, of a compound with the same composition (irrespective of

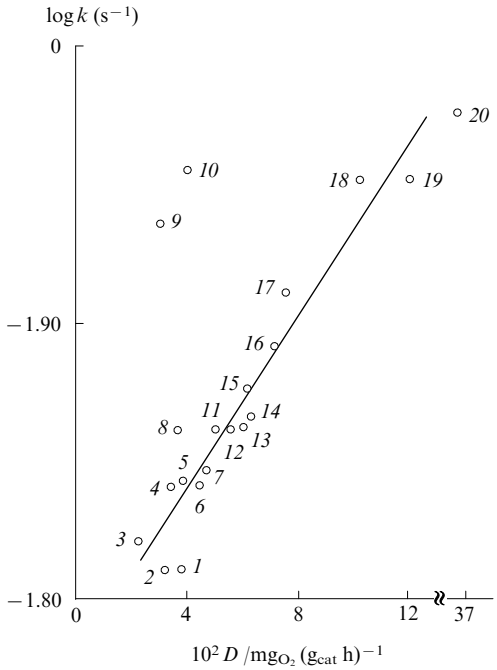


Figure 1. Correlation between the catalytic activity of the $K_3V_5M_{0.33}O_{14}$ melts in the oxidation of ethanol at 500 °C and specific desorption of oxygen from these melts at 600 °C.
M: (*1*) Ni, (*2*) Ba, (*3*) Cr, (*4*) Co, (*5*) Al, (*6*) none, (*7*) Ti, (*8*) Zn, (*9*) Fe, (*10*) Fe (V : Fe = 7), (*11*) Pb, (*12*) Sn, (*13*) Sb, (*14*) Bi, (*15*) Ag, (*16*) W, (*17*) B, (*18*) Mo, (*19*) Mn, (*20*) Cu.

the amount of MoO_3), which is thermodynamically more stable under these conditions.

A clear correlation between the catalytic activity of melts based on vanadium oxides in oxidative dehydrogenation of ethylbenzene and the content of vanadium +4 in the melts has been noted.[80] The rate of transformation of ethylbenzene into styrene on $K_2O-V_2O_5-V_2O_4$ melts was found to decrease with a decrease in the V_2O_5 concentration. The extrapolation to a zero rate shows the lack of activity for a catalyst with the composition 6 mass % V_2O_4, 69 mass % V_2O_5 and 25 mass % K_2O. In the phase diagram of the $K_2O-V_2O_5-V_2O_4$ system, this composition corresponds to the bronze $K_{(2+2x)}V_2O_{16}$ ($x = 0.35-0.45$)[89] the presence of which in solidified samples taken from the melt was proved by powder X-ray diffraction.[80] For solid-phase catalysts it was found[90] that the phase Ψ of the $K_2O-V_2O_5-V_2O_4$ system containing 3 mol % – 8 mol % V_2O_4 exhibits the lowest activity in the oxidation of *o*-xylene as compared with other formulations of the same system. In the oxidation of alcohols, the activity of the molten $K_2O-V_2O_5$ catalyst is governed by the $KV_4O_{(10.5-x)}$ concentration.[81,85] The activity of the solid catalyst with the same composition in the oxidation of naphthalene was also higher than the activity of other potassium vanadates.[91]

The similarity of action of a catalytic system in the solid or molten states can be revealed by comparing the reaction rates at temperatures above and below the catalyst melting point. The results obtained are useful for solving the problem concerning the role of the chemical composition and the solid surface in the catalysis.

The kinetic parameters for catalytic reactions proceeding on melts and on the solid phase have been compared by many researchers (see, for example, Refs 75, 85, 92–94). In particular, the activation energies of some oxidation reactions at temperatures below and above the catalyst melting points were determined.[75,85,92] Presumably, the invariable activation energy of the process on going through the melting point can serve as evidence for the predominant influence of the chemical composition of the catalyst rather than the pattern of its surface on the reaction rate. However, the decrease in the activation energy upon melting observed in some cases is attributable to the fact that the process occurs not only on the surface but also in the bulk of the molten catalyst. For example, oxidation of SO_2 to SO_3 on the $K_2S_2O_7-V_2O_5$ melt proceeds both on the melt surface and in the bulk, depending on the conditions, which was established in a study of the thickness of an 'operating' catalyst film.[76,92,95] This results in a more than twofold decrease in E_a for the reaction on melts compared with the reaction on the solid catalyst surface.[62] The activation energy also increases upon partial crystallisation of the melt.[76] High solubility of sulfur dioxide in the $K_2S_2O_7-V_2O_5$ melt was also proved.[75,76]

The decrease in the activation energy upon passing the catalyst melting point is not common to all the studied reactions. Thus the activation energy for elimination of HCl from alkyl chlorides is the same for catalysis by $ZnCl_2$ solid phase and melt,[93] which is explained by the fact that the process occurs only on the melt surface. Analogous data were obtained for oxidative dehydrogenation of ethylbenzene on the $KVO_3-V_2O_5$ catalyst applied onto alumina grains,[96] and also for benzene oxidation on vanadium oxide catalysts.[94]

A similar dependence of the activation energy on the catalyst aggregation state was found in the oxidation of hydrogen chloride on $CuCl_2$ melt.[38,97] On solidification of the molten catalyst, the activation energy of this reaction sharply increases.

Oxidation of naphthalene on the $K_2SO_4-V_2O_5$ melt has been investigated.[97] The activation energy for the reaction on the melt was found to be lower by 36 kJ mol^{-1} than that on the solid catalyst with the same composition. No data on the solubility of naphthalene in the melt of the given composition are available from the literature; however, according to calculations, molecules with sizes greater than the size of the benzene molecule (about 0.6 nm) are poorly soluble in such systems. For example, the solubility of naphthalene in potassium chloride melt was calculated to be 10^{-12} g-mol (cm^3 Pa)$^{-1}$ at 400 °C.[98] The solubility of CO_2 (the size of the molecule is ~0.3 nm) in the $Li_2CO_3-Na_2CO_3-K_2CO_3$ eutectic melt at 700 °C found experimentally equals 9.5×10^{-7} g-mol (cm^3 Pa)$^{-1}$ (Ref. 99). The enhanced solubility of CO_2 in alkali metal carbonate melts was attributed[99] to the formation of the dicarbonate ion:

$$CO_2 + CO_3^{2-} \longrightarrow C_2O_5^{2-}.$$

In the oxidation of naphthalene on the potassium–vanadium–sulfate melt, the rates of naphthalene consumption and oxygen adsorption are proportional to the surface area of the melt and do not depend on its volume.[97] Therefore, the decrease in the E_a for naphthalene oxidation upon passing of the catalyst from the solid to the molten state can hardly be attributed to occurrence of the reaction in the melt bulk.

The few kinetic data presented above were obtained for processes differing in the nature of the substrate, the composition of the catalyst and reaction conditions. The E_a values for the formation of acetaldehyde from ethanol on a number of molten

Table 1. Activation energy for the formation of acetaldehyde from ethanol on molten and solid catalysts.[85]

Catalyst composition (mol %)			T_m /K	E_a /kJ mol^{-1}	
K_2O	V_2O_5	M_xO_y		$T < T_m$	$T > T_m$
30.7	48.8	20.5 (MoO_3)	698	76	76
37.0	59.1	3.9 (NiO)	673	113	58
37.0	59.1	3.9 (Ag_2O)	673	91	94
35.6	56.8	7.6 (SnO_2)	683	118	85
37.0	59.1	3.9 (Sb_2O_5)	673	140	79
37.0	59.1	3.9 (Mn_2O_3)	668	80	80

and solid catalysts containing V_2O_5 and other transition metal oxide additives were determined [85] (Table 1). These data were obtained under identical conditions for catalysts with similar compositions; therefore, their comparison is more vivid than a comparison of the results reported by different authors. The activation energy of the reaction remains unchanged or increases on going from the melt to the solid phase. The different influence of transition of the catalyst through the melting point on E_a can hardly be attributed to the catalytic action of the bulk of the melt. It is unlikely that the addition of 4 mass % – 7 mass % of NiO, SnO_2 and Sb_2O_5 would sharply increase the solubility of ethanol in the $K_2O-V_2O_5$ melt, while the same amounts of molybdenum, silver and manganese oxides would not affect the solubility. The assumption that the mechanism of ethanol oxidation changes on passing from high to low temperatures (from 650 to 570 K) on some systems also appears doubtful in view of the fact that on other systems this mechanism is retained.

It is worth noting that the pattern of dependence of the activity of $K_3V_5O_{14}-MoO_3$ catalyst on the MoO_3 content (from 0 mol % to 60 mol %) in the ethanol oxidation is the same at 823 K (melt) and at 673 K (solid phase). Presumably, the structure of the catalyst active sites does not change significantly upon the melt solidification.

The results presented in Table 1 were obtained for catalysts in the solid and molten states. In this case, the possibility of melt solidification to give glasses cannot be ruled out. The structures of the molten and glassy catalysts are similar; therefore, their catalytic activity is the same. Raman and IR spectroscopic data show [100] that the local ordering is the same in both glassy and molten $ZnCl_2$, but differs from that in crystalline zinc chloride. The similarity of structures of glasses and melts for the $K_2SiO_5-KAlSi_3O_8$ systems was established [101] on the basis of Raman spectra. The conclusion concerning the identity of the structural units of the melts and 'quenched' glasses was also derived from the IR spectra of sodium metaphosphate.[102]

The results of X-ray diffraction studies of high-temperature melts led researchers [103] to conclusion that an increase in the temperature to a value 400 – 700 °C above the T_m changes only slightly the short-order parameters of the mutual arrangements of atoms.

In the case where cooling is accompanied by crystallisation of the system, the environment of the active sites and the distances between them can sharply change with respect to those in the liquid state. This might account for the difference in the activities of catalysts having the same composition in the solid and molten states. For example, in crystalline vanadium(V) oxide, according to the FT EXAFS X-ray absorption data, the V – O bond lengths are 0.16 and 0.19 nm, while after melting the bond lengths become equal to 0.18 nm.[104] Other researchers [105] have shown by X-ray scattering that amorphous V_2O_5 obtained by superfast cooling of the vanadium(V) oxide melt has a tetrahedral coordination with a V – O distance of 0.18 nm. The formation of either amorphous or crystalline product depends on the cooling rate of the melt. The cooling rate that is critical for the amorphisation of melts and the duration and temperature of incubation are determined by the difference between the ionic radii and the thermal conductivity of components.[106]

This phenomenon is responsible for the increase in the activity of crystalline silicate catalysts after the 'heat shock'. For increasing the activity, the catalyst is first heated at a rate of 0.5 – 560 K s^{-1} to 1200 °C, kept for 0.1 to 1200 s and rapidly cooled to 500 °C.[107, 108] A short heating of superconductor oxide compositions to a temperature of 1000 °C (above T_m) at a rate of ~2000 K min^{-1} followed by cooling at a rate of 100 K min^{-1} is also proposed in another study.[109]

The validity of assumptions that the structure of active sites and the distances between them are crucial for the catalyst activity could be verified by investigating the transition of the catalyst from the solid to the molten state: for all catalysts of the same type, the activation energy of the same reaction should decrease upon this transition. In addition, the dependence of E_a on the aggregation state of the system presented in Table 1 might change for the oxidation of other organic compounds on these catalysts. Unfortunately, no facts either supporting or disproving these assumptions are now available.

Thus, when working with molten catalysts, one can determine quickly and reliably the correlations between the structures of compounds present as catalyst components and the catalyst activity and to reproduce more precisely the definite ratios of the catalyst components, which is important for the search for conditions for selective formation of the target products.

V. Electrochemical control of the activity and selectivity of molten catalysts

Due to high electrical conductivity of molten metal oxides and salts, catalytic processes can be carried out under conditions of electrolysis.[110 – 113] The electrochemical treatment is especially topical for catalytic oxidation of organic compounds accompanied by a change in the oxidation state of transition metals in the catalyst. For example, V_2O_5 widely used as a component of oxidation catalysts is reduced to vanadium(IV) under the reaction conditions.[85, 110, 114 – 118] Vanadium(V) is regenerated ($V^{4+} \rightarrow V^{5+}$) under the action of oxygen present in the reaction mixture; as a rule, this is the rate-limiting step for the whole catalytic oxidation of organic compounds.[80, 92, 110, 119] It has been shown [80] that in the oxidation of ethylbenzene, the vanadium(IV) concentration in the molten $KVO_3-V_2O_5$ catalyst depends on the ratio of the partial pressures of oxygen and the hydrocarbon. The redox reactions in the melts containing vanadium oxides can also occur during electrolysis; by varying electrolysis parameters, one can obtain specified phases of vanadium oxide bronzes.[120] The catalytic activity of the vanadium oxide-based melts in the oxidation of organic compounds can be controlled by varying the redox potential of the medium.[121]

The changes in the equilibrium potential of the $K_2O-V_2O_5-M_xO_y$ melts depend on the amount of oxygen evolved from the melt,[83, 122, 123] which, in turn, depends on the rate constant for ethanol oxidation on these catalysts (Fig. 2). The electrochemical control of the catalyst activity includes the change in the redox potential of the medium and the shift of the equilibria in the system. The results of electrochemical studies provide grounds for predicting the catalytic activity of molten oxide – salt systems in the oxidation.

The effect of the redox potential of the $KVO_3-V_2O_5$ melt on the course of ethanol oxidation has been studied.[111 – 113] The changes in the redox (for acetaldehyde and CO_2) or acid – base (for ethylene) properties of the melt can be derived from the ratio of the products.

$$CH_3CH_2OH \rightarrow \begin{cases} CH_3CHO + H_2O \\ CO_2 + H_2O \\ CH_2{=}CH_2 + H_2O \end{cases}$$

In reality, all three reactions occur simultaneously giving rise also to by-products: C_2H_6, CO, CH_4, CH_3COOH.

The conversion and the ratio of the products of ethanol oxidation on melts containing 100 mass %, 90 mass % and 72 mass % of KVO_3 (823 K, molar ratio oxygen : ethanol = 1.5, contact time 0.5 s) depend on the electrode potential.

The dependence of the composition of ethanol oxidation products on the magnitude and sign of the working electrode potential indicates that the oxidation of ethanol under the conditions studied proceeds in the catalyst melt, and regeneration of the catalyst occurs upon electrochemical reactions on the electrodes. Thus, electrochemical processes yield mediators (electron carrier catalysts), which change the catalytic characteristics

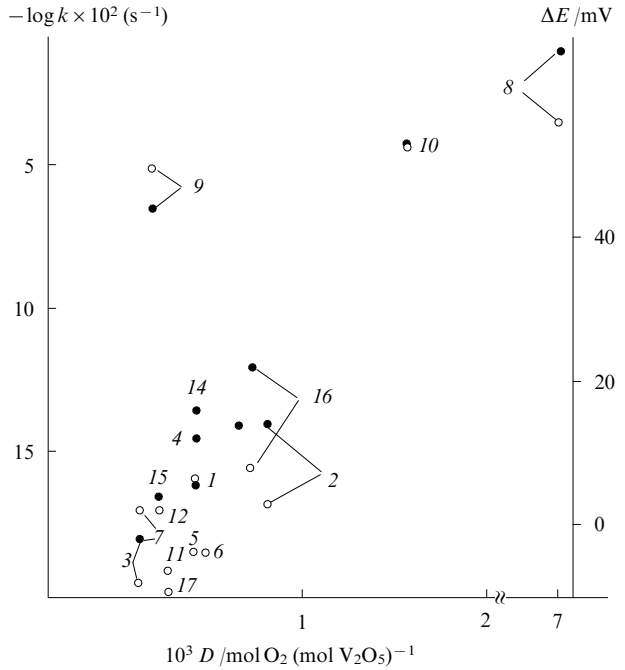


Figure 2. Dependences of the emf (ΔE) of the galvanic cell Pt, O_2|$K_3V_5O_{14}$||$K_3V_5O_{14}$ + M_xO_y|Pt, O_2 (open circles) and rate constant (at 500 °C) for ethanol oxidation (closed circles) *vs.* specific desorption (D) of oxygen from the melt for $K_3V_5O_{14}$ + M_xO_y systems with different chemical composition for M : V = 1 : 15.
Additive (M): (*1*) Al, (*2*) B, (*3*) Ba, (*4*) Bi, (*5*) Ca, (*6*) Co, (*7*) Cr, (*8*) Cu, (*9*) Fe, (*10*) Mn, (*11*) Ni, (*12*) Pb, (*13*) Sb, (*14*) Sn, (*15*) Ti, (*16*) W, (*17*) Zn.

of the melt, in particular, the reaction rate, selectivity and direction.[124]

The features of transformation of ethanol on the $K_3V_5O_{14}$ or NaOH melts and their solutions in the LiCl–KCl melt are determined by the nature, redox properties and the redox potential of the melt components.[112, 113, 115] Over the whole range of potentials studied (from +1 to −1 V), the conversion of ethanol and the yield of acetaldehyde upon electrolysis proved to be higher than in the case where the melt was not subjected to electrolysis.

VI. Oxidation of organic compounds

1. Partial oxidation

a. Alkanes and alkenes

The catalytic oxidation of methane yields ethylene (oxidative dimerisation of methane) and liquid hydrocarbons (ethylene oligomerisation). This process is important for practical purposes,[125–127] because its use on a commercial scale would provide conversion of natural gas into monomers and liquid motor fuel. However, despite the extensive research dealing with optimisation of this process, the conversion of methane in this reaction is only 3%–20%, the selectivity with respect to liquid hydrocarbons varies from 40% to 70%, and the yield of C_2 hydrocarbons does not exceed 25%.[125]

A number of patents[125, 128, 129] propose the use of melts as catalysts for the oxidative dimerisation of methane. The molten catalysts are composed of mixtures of metal oxides, alkali metal carbonates or sulfates and a reducible transition metal oxide (Mn, Sn, Sb, Pb, Bi, *etc.*). Transition metal oxides insoluble in the melt and not melting at the reaction temperature should better be fixed on a support that forms a suspension in the salt melt. For better dispersion of the initial gas mixture, particles inert with respect to the melt (the so-called immersed packing) can be added. When the melts are used, the methane conversion is carried out at a temperature of 500–1000 °C and at a pressure of 0.01–3 MPa. The methane to oxygen volume ratio in the initial mixture varies from 1 to 50. The methane conversion reaches 24%, while the selectivity with respect to higher hydrocarbons, equal to 57%, increases upon a decrease in the methane conversion, as the process follows a parallel-consecutive mechanism.[125]

Lithium carbonate melt was used as the catalyst of oxidative coupling of methane.[130] The experiments were carried out in a bubble column reactor. In order to keep lithium in the form of carbonate, CO_2 was added to the reaction mixture. It was found that on a Li_2CO_3–MgO melt (powdered magnesium oxide), the selectivity with respect to hydrocarbons markedly increased with temperature, while the yield of CO decreased with the amount of CO_2 remaining the same. The researchers note that no catalyst deactivation usual for fixed-bed reactors takes place in the bubble reactor.

The oxidative dimerisation of methane on a $Ba(OH)_2$ melt at a temperature of 800 °C and the ratio $CH_4 : O_2 = 3 : 1$ has been studied.[131] The conversion of methane reaches 20%, while the selectivity of formation of C_2 products equals 33%–38%. The authors assumed[131] that the process involves peroxide structures such as the superoxide ion O_2^{2-}, which are stabilised upon enhanced basicity of the medium due to dehydration of $Ba(OH)_2$. An increase in the basicity increases also the conversion of methane and the yield of C_2 hydrocarbons.

The oxidation of methane to give formaldehyde on a potassium nitrate melt has been studied.[132, 133] The process is catalysed most likely by NO species formed upon decomposition of potassium nitrate.

The oxidation of methane on sodium metaphosphate-based melts containing transition metal compounds was accompanied by reduction of Cr(VI), V(V) and Co(III) to lower oxidation states.[133] The concentration ratio of ^{18}O and ^{16}O isotopes in the melt on bubbling of air or a methane–air mixture was studied by mass spectrometry. The results led the authors to a conclusion that the oxidation of methane on a Na_3PO_3 melt containing d-metal ions involves both reversibly dissolved molecular oxygen (extensive oxidation of methane) and oxygen incorporated into an oxygenated metal complex (partial oxidation of methane).

Oxidation of methane with oxygen on a Na_2MoO_4 melt containing V_2O_5 and $K_4B_2O_7$ has been reported.[134] Despite the changes in the temperature, catalyst composition, the volume feed rate of the reaction mixture and the methane : oxygen ratio, high yield of formaldehyde could not be attained. Similar results have been obtained on an HPO_3 melt with iron oxide additives.[32] It is noteworthy that methane conversion and the selectivity of formation of partial oxidation products on solid catalysts are also low.[135]

The oxidation of alkanes and alkenes in molten media are widely studied in order to develop methods of preparation of commercially important monomers, buta-1,3-diene (divinyl) and 2-methylbuta-1,3-diene (isoprene). In the oxidative dehydrogenation, oxygen and its mixtures with hydrogen sulfide, ammonia and sulfur dioxide are used as hydrogen atom acceptors. Eutectic mixtures of metal chlorides, *viz.*, lithium and potassium, sodium and potassium, and magnesium and calcium chlorides serve as molten catalysts, which also contain up to 20 mass % of Group II, IV and VII metal chlorides as promoters.[136] Presumably,[133] the use of melts provides easy solution of the problem of heat withdrawal from the reaction zone owing to high thermal conductivity and melt circulation. The isothermal character of the process results in a higher selectivity with respect to the oxidative dehydrogenation products. For example, bubbling of a butane, hydrogen sulfide, air and ammonia mixture in a 1 : 4 : 2 : 8 molar ratio through molten lithium, potassium and manganese chlorides at 650 °C affords divinyl in a 52% yield, the total yield of divinyl and butenes being 70%.

The dependences of the degree of conversion of n-butane and selectivity of formation of C_4 alkenes on the nature of the melt have been studied.[28] The relatively high yields of alkenes are also

observed for molten sodium, potassium and cadmium chlorides (39.9 mass % Cd) or molten lithium and potassium chlorides (37.2 mass % K). The effect of addition of some other metal chlorides on the oxidative dehydrogenation of butane was studied. It was found that barium and manganese chloride additives decrease the conversion of n-butane but increase the yield of alkenes. The conversion of butane increases with an increase in the hydrogen sulfide concentration in the mixture. The selectivity with respect to C_4 alkenes is maximum at a hydrogen sulfide to butane molar ratio of four and decreases upon further increase in the amount of H_2S due to extensive oxidation of hydrocarbons and the formation of sulfur-containing compounds (mainly, thiophene) and elemental sulfur.

It has been proposed [137] to carry out the oxidative dehydrogenation of alkanes and alkylbenzenes on molten lithium and lead iodides at 500–650 °C in the presence of iodine for hydrocarbon oxidation in a two-chamber reactor. The process is described by the following reactions (for a divalent metal):

$$MI_2 + H_2O + 0.5\,O_2 \longrightarrow M(OH)_2 + I_2,$$

$$I_2 + C_nH_{2n+2} \longrightarrow C_nH_{2n} + 2\,HI,$$

$$2\,HI + M(OH)_2 \longrightarrow MI_2 + 2\,H_2O,$$

$$0.5\,O_2 + C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2O.$$

Molecular iodine is generated *in situ* upon the oxidation of metal iodides. Saturated hydrocarbons react with iodine to give the target products and HI, which is absorbed by the melt. The metal iodides present in the melt are reoxidised by oxygen in another compartment. This allows one to eliminate direct contact of the hydrocarbon with oxygen, which is a stronger oxidant than I_2 and thus to decrease the formation of complete oxidation products. The results of a study of hydrocarbon reactivity suggest a free radical mechanism of oxidative dehydrogenation of alkanes in the presence of iodine.[137] Despite the high conversions of hydrocarbons and the selectivity of alkene formation (for ethane, these values are ~80% and >90%, respectively), industrial implementation of this method is precluded by high cost, volatility and high corrosion activity of iodine.

The CuCl–KCl melt pre-saturated with air was used [138] to convert ethane into acetaldehyde in ~75% yield. On air bubbling, CuCl in the melt is oxidised to $CuO \cdot CuCl_2$. Apart from acetaldehyde, this reaction affords vinyl chloride.

The results of kinetic and mechanistic studies of the oxidative dehydrogenation of propane on a LiOH–LiI melt have been reported.[139] At 600 °C and a propane : air ratio of 1 : 2, the selectivity with respect to propylene is equal to ~75% and that with respect to benzene is 7%–14%. The reaction proceeds by a radical mechanism, the yield of propylene being mainly governed by the concentration ratio of the $(Pr^n)^{\bullet}$ and $(Pr^i)^{\bullet}$ radicals.

A patent [140] describes a process of preparation of acetaldehyde from C_2 hydrocarbons (ethane with ethylene impurity) on transition metal (Mn, Ni, Fe, Cu, Co, Cr) chloride melts in an air flow in the temperature range of 370–540 °C at a pressure of 0.1–1.5 MPa and a contact time from 1 to 60 s. At a <12% conversion of ethane, the selectivity with respect to acetaldehyde reaches 50%–80%.

The oxidation of propylene with oxygen on bubbling the reaction mixture through a KVO_3 melt in the temperature range of 500–650 °C has been studied.[141] Since the optimum temperature was lower than the melting point of the catalyst, the yield of aldehydes decreased with increasing temperature.

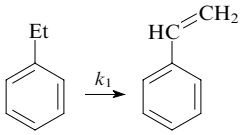
The partial oxidation of propane on melts representing complex mixtures of potassium, sodium, tungsten, molybdenum and vanadium oxides as well as B_2O_3, $K_2Cr_2O_7$ and NaOH has been studied.[142] It was found that, for some melts, the conversion of propane in a flow-type bubble reactor at 580–600 °C reaches 70%–90% at rather high yields of carbonyl compounds. $K_2Cr_2O_7$, NaOH and B_2O_3 melts proved inapplicable for this reaction due to irreversible changes in the catalyst, including reduction, transformation into carbonate and sublimation, respectively.

b. Aromatic hydrocarbons

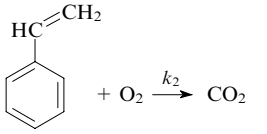
Oxidative dehydrogenation. Alkylbenzenes, for example, ethyl- and isopropylbenzenes are readily converted into the corresponding alkenylarenes on LiI and PbI_2 melts in the presence of iodine. At a high conversion of the starting hydrocarbon (up to 99%), the reaction selectivity reaches 95%.[137] Propylbenzene is converted into a mixture of allyl- and *cis*- and *trans*-propenylbenzenes. As the side chain of the hydrocarbon becomes longer, the fraction of the cracking products increases. Indeed, ethane and styrene are produced in almost equal amounts upon dehydrogenation of n-butylbenzene, while the major reaction product is naphthalene resulting from dehydrocyclisation (yield 72%).[137]

The oxidative dehydrogenation of ethylbenzene by oxygen on a molten KVO_3–V_2O_5 catalyst has been studied in most detail.[46, 56, 79, 80, 96] In particular, the activities of the catalyst in the molten and the solid states were compared and the mechanism of the process and its separate steps was studied.[56, 80, 96]

The kinetics of the oxidative dehydrogenation of ethylbenzene on an alumina-supported melt KVO_3–V_2O_5 (22 mol %) has been studied in a flow-type setup with a rotating catalyst, which ruled out the influence of mass transfer on the process rate.[96] This reaction gave styrene (St) and CO_2.



(1)



(2)

At temperatures of 450–550 °C and ethylbenzene and oxygen partial pressures of 3.7×10^{-3}–6.7×10^{-3} MPa and 3.3×10^{-3}–6.25×10^{-3} MPa, respectively, this process is described by the following kinetic equations:

$$V_{EtPh} = k_1[EtPh]^{1.12}[O_2]^{0.68},$$

$$V_{St} = k_1[EtPh]^{1.12}[O_2]^{0.68} - k_2[St]^{0.53}[O_2]^{0.53},$$

$$V_{CO_2} = k_2[St]^{0.53}[O_2]^{0.53},$$

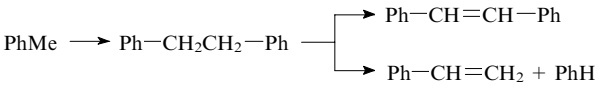
where V_{EtPh}, V_{St}, V_{CO_2} are the consumption rate of ethylbenzene and the formation rates of styrene and carbon dioxide, respectively, k_1 and k_2 are the rate constants for reactions (1) and (2).

It was found [80] that the accumulation of V_2O_4 in the melt is accompanied by the formation of a complex, inactive in oxidative dehydrogenation of ethylbenzene, with a composition corresponding to the bronze χ. From the temperature dependence of the rate constants for oxygen sorption in the KVO_3–V_2O_5 melt, it was found that oxygen is sorbed by the melt in two forms differing in the activation energies: 170.8 kJ mol^{-1} at 500–550 °C and 327.3 kJ mol^{-1} at 550–600 °C. In the temperature range of 500–550 °C, the removal of oxygen from the melt results in an increase in the catalyst activity in oxidative dehydrogenation of ethylbenzene.

Molten catalysts are suitable not only for the oxidation of organic compounds, but also for the synthesis of complex molecules containing more carbon atoms than the starting compound. Alkyl-substituted aromatic hydrocarbons (for example, toluene and xylenes) and heteroaromatic compounds [for example, picolines (methylpyridines)] form dimerisation products on alkali metal hydroxide melts.[143–145] These oxidative dehydrodimerisation reactions are currently the subject of extensive research,

because their mechanism resembles that of methane conversion into liquid hydrocarbons.

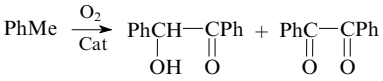
It was found [144] that the transformation of toluene on alkali metal hydroxide melts proceeds as follows:



The bibenzyl formation step is highly sensitive to the nature of the melt. The melts with high basicity catalyse efficiently dimerisation of toluene. The conversion of toluene on the NaOH and KOH melts and their mixtures is much higher than on the melt composed of a sodium and potassium chloride mixture. The conversion of toluene increases if up to 10 mass % of vanadium(V) or phosphorus(V) oxide is added to the alkali metal hydroxide melt.[144]

A study of the transformations of *o*-, *m*- and *p*-xylenes on a sodium hydroxide melt has shown that, apart from the dimerisation products, the reaction mixture contains the corresponding methylstyrenes.[122] The reactivities of the *meta*- and *para*-isomers were almost the same; the selectivity of formation of *m*- and *p*-methylstyrenes, respectively, from these isomers was also the same. The selectivity of formation of *o*-methylstyrene was almost four times lower due to steric effect on the dimerisation. This is consistent with the assumption that transformations of methylbenzenes (in particular, toluene and xylenes) involve the intermediate formation of benzyl radicals. Thus the enthalpies of formation of *meta*- and *para*-methyl-substituted benzyl radicals are 124 kJ mol^{-1} (Ref. 146) and the enthalpy of formation of unsubstituted benzyl radical is 188 kJ mol^{-1}. This is why the observed conversion of toluene is much lower than that of xylenes.

An increase in the catalyst acidity decreases the yield of dimers, while the yield of products of more extensive oxidation of hydrocarbons increases. An acidic catalyst, namely, $V_2O_5-K_2SO_4$ melt supported on SiO_2 converts toluene into oxygen-containing products, benzoin (2-hydroxy-1,2-diphenylethanone) and benzil (diphenylethanedione), in the presence of atmospheric oxygen at 400–450 °C.[144] No stilbene or bibenzyl were detected among the reaction products.

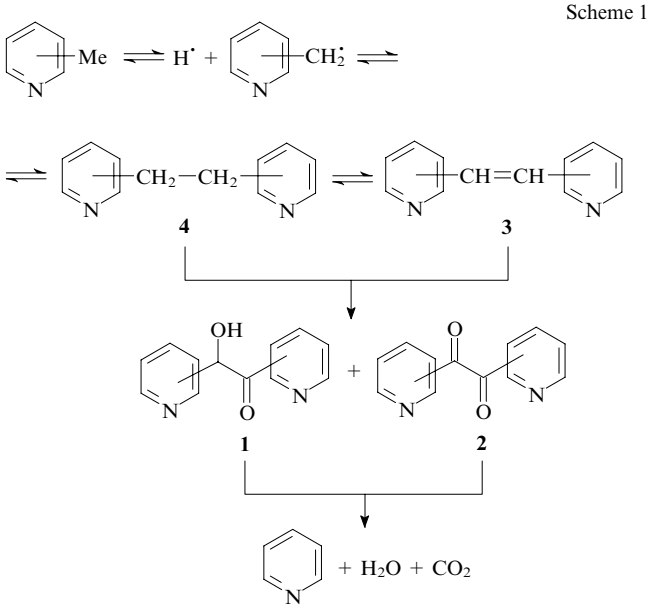


In a similar experiment, 2-methylpyridine was converted into 2-pyridoin (**1**) and 2,2′-pyridil (**2**). The proposed reaction mechanism involves the formation of a benzyl-type heterocyclic radical (Scheme 1).

On an eutectic melt $KVO_3-V_2O_5$ containing 12 mass % of MoO_3, toluene is converted into benzaldehyde and benzoic acid, and methylpyridines are converted into pyridine. In the presence of γ-Al_2O_3-supported K_2CO_3, KOH, KCl and KNO_3 catalysts, methylpyridines are converted into pyridine, CO_2 and water. No methylpyridine dimerisation products were detected. An increase in the temperature, content of air in the reaction mixture or the contact time results in higher yields of 1,2-dipyridylethylenes **3**. Note that the conversion of 3-methylpyridine is lower than that of 4-methylpyridine.[145]

As noted above, the mechanisms of dehydrodimerisation of methylbenzenes and methylpyridines on basic catalysts are similar to the mechanism of oxidative dimerisation of methane. In the latter reaction, the formation and dimerisation of radicals occur on the catalyst surface and subsequently the dimerisation products pass to the gas phase. Presumably, oxygen-containing products are formed from ethane **4** and ethylene **3** derivatives (see Scheme 1), which were found among the reaction products.

Scheme 1

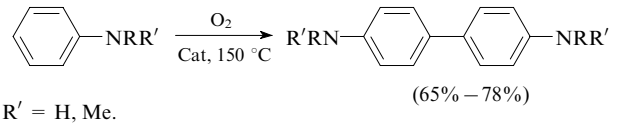


However, upon the toluene oxidation catalysed by $V_2O_5-K_2SO_4/SiO_2$, no toluene dimerisation products (bibenzyl or stilbene) were detected.

The difference between the composition of products formed on basic and acidic catalysts is due to the difference between the heats of adsorption of organic molecules on different surfaces. Higher heats of adsorption of aromatic and heteroaromatic molecules on acidic catalysts and, as a consequence, an increase in the contact time of the molecule with the catalyst account for more extensive oxidation of the dimerisation products of methylpyridines on the $V_2O_5-K_2SO_4/SiO_2$ catalyst.

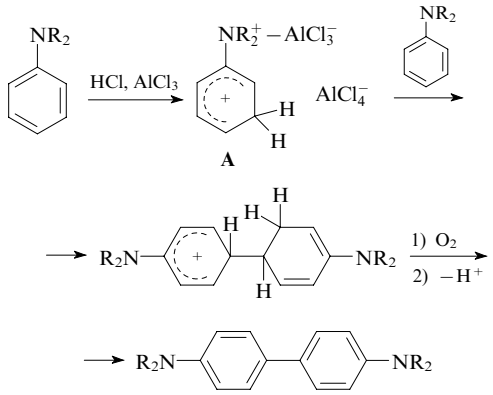
Apparently, the reaction of toluene or picolines with a basic catalyst involves the methyl groups (as in the case of oxidative dimerisation of methane), while in the case of acidic catalysts the substrate is adsorbed upon interaction of the catalyst with the aromatic π-system.

Dimerisation of aromatic amines PhNRR′ (R, R′ = H, Me) in a NaCl–KCl mixture of molten salts containing Lewis acids ($AlCl_3$ or $ZnCl_2$) to give benzidines has been studied with varied temperature, reaction time, reactant ratio and salt and gas phase compositions.[147]



R, R′ = H, Me.

The highest yield of benzidines was obtained at 150–200 °C in the presence of oxygen. If amine is used as a base, small amount of chlorobenzidines is formed, whereas the use of aniline hydrochlorides results in chlorinated derivatives as the major products (> 50%). The molecular chlorine formed *in situ* upon the oxidation of HCl serves as the chlorinating agent. The dimerisation of amines is markedly influenced by the nature of the Lewis acid, weaker acids such as $ZnCl_2$ or $SnCl_4$ being inefficient in this reaction. When two different amines are introduced in the reaction, a mixture of two symmetrical and one asymmetrical benzidines is formed. High regiospecificity of aniline dimerisation was noted: the reaction involves exclusively the *para*-position with respect to the amino group of the most stable σ-complex **A** formed upon the reaction of aniline with the Lewis acid.



Ammoxidation process. A number of US patents describe one-step synthesis of nitriles, amides, amines and other nitrogen-containing compounds by conjugated oxidation of organic compounds and ammonia on treatment with molecular oxygen in the gas phase on transition metal oxide melts.[61, 148–152]

For example, ammoxidation of propane on Mn, Co, Cr, Cu chloride and oxychloride melts yields acrylonitrile.[149] In the ammoxidation of the reaction mixture composed of propane, ammonia, air and oxygen on molten copper and potassium chlorides at a contact time of 4.8 s, the conversion of propane was 21%, while the acrylonitrile content in the products was 52.8%.

An eutectic $K_2O-V_2O_5$ mixture was proposed as the MC for ammoxidation.[61, 150–152] In this case, the process can be carried out in the absence of oxygen in the reaction mixture.[150] For example, a mixture of *m*-xylene and ammonia (molar ratio ~ 0.3) was converted into a mixture (mol %) of benzonitrile (9.49), tolunitrile (58.05) and isophthalonitrile (4.02). The conversion of *m*-xylene was 15.23%.[150] For implementing a continuous process, simultaneous melt regeneration under the action of atmospheric oxygen has been proposed.[61]

Benzaldehyde and phthalic anhydride. The oxidation of alkyl-aromatic hydrocarbons or naphthalene to give benzaldehyde or phthalic anhydride is accompanied by evolution of a large amount of heat, resulting in a sharp increase in the temperature in the reaction zone, which may induce thermal decomposition of the target products. In order to withdraw heat evolved upon toluene oxidation, Volynkin [153] proposed placing the suspended or floating catalyst, molybdenum oxide supported on ferrochrome grains or crushed MoO_3, into molten metals or alloys. The yield of benzaldehyde increased in this case to 20%–30% (based on the converted toluene). The product composition depended on the nature of the molten metal. In particular, the yield of benzaldehyde was higher when MoO_3 was suspended in an aluminium alloy. Meanwhile, molten lead was converted into lead oxide under the reaction conditions, and lead oxide catalysed further oxidation of benzaldehyde.

The oxidation of toluene to benzaldehyde on a series of molten catalysts consisting of vanadium or molybdenum oxide or their mixtures doped with sodium, potassium, copper, silver and tin oxides has been studied.[154] As the temperature of the liquid catalyst decreased from 670 to 550 °C, the yield of benzaldehyde sharply decreased, as on solid catalysts. Volynkin studied the oxidation of benzene and phenol into maleic anhydride using the same catalytic systems. The highest activity was found for the catalysts the electrical conductivity of which does not change much upon melt solidification.

The oxidation of *o*-xylene on the $K_2S_2O_7-K_2SO_4-V_2O_5$ melt using electrochemical methods has shown that potassium sulfate not only serves as the solvent for V_2O_5 but also as a reactant involved in the oxidation.[110] Regeneration is carried out using the V^{5+}/V^{4+} redox system, which serves as a 'relay switch' between the S^{6+}/S^{4+} and O^0/O^{2-} electrochemical pairs. The reduction of the sulfate by the hydrocarbon and the oxidation of vanadium(IV) by molecular oxygen may be the rate-limiting steps. The reaction orders for the overall oxidation process with respect to *o*-xylene and oxygen are 0.5 and 1.2, respectively. The activation energy is 79 kJ mol^{-1}, which almost coincides with the activation energy for the oxidation of *o*-xylene on solid vanadium catalysts reported in a review.[155]

The major naphthalene oxidation products in a molten eutectic mixture of K_2SO_4 and $K_2S_2O_7$ in the presence of V_2O_5 include phthalic and maleic anhydrides and naphthoquinone, the last-mentioned compound being an intermediate in the anhydride synthesis.[156, 157] For a constant air to naphthalene volume ratio, the yields of the products depend most appreciably on the V_2O_5 concentration.

c. Oxygen-containing organic compounds

The vapour-phase oxidation of C_1-C_4 aliphatic alcohols on heterogeneous catalysts is an industrial method for the production of carbonyl compounds. The oxidation of ethyl and propyl alcohols on $K_2O-V_2O_5$ (5 mass %–24 mass %) melts by a flow-type bubble method has been studied.[45, 158–162] As the catalyst operates and vanadium(IV) is being accumulated in the melt, the yield of aldehydes somewhat increases. After the equilibrium between the oxidation and vanadium reduction has been attained, the degree of conversion of the alcohol becomes constant.

Studies of the transformation of alcohols in an oxygen and nitrogen atmosphere have shown [159] that the qualitative composition of the products in these reactions is the same. It was thus concluded that the process follows a redox mechanism at the expense of oxygen atoms contained in the melt components. The presence of molecular oxygen in the reaction mixture promotes oxidative dehydrogenation, while the lack of oxygen is favourable for dehydration of the alcohol.

The oxidation of isopropyl alcohol on the $KVO_3-V_2O_5$ eutectic melt in a flow mode has been studied.[132, 163] On the basis of IR, ^{1}H NMR and EPR spectroscopic data, it was assumed that the alcohol is first oxidised by vanadium compounds and then the reduced forms of vanadium are reoxidised by molecular oxygen.[163]

$$V_2O_7^{4-} + \begin{matrix}Me\\ \diagdown\\ CH-OH\\ \diagup\\ Me\end{matrix} \rightleftharpoons \begin{matrix}Me\\ \diagdown\\ C=O\\ \diagup\\ Me\end{matrix} + V_2O_6^{4-} + H_2O,$$

$$V_2O_6^{4-} + 0.5\,O_2 \rightleftharpoons V_2O_7^{4-}.$$

The kinetics of the oxidation of n-butanol, n-butanal and n-butyl n-butyrate ($Pr^nCO_2Bu^n$) by chemically bound (lattice) oxygen of the melt with the empirical formula $K_{21}V_{35}O_{107}$ has been studied by pulse chromatography.[47] The studies were carried out in the temperature range of 430–550 °C in a bubble-type reactor with the bubbling height of the melt varying from 2 to 16 cm. The qualitative composition of the oxidation products proved to be the same for all three compounds; however, their ratios were substantially different.[47] Under the experimental conditions, the degree of conversion (x) of the initial compounds reached 80%–90% and the reaction slowed down with time. From the decrease in the process rate with an increase in x, it follows that the kinetic dependences are described by the Frost equation

$$k = \frac{1}{\tau}\log\frac{1}{1-x} - \frac{\beta x}{\tau}, \qquad (3)$$

where the parameter β (inhibition coefficient) is the slope of the straight line $(1/\tau)\log[1/(1-x)]$ *vs.* x/τ (τ is time).[164] A comparison of the k values calculated from Eqn (3) and the E_a values demonstrated that in terms of stability against oxidation, these compounds can be arranged in the sequence: butyl butyrate > butanal > butanol.

