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Zeolite and Mixed Oxide Catalysts for VOCs Oxidation

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Abstract: - Zeolite (NaX, NaX-CeO$_2$) and mixed oxide (Co4MnAl, NiMgMn) catalysts were tested in catalytic oxidation of volatile organic compounds (VOCs). The different kinds of catalysts proved remarkable activity in catalytic oxidation of ethanol and isopropanol respectively. The deepen comparison revealed that basic zeolite NaX-CeO$_2$ is more suitable for oxidation of isopropanol while oxidation of ethanol is faster in a presence of the metal mixed oxides, Co4MnAl and especially NiMgMn. The results of catalytic testing were linked to certain catalysts´ properties. Basicity/acidity and oxygen storage capacity (OSC) appeared to be the crucial parameters for selected tested alcohol oxidation.

Key-Words: - Ethanol, Isopropanol, Metal mixed oxide, Oxidation, and Zeolite

1 Introduction

Isopropyl alcohol (IPA) is one of the most widely used solvents in the world. It is particularly popular for pharmaceutical applications and is a major ingredient in "gas dryer" fuel additives. *Ethanol* (EtOH) was selected intentionally to focus on the emerging environmental problems of nowadays such as E-85 combustion (linked to the rising biofuel production), which actually augments the output of two different carcinogens such as formaldehyde and acetaldehyde. IPA and EtOH are volatile organic compounds (VOCs): organic compounds having an initial boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa. VOCs are harmful to human health and recognized as major responsible for the increase in global air pollution. They can also react with NO$_x$ and oxygen to form ozone: VOC + NO$_x$ + O$_2$ + $h\upsilon \rightarrow$ O$_3$ + other products. Ozone causes human health problems, affects DNA and enzyme functions, is toxic for vegetation, impairs quality of some materials, etc. Fortunately, the clean technologies and the regulations covering VOCs are permanently improving. *Catalytic oxidation* at low temperatures provides the safe and efficient way for removing dangerous VOCs. Catalysts with noble metals are currently preferred for this process, as they are highly active and stable [1], [2]. However, cheaper alternatives such as metal oxide catalysts or zeolites approved their suitability as catalysts for VOCs oxidation too [3]-[6].

Metal oxide catalysts (mainly Cu, Mn, Cr, Co, Mn, and Ni oxides) are appreciably active; though, their week point is a lower stability then in the case of noble metal catalysts [7], [8]. They are often obtained by controlled thermal decomposition of layered double hydroxides (LDHs). Chemical composition of LDHs can be represented by the general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]_x+[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n-valent anion and x has usually values between 0.20 and 0.33. After heating at moderate temperatures, LDHs give finely dispersed mixed oxides of M^{II} and M^{III} metals with a sufficiently large surface area and relatively good thermal stability [9]. Metal nitrates are usually used in preparation of such heterogeneous catalysts, as

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

nitrates can be easily removed from the catalysts by calcination. However, metal nitrates are rather expensive and so, other cheaper metal salts like sulphates, could be interesting for catalyst preparation.

The zeolites are crystalline microporous materials with a high surface to volume ratio. They are constituted of three-dimensional tetrahedral units (TO_4), bonded by oxygen atoms. The T atoms can be aluminium, silicon, and iron, copper or other. The combination of these units leads to particular arrangements with the formation of intra-crystalline channels and cavities, with dimensions in a molecular order of magnitude of 3 to 30 Å. The primary structure of the zeolite (faujasite) used in this work is composed of tetrahedral units with aluminium as central atom (AlO_4^{5-}), and silicon (SiO_4^{4-}). Faujasite zeolites are characterized by the presence of one type of large cages (supercages), 13 Å in diameter and ball-shaped, accessible through a 12 ring window with a free aperture of 7.4 Å, which is larger than the size of most of the organic molecules. Basic zeolites and particularly faujasites ones (NaX) showed interesting properties for oxidation of VOCs [10], [11].

The metal oxides (Co_4MnAl and NiMgMn) as well as the zeolite (NaX and its modification by CeO_2, well known in literature for its oxygen mobility [12]) have been recently examined by our groups as catalysts for deep VOCs oxidation. The catalysts selected for our research do not differ only in their structure, but also in acid-base characteristics and redox properties. It is known that alcohols can react as both acids and bases in solution phase chemistry depending on the acid-base characteristics of the reaction medium [13]. Scientists suggest that the presence of strong base sites such as O^{2-}, O_2^-, or HOO^-, advances the dehydrogenation of alcohol [14]. Thus, acidic (Co_4MnAl, NiMgMn) or basic (NaX, NaX-CeO_2, CeO_2) catalysts may become attractive way of varying alcohol oxidation selectivity and activity. Another approach, how to clarify divergent selectivity of catalysts is to evaluate their redox properties [15], [16]. Finally, diverse physical chemical nature of the surface of catalyst leads to promising model systems permitting to give details about the relations between acid-base or redox characteristics of solid phase and catalytic activity in total oxidation of more or less polar chemical compounds.

The additional contributions of present article are characterizations such as BET, XRD, TPR, TPD or determination of oxygen storage capacity of all catalysts.

2 Experimental

2.1 Preparation of the catalysts

The metal mixed oxide Co4MnAl was prepared by coprecipitation from hydrotalcite-like precursors with Co, Mn and Al molar ratio of 4:1:1. An aqueous solution of metal nitrates was added with flow rate of 7.5 ml/min into 1000 ml batch reactor containing 200 ml of distilled water. The flow rate of simultaneously added alkaline solution of 0.5 M Na_2CO_3 and 3 M NaOH was controlled to maintain reaction pH = 10.0 ± 0.1. The coprecipitation was carried out under vigorous stirring at 25 °C. The resulting suspension was stirred 1 h at 25 °C, the product was then filtered off, washed thoroughly with distilled water and dried overnight at 60 °C in air. The dried and powdered product was formed into pellets and calcined at 500 °C for 4 h in air.

The metal mixed oxide NiMgMn was prepared by coprecipitation from hydrotalcite-like precursors with Ni, Mg and Mn molar ratio of 1:1:1. The preparation process differs from the one of Co4MnAl only in the fact that metal sulphates were used instead of metal nitrates.

Zeolite NaX was supplied by Axens (Si/Al = 1.2).

Ceria (CeO_2) was prepared by calcining a cerium nitrate salt ($Ce(NO_3)_3,6H_2O$, Fluka, purity > 99.0%) under air flow (200 ml/min) with a heating rate of 1 °C/min from room temperature to 110 °C with a hold of one hour. Then the samples were heated overnight up to 550 °C (2 °C/min).

The hybrid catalyst (NaX-CeO_2) is a mechanical mixture of ceria and faujasite in equal mass. The mixture was then pelletized under 1.5 ton/cm² pressure and sieved between 0.2 and 0.4 mm. The sieved sample was then calcined under air flow (150 ml/min) at 100°C (1 °C/min) for one hour and at 600°C (1 °C/min) overnight.including a subsection you must use, for its heading, small letters, 12pt, left justified, bold, Times New Roman as here.

2.2 Characterization of the catalysts

The specific surface areas and pore volumes of the samples were determined by adsorption-desorption isotherms of nitrogen at -196 °C with a Micromeritics ASAP 2010 apparatus after evacuation at 90 °C for one hour followed by a hold for three hours at 350 °C. