A review of the catalytic oxidation activity of mixed and pure tin-antimony oxides: Part-I

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Abstract- This paper covers the extensive review of the work done on the catalytic oxidation characteristics of tin-antimony oxides which are excellent oxidative de-hydrogenating catalysts as Part-I, which is covering the work done till the year 1980 and Part-II would cover the work reported from the year1980 and onwards. The reported work on catalytic oxidation activity of catalysts has been discussed in the light of studies related to surface area, Temperature Programmed Desorption (T.P.D.), surface acidity, x-ray diffraction, Mössbauer effect keeping basic reaction of oxidation of methyl alcohol in focus.

Index Terms- Antimony, binary liquid solutions, catalytic oxidation, preferential adsorpotion, mixed and pure metal oxides, Mössbauer effect, review, surface excess oxygen, tin, T.P.D., Temperature programmed desorption

I.   INTRODUCTION

The concept of geometric and energetic heterogeneity of solid catalyst surfaces was introduced by Taylor [1,2] in 1925. Since then, the importance of heterogeneity in chemisorption and catalytic processes is well accepted. Catalytic activity is now invariably attributed to the surface coordinative unsaturation rather than the bulk properties of the solid. It is also well known that the occurrence of different crystallographic faces of edges of intersecting planes, steps, point defects and dislocations are taken into account, the coordination numbers of surface atoms may vary over wide ranges. The experimental evidence in general, indicates that the surface atom with lowest coordination number or highest valence unsaturation is the site responsible for highest valence unsaturation is the site responsible for highest activity. The low sensitivity versus valence unsaturation exhibited by some solids have also been successfully explained by various researches with the help of internal compensation effects [3] or surface reconstructions during the course of the reaction. The problem, however, does not appear to be well understood still [4]. Information regarding the effect of environments on the nature of the active sites has been reported by Cimino and Pepe [5,6], Stone and Vickerman [7] and Pepe and Stone [8]. They have reported that when a catalytically active ion such as Cr^{3+} is embedded in an inactive oxide matrix i.e. α-Al_2O_3, the oxides expose the cations to oxygen ions and hydroxyl group(s) often in the unusual coordination numbers. Thus, the surface coordinative unsaturation may be considered as the cause for the activity of the various surface sites. Similar information is available in the studies reported by many other workers as well [9-11]. A wide variety of potentially active single or multicentre sites may be present on the oxide catalyst surface. There may be sites that are distinct with respect to their chemical nature and there is a certain energy distribution for chemically equivalent sites. Thus, in heterogenous catalysis, a vital interest for study is the chemical nature of surface sites in general and information regarding catalytically active sites, in particular their energy distributions and their absolute umber per unit area. Independent knowledge of the chemical nature of an active site will provide an important and complementary information in addition to more easily accessible data on the behaviour of reactant. Many attempts have been made in correlating catalytic activity with electrical conductivity, magnetic permeability surface morphology, porosity and crystal geometry etc. With the help of a number of sophisticated instrumental methods of analysis such as thermal methods of analysis, micro-calorimetry, magnetic susceptibility, x-ray analysis, x-ray fluorescence (XRF) spectroscopy, low energy electron diffraction (LEED), transmission electron microscopy (TEM), scanning electron microscopy (SEM), infrared (IR) and ultra violet (UV) spectroscopy, field ion spectroscopy and Mössbauer spectroscopy etc. which have opened a new Vista in the field of catalytic research. Several reviews, articles and monographs [12-19] are available for updating the knowledge of the research done and being carried out in the field of catalysis.

Among the industrially important catalysts, the most common active components are the metal oxides. Balandin *et al* [20] have attempted to correlate the catalytic activities of the metal oxides with the position of the metal in the periodic table. Emmett [21] has made a classification of various metal oxides according to the type of catalytic reaction involved.

Of the numerous oxides, oxides of tin and antimony [22] you have become important, particularly because of the selective oxidation and the ammonoxidation of n-propane for the manufacture of acrolein and acrylonitrile. Similarly, tin and molybdenum oxides are very useful for the conversion of propylene to acetone, acrolein and acetic acid. The importance of tin-molybdenum oxide is further established by the fact that till 1970, the synthetic method of the selective formation of ketone [23] by one step oxidation of olefins was not reported except the oxidation using $PdCl_2$-$CuCl_2$ catalyst in aqueous medium [24]. These oxides i.e. tin-antimony and tin-molybdenum, form the subject of our studies. A brief review of the work is given below.

II.   CHARACTERIZATION OF SURFACES OF MIXED AND PURE METAL OXIDES

The surface of all the oxide catalysts is generally hydrated or hydroxylated. This may be due to the reaction with solution use in the preparation or through the reaction with atmospheric moisture. Water is lost in steps when the oxide samples are activated at different temperatures and it has been shown [25] that the water present is either as bulk water or in the surface hydroxyl form. Different forms of metal oxygen functional groups are left by surface hydroxyl groups when water is removed as a result of different activation temperatures [26].

Wakabayashi *et al* [27] have studied the effect of composition of the catalyst and the temperature of activation the colour and catalytic activity. Hernimann *et al* [28] investigated the relationship between the bulk and surface composition of tin and antimony oxide catalysts and oxidative dehydrogenation of 1-butane to butadiene in the light of calcination temperature. It was show that the specific activity for the formation of butadiene from 1-butene maybe directly related to the concentration of antimony cations at the surface. It was proposed that the isolated antimony cations surrounded entirely by Tin ions in nearest neighbour sites constituted and active site for the formation of butadiene. Lazukin *et al* [29] have reported the presence of Sb (III) and Sb(V) in solid solution in SnO_2.

On the basis of X- ray data, they have shown [27] that the colour of the catalyst was attributed to the formation of solid solutions. They also concluded that the formation of acrolein from propylene is closely connected with the formation of solid solution formed between Sn and Sb oxides. Trimm and Gabbay [22] have also shown that the oxidation of butene isomers to butadiene occurs over solid solutions of Sb_2O_5 in SnO_2, in which Sn^{4+} ions play an important role.

Goldin *et al* [30] have shown that catalytic oxidation of propylene to acrolein occurs over the SnO_2+Sb solid solution component and is attributed to a reaction of Sb^{5+} ions in octahedral coordination sites. The selectivity was shown to be affected by physical structure of the catalyst and shows a decrease with surface area.

Sala and Trifiro [31] have studied the effect of heating in solid state on the bulk and surface properties by spectroscopic and thermogravimetric methods and have concluded that Sb_2O_5 present on the surface makes the catalyst active for oxidizing and isomerization reactions. The oxidizing sides of Sb_2O_5 were attributed to the presence of double bond between antimony and oxygen atoms or to surface defects. Calcination was found to destroy the surface reactivity of pure oxides but not of the mixed ones. Roginskaya *et al* [32] suggested that transformation of Sb^{5+} to Sb^{3+} must be obtained. Lazukin *et al* [33] have studied the mixed oxides containing tin and antimony in 90: 10 to 10: 90 ratios. They have attributed the catalytic activity to the solid solution and no effect was noticed for the catalyst composition. Bakshi at al [34] have studied the catalytic oxidative dehydrogenation of n-butene and have reported optimal reactivity and selectivity for catalysts having atomic ratio Sn:Sb in the range of 1:1 to 1:4. Sala and Trifiro [35] investigated the relationship between structure and activity of antimony mixed oxides in 1-butene oxidation. It was proposed that the oxidative dehydrogenation properties of the catalysts are due to two: "gem", i.e. Sb^{5+}=O groups and that the role of second metal is to adsorb the gaseous oxygen to re-oxidize the reduced antimony ions. Free antimony oxides dispersed in mixed oxides exhibited reduction rate higher than pure antimony oxides. This property was found to be decreased by a high temperature calcination.

Trifiro *et al* [36-38] have studied the oxidative dehydrogenation and isomerization of n-butene and have attributed the catalytic activity to the presence of Sn at valence lower than 4 and attributed to deactivation observed during the oxidation reaction of low amount of reaction lattice oxygen in Sn-Sb oxides. Irving and Taylor [39] studied the acidic properties of mixed tin and antimony oxide catalyst in relation to the isomerization of olefins. They have shown that isomerization takes place at the Brönsted acid sites which acts as a source of protons. However, no relationship between surface acidity and oxidative activity was found.

Irving and Taylor [40] in other studies have proposed that dehydrogenation involved a π- allyl intermediate, while isomerisation occurred through carbonium Ion formation tin- antimony oxide. The conclusions of Boudeville *et al* [41] are in good agreement with that of Cross and Pyke [42] who also studied the XPS spectra of the surface composition of tin and antimony mixed oxide catalysts and have shown that, at elevated temperatures, the surface became rich in antimony composition.

Molybdenum based oxide catalyst has been studied by Chopra *et al* [43]. They have studied the effect of catalyst composition the H_2O_2 decomposition. Catalytic oxidation of olefins over oxide catalysts containing molybdenum were studied by Tan *et al* [44]. They selected Co_3O_4- MoO_3 and SnO_2-MoO_3 catalysts. The surface area of the Sn-

Mo oxides catalyst was 45.6 m²/g. Propylene was converted to acetone at 100- 160°C with more than 90% selectivity over SnO_2- MoO_3. Isobutene was converted to t- butyl alcohol and di- isobutene over SnO_2-MoO_3 and to α-methyl acrolein over Co_3O_4- MoO_3. The proposed that the active sites seemed to involve an acidic point which was formed by the combination of tin or Cobalt oxide with molybdenum oxide. Moro-Oka et al [23] found that Co_3O_4-MoO_3 was an excellent catalyst for the oxidation of propylene to acetone. They have also shown [45] that systems containing SnO_2, Cr_2O_3, NiO and Fe_2O_3 were also found to be effective for that reaction.

Buiten [46] has found that MoO_3 did not form a bulk compound with SnO_2. It could be found at the SnO_2 surface, which then exhibited a peculiar catalytic activity for the oxidation of propylene by molecular oxygen mainly to acetic acid along with acetone while pure SnO_2 oxidized propylene mainly to CO_2 and CO and a considerable portion was converted into acrolein. MoO_3 was found to be much less active. Buiten [46] prepared Sn-Mo catalyst by mixing SnO_2, MoO_3 and SiO_2 in desired ratio and activating at 450°C. X-ray examination did not indicate any compound formation. These results were supported by Doyle and Forbes [47]. On the other hand, Lazukin et al [48] activated the Sn-Mo catalyst at less than 600°C and reported that their catalyst contained solid solutions of MoO_3 in SnO_2 and the compound SnO_2. $2MoO_3$.

Moro-Oka et al [49,50] have studied the oxidation of propylene to acetone over molybdenum oxide with TiO_2, Fe_2O_3, Cr_2O_3, CrO_3, SnO_2, V_2O_5, NiO, CuO and ZnO. Of all the above mixed oxides, SnO_2-MoO_3 showed the highest activity for oxidation. X-ray, IR and Diffuse reflectance spectroscopic studies were made for Bi_2O_3. MoO_3 with effect of promoters such as $BiPO_4$, Fe_2O_3 and Cr_2O_3 by Batist et al [51]. A new compound was detected and was supposed to be responsible for the catalytic activity of Bi_2O_3.$3MoO_3$+Fe_2O_3.$3MoO_3$ catalyst for the conversion of butene to butadiene.

The surface and catalytic properties of mixed oxides have been a subject of a large number of studies. Vadekar and Pasternak [52] have reported that the efficiency of the hydrogenation catalysts is increased by the presence of hydrogen halides in the reacting gases. A patent of Imperial Chemical Industries. [53] mention that tin-antimony oxide catalyst gives higher yields in ammonoxidation of propylene in the presence of volatile halogen compound in the reacting gas. It may be due to an inorganic halogen compound on the surface of the catalyst. It has been shown that the activity and selectivity of the catalysts depend on the composition among other things [27, 29, 34].

The work of Maslyanskii and Bursian [54] and of Givaudon et al [55] on chromia-alumina catalyst implied that chromia contains adsorbed, or excess oxygen when oxidised. The surface excess oxygen was held responsible for the production of water as indicated by heat effects during oxidation- reduction cycle on chromium oxides by Dickinson [56]. The catalytic activity of certain metal oxides has been successfully correlated with their surface oxygen.

Mellor et al [57] have used KI oxidation to estimate the surface density and strength of oxidizing centres on silica-alumina catalysts. They concluded that salts interact strongly and directly with the oxidizing centres in silica-alumina catalysts and the anions compete successfully with water for adsorption. Flockhart and Pink [58] have also found that treating silica- alumina with salts with their activity for forming cation-radicals from perylene.

Uchijima et al [59] used potassium iodide solutions of pH between 7.5 and 11.5 to establish a distribution in the oxidation power of surface excess oxygen has been found to be a useful variable to represent the activities of various catalysts; for example, in the oxidation of ammonia on Nickle oxide, Cobalt oxide and manganese oxide catalysts [60]. The decomposition of hydrogen peroxide on Nickel oxide [61] and chromia catalysts [62-65] has revealed a good correlation between their catalytic activities and their amount of excess oxygen. Bielanski et al [66] and Weller and Voltz [67] have determined the surface excess oxygen by reduction with Cl^- or I^- ion in strongly acidic medium. Yoneda [68] proposed regional analysis and reported that the catalytic activities of some solid acids were duly represented by a linear combination of the acidic strength distribution of the catalysts. The quantitative correlation for excess oxygen distribution over oxides for an oxidation- reduction catalysts also discussed.

Alkhazov et al [69] have studied the isomerization normal molybdates and tin containing molybdates. On the basis of the results, it was suggested that the isomerizing capacity of a catalyst may be used to evaluate its acidic properties. They also proposed that the activity of the catalyst increased as the more electronegative metal was introduced. They also discussed the advantage of their methods for the determination of acidity over the methods proposed such as Hammett indicators [70] and those involving adsorption of ammonia and pyridine [71]. A clear relationship between the activity and acidity of a large group of oxide systems supported an earlier suggestion

[72] that the acidity of the catalyst under conditions for the catalytic oxidation of olefins can characterize their activity for the isomerization of butene. Formation of peroxo radicals on the tin oxide surface was detected by Hoof and Helden [73] during ESR studies. The role of surface acidic centres in the extensive oxidation of 1-butene over molybdenum oxide- based catalyst was studied by Forzatti *et al* [74]. They proposed that Brønsted sites were transformed into Lewis sites at high temperature.

Ai [75-80] has concluded that the catalytic activity is well interpreted in terms of the acid- base properties of the catalysts, such as in the case of many other V_2O_5 or MoO_3 containing catalyst. Ai [76] studied oxidation activity and acid-base properties of SnO_2-MoO_3 and SnO_2-P_2O_5 system. The acidities of the SnO_2-MoO_3 catalyst were dramatically high when the molybdenum content was in 32-60 atom % range and those of tin oxide rich (Mo < 20 atom%) and molybdenum oxide rich (Mo >80 atom %) catalysts were fairly low. The basicity remarkably enhanced by the introduction of small amount of MoO_3 (Mo <5 atom%). It was inferred that the catalysts are basic in the MoO_3 poor compositions.

Buiten [81] has proposed that reaction between propylene and acidic surface hydroxyl groups yield surface bonded isopropyl groups which constituted the intermediate species in the oxidation of propylene to acetone and acetic acid. Infrared measurements revealed that deuterium appears preferably in the methylene group (as was confirmed by Proton magnetic resonance measurement) and for the greater part in the cis-position with respect to methyl group.

III.   TEMPERATURE PROGRAMMED DESORPTION (T.P.D.) STUDIES

It is a well- accepted fact that the catalytic reactions occur on the active centres which are specific and thorough information is very necessary for the preparation of a good catalyst. Today many desorption techniques are available for obtaining the information about the active centres present on the surface. The important desorption methods used are Thermal Desorption, Electron Stimulated Desorption, Field Desorption, Mass spectrometry, Photon and phonon Desorption etc. The information about the surface concentration, stoichiometry and nature of the surface species can be obtained by these methods. The desorption process kinetics and surface reactions preceding desorption can be deduced and are of importance in understanding of the mechanism of catalytic processes. If the amount of the gas can be measured then surface analysis can be made, but equally important is the kinetic information which can be derived from the rate of desorption. The desorption rate is generally governed by Arrhenius (or Polanyi-Winger) equation,

$$-\frac{dn}{dt} = k_d n^x = v_x \exp\left(-\frac{E^+}{RT}\right) n^x$$

Where n is the surface concentration of the desorbing species per unit area, K_d the rate constant for desorption, "x" the order of desorption process, v_x the pre- exponential (or frequency factor) and E^+ the activation energy for desorption. Thus, the desorption rate is extremely temperature sensitive. A temperature programmed desorption method is in principle similar to flash- filament desorption method reviewed by Ehrlich [82]. However, it differs from it in several respects. In T.P.D. studies, information can be obtained for the conventional metal oxides catalysis in addition to metal catalysts. The conditions employed in T.P.D. studies are much more similar to those ordinarily used in the catalytic reaction than in the case with the flash-filament method. T.P.D. technique has been successfully employed for the study of active sites for olefin chemisorption by Amenomiya *et al* [83]. They studied temperature programmed desorption of ethylene from alumina surface and concluded that two types of active sites are present on the alumina surface for the chemisorption of ethylene. When higher olefins, such as propylene [84] and trans-butene-2 [85], were adsorbed on alumina and were evacuated at room temperature and then subjected to temperature- programmed desorption, a larger peak with a small shoulder on the high- temperature side was obtained. It was concluded that sufficient amount of physically adsorbed olefins was left on alumina, presumably because of their higher boiling points. Amenomiya and Cvetanovic [84,85] concluded that olefins are selectively adsorbed on the active sites rather than a random adsorption the whole surface. Ohno and Yasumori [86] also studied the T.P.D. of ethylene on γ- alumina. Amenomiya and Cvetanovic [87] found by T.P.D. technique that active sites of alumina developed sharply when the evacuation temperature was increased beyond 520°C. Amenomiya *et al* [88] demonstrated in a study of the polymerization of ethylene on alumina that T.P.D. is useful not only in identifying adsorbed states or active sites but may also help in understanding reaction mechanisms. T.P.D. technique is also useful in determining heats of desorption and surface heterogeneity. The values of heat of desorption of butene on alumina on site- I are in good agreement [85] with the values determined by

conventional desorption methods. The T.P.D. technique is also employed for calculating the activation energy of desorption. Amenomiya *et al* [89] studied the adsorption of ammonia on an alumina catalyst and its effect on the subsequent adsorption of ethylene was studied by flash- desorption technique. It was calculated that activation energy of desorption of ammonia increase from 7 to 18 kcal/mole as the surface coverage decreases from 29 to 1.5%. Finally, they concluded that the active sites for ethylene adsorption do not coincide with the highest energy sites for ammonia adsorption though they were within the distribution range for ammonia. Amenomiya *et al* [84,89] have shown that the peak shapes and desorption temperature peak maximum vary with the amounts of the adsorbed species for the systems propylene- alumina and ammonia- alumina respectively. From the values of T_M at different Q_i the surface coverage and the average activation energies of desorption E_d can be calculated as a function of surface coverage by using equation 2, if the corresponding pre-exponential factors are known.

$$2 \log T_M - \log \beta = \frac{E_d}{2.302 R T_M} + \log \left(\frac{E_d}{AR}\right) \text{-------(2)}$$

Where, T_M is peak maximum temperature

β = heating rate

R = Rydberg constant

E_d = Activation energy of desorption

A = pre- exponential factor.

T.P.D. techniques have been used in the study of surface reactions [88] where Amenomiya *et al* studied the polymerization and hydrogen- deuterium exchange of ethylene on alumina. They concluded that as polymerization proceeds the ethylene peak gradually decrease with the simultaneous increase of the product peak. The position of product peak coincides with that of the second peak in butene desorption. Also, as the reaction proceeds, the front edge of the product peak gradually extends to lower temperatures while the rear edge remains unchanged. Simultaneously, the rear edge of ethylene peak gradually recedes from the high- temperature side. Thus, two molecules of ethylene were polymerised to give butene. Hydrogenation of ethylene on alumina have been reported by several investigators [90-93] at relatively high temperature (between 120°C and 500°C). However, the reactions have been found to occur even at room temperature and T.P.D. technique was used to study the reaction by Amenomiya *et al* [94]. They studied the hydrogenation of ethylene on alumina at low temperature (-20°C to 90°C). The reaction was found to occur at room temperature. Two different types of active sites were found to be present on the surface of alumina for the hydrogenation of ethylene. These were the same sites which were previously found by the same authors to be responsible for chemisorption and polymerization of olefins. However, the hydrogenation was found to occur more readily on the active sites on which chemisorption was weaker while polymerization of ethylene took place preferably on the other site. The surface was found to be heterogeneous as the results of hydrogenation suggested. Rivin and Illinger [95] studied the chemisorption of acetone on carbon blacks by T.P.D. technique. They proposed that chemisorbed molecules were present in a mobile phase and underwent a loss of translational entropy prior to desorption. When acetone was desorbed from the surface only one peak was observed at about 200°C which was resolve by analogue curve generator in four peaks with maxima at 140, 180, 230 and 280°C respectively. The study was also extended to silica gel [96] and the peaks observed were again resolved into four component peaks. Kondo *et al* [97] studied T.P.D. of carbon dioxide on nickel oxide catalyst and the oxidation of carbon monoxide to obtain information on the surface heterogeneity of the catalyst. Two peaks of CO_2 were observed in 80°C-120°C and 300°C-370°C range, with the activation energies of desorption of 8 and 25-27 kcal/mole respectively. From the studies, it was concluded that nickel oxide surface has two kinds of active sites and that the oxidation of CO at low temperature takes place on the stronger sites, characterized by the higher temperature peak of CO_2, while the weaker sites were held responsible for the higher temperature reaction. It was also suggested that the stronger sites were composed of relatively labile and weakly bound oxygen atoms and the weaker sites of stable and strongly bound oxygen atoms. The chemisorbed state of oxygen on NiO was studied by Gay [98]. The T.P.D. study was carried out in vacuum when oxygen was adsorbed

at room temperature. T.P.D. study gave two major peaks, at about 70°C and 650°C-750°C respectively while at adsorption temperatures higher than 150°C another type of chemisorption characterized by a peak appearing at 320°C-360°C was obtained.

Desorption of some aliphatic alcohols (C_1- C_8) and fatty acids (C_1- C_5) on a rutile pigment surface was studied by Schreiber and Mackinnon [99]. They found that peak maximum temperatures were shifted to higher temperatures and as the boiling point of alcohol increased, all alcohols gave single peak of similar shape. However, the peak areas markedly decreased as the alkyl group became larger even after the areas were correlated for the sensitivity of detection. This was ascribed to steric barriers due to the adsorbate orientation on the surface. On this basis, the authors were able to calculate the average angle of inclination of the alkyl chain on the surface. Similar steric hindrance was also found for the fatty acids, but two desorption peaks were observed with formic and acetic acid at about 120°C and 290°C. The two peaks of formic acid on titanium dioxide were also observed by Munuera [100], who studied the mechanism of formic acid dehydration on titanium dioxide by I.R., T.P.D. and adsorption measurements during the reaction. Water on titanium dioxide was also investigated by T.P.D. The four peaks appeared at 250°C, 370°C, 400°C and 500°C respectively. From the results, it was concluded that the high temperature decomposition takes place through formate, whereas the low temperature reaction involves the formation of a protonated formic acid molecule. The adsorption of isopropyl alcohol on a zinc oxide catalyst by a T.P.D. technique was investigated by Kolboe [101]. By varying the experimental conditions, purposely such as very slow rate of N_2 (the carrier gas) and heating rate 4°C/min the obtained desorption spectrum indicated the existence of five different groups of adsorption sites. Further, the kinetics of dehydration of isopropyl alcohol on zinc oxide was explained by the same author [102]. Thermo-desorption of methanol, isopropanol, di-isopropyl ether and water were studied on alumina, and studies of benzene on nickel oxide- alumina were made by Yakerson *et al* [103]. They established multiple forms of adsorption and irreversible nature of chemisorption by studying chromatographically the thermo-desorption of methyl and isopropyl alcohols and di-isopropyl ether from alumina surface. On 40% NiO-Al_2O_3 benzene gave one symmetric peak at 190°C in T.P.D. carried out at a heating rate of 13.6°C/minute suggested that benzene was adsorbed in only one form. No decomposition occurred during adsorption and desorption. On 70% NiO-Al_2O_3 catalyst, however, two forms of adsorption were indicated by peaks appearing at 175°C and 321°C respectively. Thermo-desorption of oxygen from powdered transition metal oxide catalyst was studied by Halpern and Germain [104]. The spectra showed a small number of well resolved peaks. One, two or three states of binding were found for oxygen, each population of those states changed with preliminary treatment of the metal oxides. The oxides studied were TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, NiO and ZnO.

IV.   PREFERENTIAL ADSORPTION FROM BINARY LIQUID SOLUTIONS

Temperature programmed desorption technique provides the information about the types of active centres present on the oxide surfaces. Useful information about the nature of the active sites, and their specificity for the adsorption can be easily obtained by the study of the adsorption from carefully selected binary solutions.

Kipling [105], Everett [106], Puri *et al* [107-110], Schay and Nagy [111-114], Goodrich [115] and Aveyard [116], Suri and Ramakrishna [117-121] and Sandle *et al* [122] have contributed a lot on this subject.

It is understood that in adsorption studies from binary liquids, the distinction of soluble and solvent becomes arbitrary and both the solute and the solvent are considered to be also adsorbed and most probably both of these are adsorbed simultaneously. The adsorption isotherms obtained by plotting the change of concentration against the equilibrium concentration is a composite isotherm which is not a true adsorption isotherm of that component when change of concentration is taken into account. The significance of the composite isotherm is shown by deriving an equation to relate the preferential adsorption from a two- component mixture to the actual adsorption of each component. The derivation is based on the assumption that each component of the liquid mixture may be adsorbed at the interface.

When a weight "m" of a solid is brought into contact with n_o moles of a liquid mixture, the mole fraction of the liquid, changes by Δx_1^L with respect to component 1. This change in concentration is brought about by the transfer of n_1^S moles of component 1 and n_2^S moles of component 2 onto the surface of unit weight of the solid. At equilibrium the two components consisting of n_1 and n_2 number of moles remain liquid phase and results in mole fraction, x_1^L, with respect to component 1, the initial mole fraction having been x_o. Then by using the mass balance, the equation may be written as:

$$n_0 = n_1 + n_2 + n_1^S m + n_2^S m \quad \text{and}$$

$$x_0 = \frac{n_1 + n_1^S m}{n_0^-},$$

$$x_1^L = \frac{n_1}{n_1 + n_2}$$

$$1 - x_1^L = \frac{n_2}{n_1 + n_2}$$

$$\therefore \ x_1^L = (x_0 - x_1^L)$$

$$= \frac{n_1 + n_1^S m}{n_1 + n_2 + n_1^S m + n_2^S m} - \frac{n_1}{n_1 + n_2}$$

$$= \frac{n_1^2 + n_1 n_2 + n_1 n_1^S m + n_2 n_1^S m - n_1^2 - n_1 n_2 - n_1 n_1^S m - n_1 n_2^S m}{(n_1 + n_2)(n_1 + n_2 + n_1^S m + n_2^S m)}$$

$$= \frac{n_2 n_1^S m - n_1 n_2^S m}{(n_1 + n_2) n_0}$$

$$= \frac{n_0 \Delta x_1^L}{m} = n_1^S (1 - x_1^L) - n_2^S x_1^L$$

$$or \ \frac{n_0 \Delta x_1^L}{m} = n_1^S x_2^L - n_2^S x_1^L$$

Where $x_1{}^L$ and $x_2{}^L$ refer to the fractions of component 1 and 2 respectively. The liquid phase. The function $\frac{n_0 \Delta x_1^L}{m}$ has been plotted as "adsorption" to give composite isotherms which is however, being used most frequently [123]. The plot of $\Delta x_1{}^L$ measured experimentally against $x_1{}^L$ is the isotherm of concentration change for component 1 i.e., the composite isotherm. This isotherm shows which component is preferentially adsorbed. It has been stressed by many workers that the following factors were attribute to the preferential adsorption:

1. The nature and interaction between the molecules of the binary mixtures.
2. The mode of orientation of the adsorbed molecules at the surface.
3. The thickness of the adsorbed layer.
4. The nature of the solid adsorbent surface, the chemical nature of the surface is of prime importance.

The force field is such that preferential adsorption by a solid is appreciably greater than which occurs at other interfaces, but the extent and the sign of the selectivity vary considerably and this is evident when adsorption takes place from a mixture of polar and a relatively non-polar liquid. Alcohol was adsorbed preferentially on silica gel from alcohol and iso- octane [124] and from alcohol and benzene [125-128] mixtures.

In the absence of specific polar groups, the π- electrons of an aromatic system ensure that the aromatic compounds are adsorbed preferentially the corresponding aliphatic compound by polar solids [129-131]. Madan at all [132] have studied the adsorption from benzene and cyclohexane and have shown that the π- electrons cause the preferential adsorption of benzene on the tin oxide surface.

The effect of chemical, geometrical and steric factors was discussed by Zhdanov *et al* [133]. They have studied the benzene- n- hexane system on Linde Molecular Sieve 5A. The interaction between the π- electrons system of the benzene and the ionic lattice of the zeolite is so strong that the n-hexane is completely excluded virtually on the whole range of concentration. Change of temperature and pressures of adsorption from the completely miscible liquids affect the selectivity. The selectivity generally decreases with rise in temperature and with fall in temperature multilayer adsorption is likely to occur as the critical solution temperature is approached. Chopra [134] and Anand [135] have reported the effect of the change of temperature on the change of preference. The effect of pressure on adsorption is of little interest. However, it has been studied by Rosen [136] and shown that the adsorption of acetic acid by charcoal from aqueous solution increased slightly as the external pressure is increased from 1 to 2000 atmospheres. For this, no explanation was put forward.

Kipling [13], Everett [106,137], Schay-Nagy [111-114], Sircar and Myers and Larinov and Myers [138,139] have put forward the various models for the adsorption phenomenon.

It was proved by Winter [140] that surface heterogeneity in most of the oxide adsorbents is due to the surface oxygen present. Metal oxides prepared by precipitation method [25] have surface hydroxyl groups which on heating lose water and leave different metal oxygen groups which make the oxides non- stoichiometric and changed their adsorption behaviour.

Madan [141] performed the binary liquid adsorption tin oxide gel and tin- oxide precipitates. It was reported that both the tin oxide gel and precipitates preferred alcohol from alcohol- hydrocarbon mixtures which was attributed to acidic nature of oxides and the presence of hydroxyl groups on their surfaces. The surface of the tin oxide precipitate had adsorbed layer which was half molecule thick indicating that the surface has been partially covered while the thickness of the adsorbed layer on tin oxide gel was multimolecular in nature. This was attributed to the reason that tin oxide gel surface had hydroxyl groups profusely on its surface while the extent of abundance on tin- oxide precipitate was lesser. It was also shown [142] that powdered solids have cracks, crevices which result in the formation of a large number of edges and corners as compared to the plane surface. The crevices and cracks hold the physically bonded molecules, more energetically, then the plane surfaces. Surfaces are generally rich in impurities thus chemical heterogeneity is introduced and consequently the adsorption behaviour is changed. In the case of homogeneous surfaces, which can adsorb one component strongly, a U-shaped composite isotherm is obtained. S-shaped composite isotherms are obtained in the case of heterogeneous surfaces, which have affinity for the adsorption of both compounds. Thermodynamic properties of the binary liquid mixtures have also been used to predict the preferentially adsorbed component. Komorov and Ermolenko *et al* [143] have inferred that if the solutions show negative deviation from ideality, the component present in excess, is selectively adsorbed; if the solution shows positive deviation the component present in lower concentration is selectively adsorbed. This was attributed to the escaping tendency of the component in the liquid mixture, especially when it is present in small concentrations thus S-type adsorption isotherms were obtained. A number of workers [144,145] have investigated the effect of porosity on the adsorption of binary liquids. It was inferred that higher the porosity, higher the extent of absorption of the liquid. The effect of hydrogen bonding between the solid and the adsorbent or between the two components of the liquid affect the preference of absorption [146-148].

The literature survey clearly indicates that careful study of absorption from binary solution can provide very useful information about the nature of the surface and the surface-active centres.

V.   THE MÖSSBAUER EFFECT

R.L. Mössbauer first reported the phenomenon in 1958 [149-151]. By Mössbauer effect, it was found possible to evaluate the electron density at each Mössbauer nucleus, which is related to valency of the atom, and to examine the crystal field produced by the neighbouring atoms. Because of the diversity in the applications of Mössbauer spectroscopy the literature is scattered throughout the journals of different disciplines. The literature coverage in "Mössbauer Effect Data Index" is very useful for workers in this field [152,153]. The literature regarding the interest of catalytic chemists has been summarised in recent reviews [154-165] and several other monographs [166,167].

The [119m]Sn Mössbauer spectra of some inorganic compounds and twenty alloys are given by Hayes [168]. The parameters which are of direct chemical interest such as the isomer shift and the quadrupole splitting are discussed.

Goldanskii [169] has reported that in case of SnO_2 a polymeric structure exists in which the oxygen forms a distorted octahedron around the metal atom. Herber and Spijkerman [170] have suggested that the small quadrupole splitting observed in this compound arises from this distortion as well as an additional twinning deformation of the octahedron of oxygen ions that surround the tin ion. Mössbauer spectra of a series of molecular Tin (II) oxides, isolated in solid nitrogen at 5K were measured by Bos *et al* [171] and found that for SnO, the Sn 5s population is only slightly less than 2, and predicted a point on the isomer shift against electron density scale in support of that previously obtained from Sn atoms. Donaldson *et al* [172] have reported 119 Sn Mössbauer spectra of the precipitates, obtained when the pH of mixed Sn(II)–Sn(IV) solution was raised. Fabrichnyi *et al* [173] investigated the phase transition of VO_2 doped with 0.16 atom % Sn^{4+} by Mössbauer spectroscopy of [119]Sn and hyperfine magnetic fields were observed on [119]Sn nuclei below transition temperature. The tin- 119 Mössbauer studies were extended to iron, manganese and cobalt oxides by Sekizawa *et al* [174]. The tin-119 Mössbauer spectroscopy was also applied to the study of VO_2, a compound in which phase transition takes place at 340 K by

Fabrichnyi *et al* [175]. The Mössbauer spectrum consisted of a single line with a positive chemical shift with respect to the emission line of $BaSnO_3$. They assumed that addition of tin, because of substitution by Sn^{4+} of V^{4+}, liberates some V spins which can form antiferromagnetic pairs and magnetically ordered clusters in the structure of low temperature VO_2. The Mössbauer spectrum for 119 Sn^{4+} antiferromagnetic Cr_2O_3 was investigated by Miterofanov *et al* [176]. It had same structure as α-Fe_2O_3, but different from it in the lower value of magnetic moment of the cations. The activity of mixed lead oxide PbO_2-MO_2 (M=, Ti, Zr) catalyst in catalytic oxidation of propylene by NO was reported by Plachinda and Bllourov [177]. The activity was dependent on the bond energy of the oxidizing agent NO with the catalytic surface. The isomer shifts and the line widths were given for the Mössbauer spectra of the Sn^{4+} in Pb-SnO, SnO_2 and Pb-Ti-O (containing 3% SnO_2) catalysts. The ^{119}Sn Mössbauer spectroscopic studies made by Thornton and Harrison [178] confirmed the partial reduction of the Sn (VI) oxide to Sn (II) species when carbonate species were formed over hydroxylated tin oxide when carbon dioxide was adsorbed over it in the range 320- 618 K. Saraswat *et al* [179] made Mössbauer resonance studies to rule out the formation of any form of known oxyhydroxide in ferric oxide hydrate gel. A multicomponent molybdate catalyst was studied by Prasad Rao and Menon [180] using Mössbauer spectroscopy with ^{57}Co as a source. After use the valency of iron in $Fe_2(MoO_4)_3$ and $FeMoO_4$ reported was +3 and +2 respectively.

Antimony-121 spectra of U-Sb oxides are reported by Birchall and Sleight [181]. The antimony-121 Mössbauer investigations on Sn-Sb were also reported by Suzdalev *et al* [182].

Birchall *et al* [183] investigated the $Sn_{1-x}Sb_xO_2$ system by Mössbauer spectroscopy by means of ^{119}Sn and ^{121}Sb. The presence of an unresolved quadrupole splitting was confirmed in SnO_2. The oxidation states of Sn and Sb found were IV and V respectively. It was also reported that as the antimony content increases, the ^{119}Sn isomer shift and electron density at the tin nucleus is also increased, as expected, for a conduction band composed largely of Sn 5S orbitals. Portefaix *et al* [184] investigated mixed oxides of tin and antimony by Mössbauer spectroscopy as a function of function of composition and firing temperature. They found that at low calcination temperatures antimony was present as Sb^{5+} dissolved in the SnO_2 lattice at 5 atoms % antimony and a mixture of Sb^{5+} and Sb^{3+} at higher concentrations. They also reported that only small variations of the nuclear Gamma ray parameters were observed up to antimony content of 10%. They did not observe any unreduced species. Boudeville *et al* [41] have also reported in the Mössbauer studies performed on their samples that tin underwent no detectable reduction due to charge compensation resulting from antimony (V) incorporation into the tin oxide matrix.

In the light of solid solution study Karasev *et al* [185] investigated SnO_2-MoO_3 system. The absorber was maintained at 78 and 300 K. The isomer shift with respect to SnO_2 at 300 K reported was 0.00 mm/sec. The tin-119 Mössbauer parameters of MoO_3, SnO_2, Cr_2O_3, V_2O_5, NiO with tin oxide were also reported by Karasev *et al* [186].

Skalkina *et al* [187] found that a correlation exists between the Mössbauer parameters, for example, isomer shift and quadrupole splitting vs. catalytic activity of different catalysts, such as Fe (III) and Sn (IV) oxides with the oxides of molybdenum, antimony and chromium for oxidative ammonolysis of propylene. It was concluded that the immediate surrounding of iron or tin ions in the catalysts determine the selectivity of the catalyst in the reaction. The values of quadrupole splitting for SnO_2-MoO_3, SnO_2-Sb_2O_4 and SnO_2-Fe_2O_3 catalysts system reported were 2.04, 1.92 and 2.12 mm/sec respectively. Firsova *et al* [188] in their studies reported that Mössbauer spectroscopy proved that propylene and acrolein form surface compounds during chemisorption Sn-Mo-O films. The compounds are bound to the tin ions via oxygen causing the reduction of originally tin (IV) to tin (II). They reported that since an analogous reduction of tin (IV) is not observed during an adsorption of propylene and acrolein on pure tin oxide, so they presumed that the presence of molybdenum ions was responsible for the observed phenomenon.

Berry and Maddock [189] also reported the tin-119 Mössbauer investigation $Sn_{1-x}Sb_xO_2$ (x = 0.01- 0.10) system calcined at 600°C. The Mössbauer parameters constantly and steadily departed from those of stannic oxide but provided no localized tin (II).

VI.   CATALYTIC OXIDATION STUDIES

Oxidation of methanol over mixed oxides has been a subject of several investigations. A number of workers have tried the air-methanol oxidation to formaldehyde over MoO_3-Fe_2O_3, MoO_3-V_2O_5, MoO_3-Cr_2O_3 based metal oxide combinations and other catalysts [190-203]. Effort has been made to understand the exact route for the oxidation of methanol. The nature of active sites on the Fe_2O_3-MoO_3 catalyst for the methanol oxidation is studied by Jirů *et al* [192]. The effect of water on the catalytic oxidation of methanol to formaldehyde was studied by Pernicone

et al [204]. They inferred that water is more basic than methanol and this gets adsorbed over catalyst and inhibits the reaction.

Greco and Soldano [205] and Boreskov *et al* [206] used $Fe_2(MoO_4)_3$ with MoO_3 to oxidize methanol to formaldehyde. The nature of the active component in Fe_2O_3-MoO_3 catalyst was investigated by Trifiro *et al* [207] and concluded that ferric molybdate is the most reactive component. It was proposed that the iron in ferric molybdate seems to act as the transfer agent of oxygen and water between the surface and the gas phase. X-ray structure study of MoO_3- $Fe_2(MoO_4)_3$ catalyst used for or methanol oxidation was made by Fagherazzi and Pernicone [208]. The oxidation of methanol on molybdenum trioxide, with its lattice oxygen only, was investigated by Novakova *et al* [209]. The change of oxidation mechanism due to lowering of the valence of Mo^{6+} to Mo^{4+} was suggested. Oxidation of methanol in gaseous phase and in the presence of oxygen to formaldehyde was studied by Boreskov [210]. Formation of CO was explained as a result of consecutive reaction. No O_2 or H_2 were found in gaseous product which were attributed to the non- existence of dehydrogenation step. The reactivity of lattice oxygen and catalytic activity of MoO_3 as oxidation catalyst were correlated according to the strength of lattice oxygen bond [210-213].
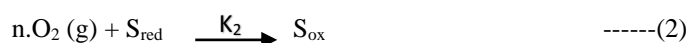
The importance of spinel formation of some mixed oxide catalysts involved in methanol synthesis stressed [214, 215]. The oxidation of methanol on pure Fe_2O_3 at 220°C was compared with the oxidation of methanol on MoO_3 and $Mo^{6+}Fe^{3+}O$ by Novakova *et al* [199]. The mechanism of methanol oxidation to formaldehyde over MoO_3-$Fe_2(MoO_4)_3$ catalyst was investigated kinetically by Pernicone *et al* [198]. Water inhibited the reaction rate. The rate determining step was proposed to be the desorption of the products. Kinetics of the vapour phase oxidation of methyl alcohol on V_2O_5-MoO_3 catalyst was studied by Mann and Dosi [202] between 250 and 530°C. The maximum yield (more than 90%) of formaldehyde (100% selectivity) was obtained at 466°C containing 8% methanol in the feed and rate expression was deduced. Tarama *et al* [216] studied the structure of the catalyst of V_2O_5-MoO_3 by X-ray, infrared, ESR and magnetic susceptibility measurements and found that MoO_3 had promotional action on V_2O_5 for oxidation reaction. The investigations of catalytic activities of V_2O_5- NiO, V_2O_5-Fe_2O_3 and V_2O_5 – Cr_2O_4 systems in the reactions of methanol oxidation to formaldehyde showed much higher selectivities for mixed oxides than pure oxides [203]. The highest yield for formaldehyde was obtained for catalysts with atomic ratios V/Me = 1. Infrared spectra were taken of the 1:1 catalyst before and after 2 hours of methanol oxidation at 410°C and showed different stabilities of V=O bond. The resulting structure modifications were most significant in the Me-O bond region. Bliznakov *et al* [217] studied tungstates of metals of the IV period with regard to their catalytic activity of methanol oxidation to formaldehyde. The highest reactivity was found for ferric tungstates; however, their reactivity was much lower than that of ferric molybdates. Partial oxidation of methanol in iron- molybdenum oxide catalyst was studied by Edwards *et al* [218]. The results suggested that OCH_3 on the surface play an important role in the reaction sequence.

Ai [219-224] studied the following oxides:

MoO_3-TiO_2, MoO_3-Fe_2O_3, MoO_3-SnO_2, MoO_3-P_2O_5, MoO_3-Bi_2O_3, P_2O_5, V_2O_5-MoO_3, WO_3 and V_2O_5 based oxides, SnO_2-K_2O_3, Co_3O_4-K_2O, Bi_2O_3-X_nO_m (X = P, Mo, W, V and S). An attempt was made to correlate the catalytic activity with the surface activity but no clear relationship is observed. Ai [219] also observed that Sn/Mo = (70/30) is highly acidic and, as a result, very active in the oxidation of methanol, but catalyses the formation of formic acid and methyl formate. It was considered that when the acidic property of a catalyst is too high, the formaldehyde product, which is an electron- donating (basic) compound, is activated by the acidic sites and, then oxidized to formic acid. A mechanism as shown below was given by Ai [219] for the oxidation of methanol to formic acid and CO_2:
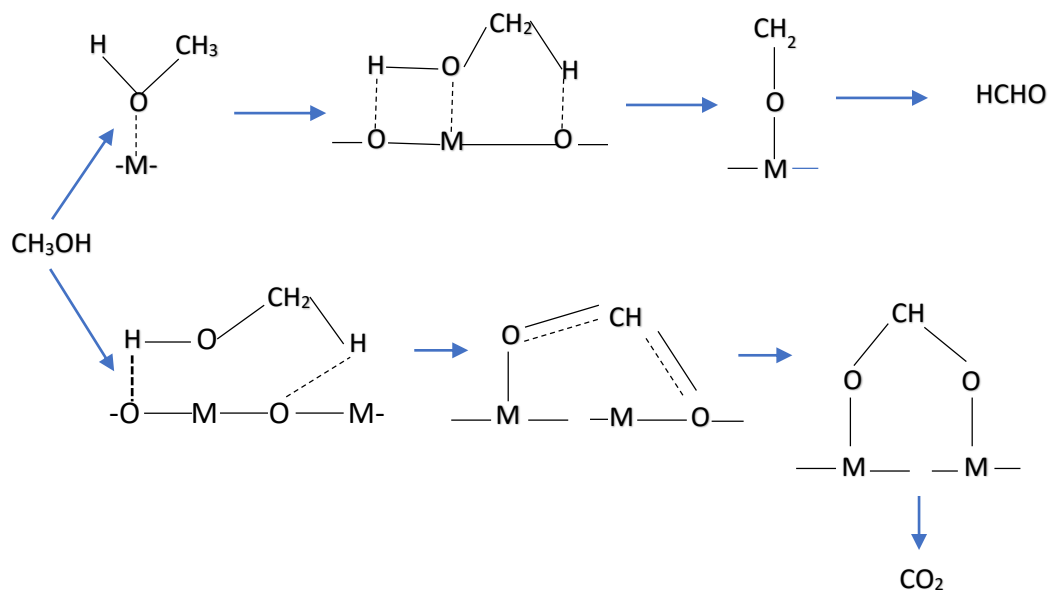
Mars and Krevelen [225] have proposed the following reaction mechanism:

$$nCH_3OH + S_{ox} \xrightarrow{K_1} HCHO \ (g) + H_2O \ (g) + S_{red} \quad -----(1)$$

$$n.O_2 \ (g) + S_{red} \xrightarrow{K_2} S_{ox} \quad ------(2)$$

Trifiro and Pasquon [194] have studied a number of mixed oxides of tin, antimony and molybdenum. In the oxidation of methanol on SnO_2-Sb_2O_3, carbon dioxide was essentially obtained while on MoO_3 at T< 350°C selectively for formaldehyde was obtained higher than 80% [226-228]. They classified the metal oxides in two groups:

    i.   Metal- oxide double bond character (M=O)
    ii.   Metal- oxide single bond character (-M-O-)

Thus, MoO_3 was placed in category (i) while SnO_2-Sb_2O_3 was placed in category (ii). Thus, the catalytic oxidation of methanol over Sn-Sb and Sn-Mo oxides along with pure oxides i.e. SnO_2, Sb_2O_5 and MoO_3 for the comparison was performed. Thus, the activities were compared with respect to the composition of the oxide catalyst of tin-antimony and tin-molybdenum for the oxidation of methanol.

VII.   CONCLUSION

The review shows that the tin- antimony and tin- molybdenum oxides have been widely used as industrial catalysts. The catalytic activity of these oxides has been shown to alter with the variation of the methods of preparation and activation temperature. Scattered attempts have been made on correlating the catalytic activity with the nature of the surface- active centres, but there is no comprehensive work available where different compositions and the surface physio- chemical and catalytic properties investigated.

The surface physico-chemical properties such as surface area, surface excess oxygen, solid state nature, and surface morphology of the different samples have been reported.

It is already mentioned that tin- antimony and tin- molybdenum oxides are very important oxidative dehydrogenation and oxidation catalysts. Not much information is available in the literature on T.P.D. (Temperature Programed Desorption) studies. The T.P.D. studies on Alumina, Nickel Oxide, TiO_2 with reference to active sites and chemisorption are reviewed

It was also seen that the study of the preferential adsorption of the binary liquid mixtures of the non- electrolytes provides useful information regarding the nature of the surface. The preferential adsorption studies of the binary

solutions like methanol + benzene etc. are, the nature and interaction between the molecules of the binary mixtures are reviewed.

The ^{119m}Sn Mössbauer spectra of some inorganic compounds and twenty alloys are given by Hayes [229]. The parameters which are of direct chemical interest such as the isomer shift and the quadrupole splitting are reported and discussed in order to highlight the nature of the active centres present on the surface of both the oxide systems,. Goldanskii [230] has reported that in case of SnO_2 a polymeric structure exists in which the oxygen forms a distorted octahedron around the metal atom. In the course of investigations, it was seen that tin was present as Sn^{4+}. No spectra corresponding to Sn^{2+} were obtained. By increasing the concentration of molybdenum S- electron density at the tin- nucleus increased.

Oxidation of methanol over mixed oxides has been a subject of several investigations. Not much information on the oxidation of methanol over mixed and pure oxides of Tin-Antimony are reported but a number of workers have tried the air-methanol oxidation to formaldehyde over MoO_3-Fe_2O_3, MoO_3-V_2O_5, MoO_3-Cr_2O_3 based metal oxide combinations and other catalysts. The other studies indicated that ferric molybdate is the most reactive component in Fe_2O_3-MO_3 catalyst. The review indicated that the iron in ferric molybdate seems to act as the transfer agent of oxygen and water between the surface and the gas phase. Similar studies are also reported on other catalysts made of mixed and pure forms of metal oxides.

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