The oxidation of dimethyl ether to formaldehyde has been studied.[165–168] The reaction was carried out with oxygen by the flow method in the bubbling mode under atmospheric pressure in the temperature range of 400–500 °C. Melts consisting of Li, K, Na, Mo, V, P oxides (>60 formulations) were used as the catalysts. In the case of melts consisting of vanadium and molybdenum oxides promoted by alkali metal oxides and small amounts of other oxides at an optimum temperature of 420–440 °C, the conversion of dimethyl ether was 45%–54% and the selectivity with respect to the target product (formaldehyde) was 90%–99%. The latter value is much higher than the selectivity (70%–80%) obtained with solid oxide catalysts. A mechanism of the process has been proposed[165] according to which the ether reacts with molybdenum(VI), which results from oxidation of Mo(V) with vanadium pentoxide, with transfer of electrons to the molecular oxygen. The degree of conversion of dimethyl ether increases with an increase in the number of reduced Mo and V ions.

2. Extensive oxidation of organic compounds

The extensive catalytic oxidation and destruction of organic compounds on molten catalysts are of interest, first of all, as environmentally safe methods for waste utilisation. Other applications of these reactions are to produce heat[169] and generate synthesis gas by the reforming of carbon black residues (tar, coke) with steam.[65]

The oxidation of formaldehyde by atmospheric oxygen in molten KVO_3–KBr (20 mol %) (T_m = 491 °C) and LiCl–KCl (47 mol %) (T_m = 352 °C) eutectic mixtures in a flow-type bubble reactor has been studied in the 550–800 °C and 400–800 °C temperature ranges, respectively.[170] At 500 °C, the conversion of formaldehyde in the lithium and potassium chloride melt exceeds 32%, whereas in the gas phase (upon thermal decomposition), it reaches 98%. The oxidation in the salt melts is more mild, as follows from the high content of CO in the products; in the gas phase, the aldehyde is oxidised to CO_2.

Complete and fast oxidation of organic wastes to carbon dioxide and water is often carried out on MC containing vanadium pentoxide.[52] Unlike the known methods of incineration of organic compounds in the media of molten metals, glasses and slags,[171] the oxidation in the presence of V_2O_5-based melts can involve not only atmospheric oxygen, but also the oxygen from vanadium(V) oxide. Hence, it is possible to supply the organic feedstock and oxygen to the reactor separately or to carry out oxidation of organic compounds with vanadium pentoxide in one reactor zone and oxidation of the formed vanadium(IV) in another zone and thus to avoid the formation of explosive mixtures.[63]

The incineration of organic wastes on molten catalysts occurs at the interface. Chain oxidation cannot immediately propagate to the bulk of compounds fed to the reactor; therefore, the process occurs smoothly, under isothermal conditions, and the heat evolved during incineration is absorbed by the molten catalyst, which has a high heat capacity and high thermal conductivity. For example, the K_2O_5–V_2O_5 melt (with a V_2O_5 content of 40 mass % to 83 mass %) was used to oxidise wastes from the production of phthalic anhydride (tar)[52] and nitrobenzene,[52,53] while their incineration in usual furnaces is accompanied by explosion. For this reason, these wastes are usually diluted with water prior to combustion, which reduces the efficiency of using the supplied heat and requires combined fuel combustion.

Molten mixtures of inorganic salts, alkali metal oxides and transition metal oxides are also used as catalysts for the oxidation of carbon monoxide.[172]

The possibility of detoxification of mixed organic wastes containing radionuclides using catalytically active melts has been studied.[172–174] Depending on the nature and concentration, the radioactive metal ions can either be retained in the melt or precipitate, which leads to the necessity of melt regeneration.[173] The oxidation of model extractants containing uranium and plutonium in melts based on alkali metal carbonate has been carried out. Analysis of the effluent gases and the melt composition after completion of the experiments showed high efficiency of oxidation of organic components from radioactive wastes and complete absorption of phosphorus and radionuclides by the melt.[173]

A method for processing of solid urban wastes by fusion in a bubbled slag melt has been proposed.[66–68,175,176] Owing to the manufacture of special design reactors in which unique aerohydrodynamic conditions are produced, solid urban waste particles of various sizes are captured by melt drops, get into the high-temperature region and pass to the liquid (molten) state. Fast heating to a temperature above 1250 °C in ambient atmosphere promotes complete oxidation of organic compounds, and fast cooling of the gaseous products contemplated by the process flow diagram prevents the transformation of the feedstock components into dioxins.[177] This process flow diagram has passed pilot tests.[68]

a. Oxidation of organohalogen compounds

Let us consider extensive oxidation processes of organohalogen compounds and disposal of polymeric materials in more detail.

Molten catalysts are suitable for extensive oxidation of halogen-containing organic compounds,[122,178–180] while their oxidation on solid catalysts is complicated by the reactions of Cl_2 and HCl formed with components of the catalyst. The demand for an effective catalyst for the oxidation of halogen derivatives is due to the fact that the amount of such wastes reaches 1.5×10^6 tpy in Russia alone.[181] In addition, neutralisation of fluorine-containing compounds, which are components of chemical weapons now becomes a highly topical problem. Extensive oxidation on molten electrolytes is also used for this purpose. Thus exhaustive oxidation of sarin and soman in molten alkali metal salts was recommended in the USA for large-scale destruction of chemical agent stockpiles.[182,183] As a method for extermination of chemical weapon components, their catalytic destruction by metal melts at high temperature has been considered.[184]

An attempt to carry out extensive oxidation of polychlorobiphenyls on the molten KVO_3–V_2O_5 (60 mass %) catalyst supported on alumina in a flow-type tubular reactor at 600–750 °C has been undertaken.[185] The kinetic and energetic parameters of the process were determined. Carbon oxides and HCl were found to be the major products under these conditions.

Chlorodioxins present in wastes are neutralised by the reaction with molten salts[173] or by incineration after pre-treatment with molten metallic sodium.[186] Pilot plant tests carried out for a long period of time demonstrated the efficiency of oxidation of toxic organic compounds such as polychlorobiphenyls and tetrachloroethylene on melts.[173]

The company ATG Inc. (USA) developed an industrial process ensuring the destruction of halogen-containing wastes based on injection of the material to be treated into a sodium carbonate melt or melts of other similar salts.[187] At 650–700 °C, organohalogen components are destroyed to give non-toxic salts (*e.g.*, sodium chloride). It was noted[187] that this process is 30%–40% less expensive than the traditional method of waste disposal by incineration followed by gas scrubbing.

The company Molten Metal Technology Inc. (USA) proposed[188] performing neutralisation of toxic chlorine-containing wastes using a reactor containing a molten metal acting as the catalyst. The wastes are thus converted into utilisable products such as CO, HCl, ceramics, metallic alloys, and the exhaust gases of the reactor do not contain dioxins or chlorodibenzofurans.

Organohalogen compounds are also oxidised by treatment in a tank with a melt through which an oxygen-containing gas mixture is passed.[189] The melt contains an alkaline earth metal and an alkaline earth metal halide. The halogen formed upon extensive oxidation of wastes reacts with the metal; as a result, the alkaline earth metal halide is accumulated in the melt. This

method is rather expensive due to the high cost of the alkaline earth metal; however, its use for treatment of highly toxic substances seems to be cost-effective.

A method for treatment of exhaust gases from waste incinerators used for hazardous wastes (chlorinated organic compounds) has been proposed [190] and prepared for commercial use. The oxidation occurring on a molten eutectic mixture of Na, Li and K carbonates at 700–800 °C does not require any expensive construction materials. The effluent gases of the reactor contain less than 0.01% of the initial organic compounds.

The results of a study on extensive oxidation of halogen-containing compounds, *viz*., $CHCl_3$, CCl_4, and fluorocarbon fluid M-1, on molten catalysts I–X (Table 2) depending on the temperature, air feed rate and the nature of the substrate have been reported.[122, 179] It was shown that the extensive oxidation of CCl_4 and $CHCl_3$ on catalyst I yields CO_2, Cl_2 or HCl. However, these compounds are absent in the effluent gases, as they are absorbed by the melt. In the oxidation of CCl_4 and $CHCl_3$ on catalyst II, carbon dioxide appears in the effluent gases in the very beginning of the experiment, and its concentration gradually increases. The degrees of conversion of CCl_4 and $CHCl_3$ increase from ~99.0% at 350 °C (the ratio air : substrate = 1.8) to 100% at 400 °C. The conversion of chlorohydrocarbons reaches a maximum with a decrease in the load on the catalyst. The reactor effluent gases first contain no chlorine (it reacts with sodium and potassium hydroxides) but after long-term experiment, chlorine appears. Chloride anions were found in the spent catalysts. The presence of sodium and potassium chlorides in the catalysts was confirmed by powder X-ray diffraction data. In the case of catalyst IV (T_m = 710 °C), no complete oxidation of halohydrocarbons is observed even at 720 °C and the reaction products contain CO.

Table 2. Composition of the molten catalysts for extensive oxidation of halogen-containing compounds.[124, 174]

Catalyst	Primary melt	Additives (mass %)
I	NaOH–KOH (eut.)	–
II	NaOH–KOH (eut.)	V_2O_5 (10)
III	NaOH–KOH (eut.)	CuO (10)
IV	Na_2CO_3–K_2CO_3 (eut.)	–
V	Na_2CO_3–K_2CO_3 (eut.)	V_2O_5 (10)
VI	Na_2CO_3–K_2CO_3 (eut.)	V_2O_5 (15)
VII	LiCl–KCl (eut.)	–
VIII	LiCl–NaCl–KCl (eut.)	–
IX	LiCl–NaCl–KCl (eut.)	V_2O_5 (10)
X	LiCl–NaCl–KCl (eut.)	V_2O_5 (15)

When air is bubbled through melt IV containing V_2O_5 (10 mass %), the reactor effluent gases contain CO_2, resulting from thermocatalytic decomposition of carbonates. Thus, during catalyst preparation, CO_2 is removed due to the reaction of sodium and potassium carbonates with V_2O_5 and oxygen. However, CO_2 formed upon passing of CCl_4 and $CHCl_3$ vapours through the melt and their oxidation is absorbed by the melt. Hence, in the early period of catalyst operation, the CO_2 concentration in the reaction products is lower than that calculated theoretically, while at 650 °C, it approaches the calculated value.

The results of investigation of the oxidation of fluorohydrocarbon fluid M-1 on melts I, IV, VI–X have been reported.[122, 179] Upon saturation of these melts with atmospheric oxygen (without supply of the fluorohydrocarbon), evolution of chlorine from catalysts IX and X was noted. The oxidation of chloride ions to molecular chlorine by V_2O_5 and atmospheric oxygen attests to the possibility of melt regeneration.

It was shown that fluorine and hydrogen fluoride formed upon decomposition of fluid M-1 are absorbed by the melt. The best properties as regards extensive oxidation were found for the melt of sodium and potassium carbonates having the eutectic composition with the addition of 15 mass % of vanadium pentoxide. However, the chloride melt X containing 15 mass % of V_2O_5 showed better stability against fluoride ions and molecular fluorine. The transformation pathway of fluorinated fluid M-1 depends appreciably on the nature of the melt. In the case of melts IV and VIII, thermal decomposition of fluid M-1 and oxidation of the pyrolysis products by atmospheric oxygen take place. In the case of doping of alkali metal chloride or carbonate melts with vanadium pentoxide, which reacts with alkali metal ions and catalyses the formation of CO_2 from carbonates and the formation of molecular chlorine from chloride ions, fluorinated fluid M-1 undergoes catalytic oxidation.

It was shown by differential thermal, elemental and powder X-ray diffraction analyses [179] that the oxidation of halohydrocarbons on molten catalysts NaOH–KOH (eut.), Na_2CO_3–K_2CO_3 (eut.) or LiCl–NaCl–KCl (eut.) containing V_2O_5 affords an equilibrium mixture containing alkali metal hydroxides, carbonates, halides and vanadates and vanadium oxide bronzes, their ratio in the mixture depending on the partial pressures of the halogen, CO_2, water vapour and oxygen. Based on these studies, a catalyst for extensive oxidation of halogenated compounds stable against halogens was proposed, in particular a LiCl–NaCl–KCl (eut.) mixture containing 15 mass % of V_2O_5.

The process of gaseous chlorine evolution from melts has been described.[122, 191] The $NaCl$–V_2O_5 (5 mass %, 10 mass %, 20 mass %) and $NaCl$–$NaVO_3$ (13.4 mass %) systems were studied in an inert atmosphere and in the presence of atmospheric oxygen at 820 and 880 °C as molten catalysts for extensive oxidation of organohalogen compounds. The derivatograms of the samples obtained by fusing NaCl with 10 mass % of V_2O_5 in air or with continuous air supply to the melt at a rate of 2.5 litre h^{-1} exhibit endothermic effects corresponding to the melting points of NaCl (780 °C), the $NaVO_3$–$Na_2V_5O_{13.3}$ eutectics (525 °C) and sodium metavanadate (630 °C). The derivatogram of the $NaCl$–V_2O_5 (10 mass %) sample molten in air shows an endothermic effect indicating the presence of the NaV_6O_{15} bronze (670 °C). The derivatogram of a sample of the $NaVO_3$ melt recorded after bubbling CCl_4 (fed as a liquid at a rate of 2 ml h^{-1}) for 3 h and air (2.5 litre h^{-1}) through the melt contains minima corresponding to the melting points of $NaVO_3$ (630 °C) and NaCl (800 °C). The endothermic effect at 525 °C is due to melting of the $NaVO_3$–$Na_2V_5O_{13.3}$ eutectics. The $Na_2V_5O_{13.3}$ bronze results from the reaction of sodium metavanadate with chlorine formed upon oxidation of CCl_4. The mass of the catalyst samples does not change over the temperature range studied.

When air is bubbled through a NaCl melt at 820 °C, no molecular chlorine is evolved. Chloride ions might be oxidised with oxygen to give oxides, peroxides and superoxides, but the equilibrium constants of these reactions are low.[192] If V_2O_5 has been added to the NaCl melt, molecular chlorine does form, its amount increasing with an increase in the V_2O_5 concentration and with increasing temperature.

The initial reaction products formed in the $NaCl$–V_2O_5 system are oxide bronzes, β-type NaV_6O_{15} and κ-type $Na_2V_5O_{13,3}$:[193, 194]

$$2\,NaCl + 6\,V_2O_5 \rightleftharpoons 2\,NaV_6O_{15} + Cl_2, \quad (4)$$

$$5\,NaV_6O_{15} + 7\,NaCl + 2.4\,O_2 \rightleftharpoons \rightleftharpoons 6\,Na_2V_5O_{13.3} + 3.5\,Cl_2. \quad (5)$$

Then the $Na_2V_5O_{13.3}$ bronze is converted into $NaVO_3$:

$$Na_2V_5O_{13.3} + 3\,NaCl + 0.85\,O_2 \rightleftharpoons 5\,NaVO_3 + 1.5\,Cl_2. \quad (6)$$

The oxidation of chloride ions in an inert atmosphere is due to the redox reaction accompanied by partial reduction of vanadium(V) to vanadium(IV) to give the β-type NaV_6O_{15} bronze [reaction (4)].

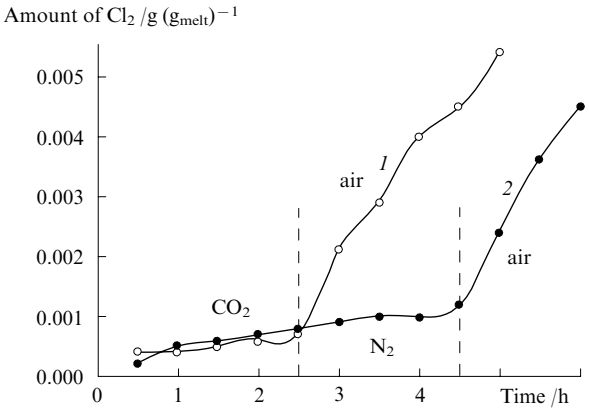


Figure 3. Kinetics of chlorine evolution from the NaCl + 10 mass % V_2O_5 melt depending on the nature of bubbled gas at 820 °C: (*1*) CO_2 then air, (*2*) N_2 then air. The gas feed rate is 2.5 litre h^{-1} (Ref. 117).

It has been found [191] that the amount of chlorine evolved upon bubbling of nitrogen or carbon dioxide through the $NaCl-V_2O_5$ (10 mass %) melt is the same and is much lower than that in the case of passing of atmospheric oxygen through this melt (the initial sections of the curves in Fig. 3). If the gas bubbled through the melt is replaced by air, the amount of the evolved chlorine sharply increases (see Fig. 3).

The dynamics of chlorine formation in the $NaCl-NaVO_3$ (13.4 mass %) melt upon bubbling of air (volume flow rate 2.5 litre h^{-1}) has been studied.[122] The concentrations of sodium metavanadate formed in this mixture and in the $NaCl-V_2O_5$ (10 mass %) system in the presence of air are the same in the case of complete transformation of V_2O_5 (Table 3). The reaction affords sodium divanadate. The amount of chlorine evolved in this case is minor and the rate constant for the reaction of $NaVO_3$ with NaCl is about two orders of magnitude lower than that for the formation of chlorine in the $NaCl-V_2O_5$ system. In an inert atmosphere (bubbling of pure CO_2), almost no chlorine is evolved.

Table 3. Rate constants for the oxidation of chloride ions according to reaction (4) for the $NaCl-V_2O_5$ systems.[122]

Air passing mode	Content of V_2O_5 (mass %)	T /°C	$10^4 k_1$ /s^{-1}
Bubbling	5	820	0.59 ± 0.03
Bubbling	10	820	0.79 ± 0.02
	10	880	1.31 ± 0.13
Surface	10	820	0.69 ± 0.03

Presumably, under these conditions, V_2O_5 is first converted into non-stoichiometric compounds corresponding in composition to vanadium oxide bronzes and then into more stable $NaVO_3$. Thus, equal rate constants for the oxidation of Cl^- with air bubbling though the $NaCl-V_2O_5$ systems suggest simultaneous existence and fast interconversion of vanadium-containing compounds.

The reactivity of vanadium compounds in the oxidation of Cl^- decreases in the sequence $V_2O_5 \gg NaV_6O_{15} \gg Na_2V_5O_{13.3} \gg NaVO_3$. Upon an increase in the temperature and partial pressures of oxygen and chlorine, the rate of transition of one species into another becomes higher than the oxidation rate of the chloride ion. Therefore, when using the $NaCl-V_2O_5$ system as the catalyst for extensive oxidation of chlorinated organic compounds, the catalyst activity can be controlled by varying the conditions of the process and the composition of the initial mixture.

The apparent activation energy for the oxidation of Cl^- in the $NaCl-NaV_6O_{15}-O_2$ system was determined. The relatively high value (109 kJ mol^{-1}) indicates that diffusion has a slight influence on the chlorine evolution.

The interactions in the $NaCl-M_xO_y$ (where M = Cu, Co, Cr, Mo, Sb) and NaCl–CuCl systems in air or nitrogen atmosphere were studied by differential thermal, powder X-ray diffraction and elemental analyses. The activity of these catalysts in the oxidation of chloride ions was found to depend on the nature of the metal oxide and to decrease in the sequence:[195] $CrO_3 > V_2O_5 > V_2O_5 + Sb_2O_5 > MoO_3 > Sb_2O_5 > Cr_2O_3 > Co_3O_4 > CuCl$.

In the absence of oxygen, the oxidation of chloride ions takes place in the reaction of sodium chloride with vanadium, chromium(VI) and molybdenum oxides. When the reaction mixture contains oxygen, metal oxides act as catalysts of the oxidation of chloride ions by oxygen; as a result, regular evolution of chlorine is observed.

The results of studies of chloride ion oxidation to chlorine indicate that one can select $NaCl-M_xO_y$ systems containing mixtures of transition metal oxides that would ensure that a rate of chlorine formation and evolution from the melt would be commensurable with the rate of chlorine supply from extensive oxidation of halohydrocarbons. Thus, these catalysts would also be suitable for the latter process.

b. Disposal of polymers

It has been proposed [71] to clean metal cord and fixtures from polymeric materials by extensive oxidation of the polymers (burning at 350–600 °C) in a molten catalyst with air bubbling through the melt. The NaOH–KOH melt with 5 mass % – 10 mass % of transition metal oxide added is used as the catalyst. The relatively low temperature of the process rules out the formation of nitrogen oxides and the catalytic oxidation of compounded rubber is not accompanied by evolution of gaseous organic compounds or soot. The metal wire is recovered from the processed wastes from reinforced hoses, where the polymers contain mixed rubbers, low density polyethylene, plasticisers (dibutyl phthalate, paraffin, rosin, *etc.*), or from cord debris obtained from waste automobile tyres by pressing,[196] where different amounts of compounded rubber could be present.

The rate of extensive oxidation of compounded rubber and polymeric materials depends on the amount and the nature of transition metal oxides added. The carbon dioxide formed upon the oxidation of polymers is partly absorbed by the melt, together with the sulfur (IV and VI) oxides formed upon oxidation of compounded rubber. This yields a mixture of salts. In the presence of atmospheric oxygen and water vapour, alkali metal carbonates present as components of the melt can partially decompose to give carbon dioxide; therefore, the spent catalyst represents a mixture of carbonates, sulfites and sulfates as well as transition metal salts; as a result, the melting point of the mixture increases.

VII. Conclusion

Analysis of the properties and possible applications of MC demonstrates that molten metals, metal oxides and salts can be successfully used as the media and the catalysts for various processes. Depending on the melt composition and the nature of the organic compound that reacts with the melt, this can function as a solvent, a chemical reagent or heterogeneous or homogeneous catalyst. The high rate of heterogeneous exchange of the components of a melt containing transition metal oxides with the gas-phase oxygen, the high thermal and electrical conductivities of these systems and the simplicity and reproducibility of the catalyst preparation stage and the activity parameters allow researchers to use molten oxides and salts for mechanistic studies of catalytic reactions and for establishing the composition–catalytic activity relationships. The physicochemical properties attest to advantages of molten catalysts over other types of catalysts, especially as

regards oxidation of organic compounds accompanied by substantial heat evolution, coking or formation of explosive mixtures.

The electrical conductivity of molten oxides and salts allows one to use electrochemical methods for increasing the catalytic activity; this enhances the reliability of operation of reactors in the case of violation of the organic compound to oxygen ratio.

Promising applications of molten electrolytes are those for treatment of exhaust gases and destruction of chemical production wastes. By varying the physicochemical properties of these systems over wide limits, it is possible to use diverse techniques and equipment for the treatment processes and separate and utilise compounds with complex chemical compositions and aggregation states present in the wastes.

Molten salts and oxides demonstrate high stability and capacity (the bulk of the melt rather than only the surface, as in the solid catalysts, is involved in operation) with respect to impurities, which are often poisonous for solid catalysts even when present in minor concentrations. Therefore, the starting compounds can be used without pretreatment and complex mixtures can also be processed using melts.

The use of melts based on alkali metal chlorides containing transition metal oxides, most often V_2O_5, appears to be promising for the oxidation of chlorine-containing organic compounds. Vanadium(V) oxide increases the catalytic activity and durability of melt performance and improves the heterogeneous exchange between the catalyst and oxygen; thus, it becomes possible to separate the zone for melt saturation with oxygen (catalyst regeneration) and the zone for oxidation of organic compounds. Besides, the addition of V_2O_5 increases the catalyst service life, as it favours the evolution of CO_2 and Cl_2 from the melt giving rise to an equilibrium mixture of K, Na, OH, CO_3, Cl and V ions in the reactor. The presence of V_2O_5 in the molten catalyst favours oxidation of aromatic hydrocarbons.

Molten catalysts can act as reagents with respect to the halogen evolved upon extensive oxidation of organic compounds; hence, trapping of toxic products by adsorbents is not required. According to published data,[173] burial of organohalogen compounds formed in the deactivation is more cost-effective than absorption of effluent gases in absorbing towers followed by neutralisation.

Due to the specific character of the catalysts and high cost of reactors used for the melt-catalysed oxidation, it is expedient to use this technique for combusting highly toxic wastes or wastes containing metals and halogens. Thus, it is better to design small-capacity units which can be combined into blocks if necessary. For destruction of highly toxic wastes, the incineration units can be placed into boxes and an additional treatment of the gaseous products formed can be provided.

Molten catalysts are promising systems for effective disposal of solid polymeric and metal polymeric wastes.

Thus, the prospects of development of this field are related to practical implementation of extensive oxidation and destruction of diverse wastes.

In conclusion, we would like to mention one more application of molten catalytic systems, which has not yet been practically implemented, namely, their use as solvents for metal complex catalysts of high-temperature processes such as dehydrogenation.[197]

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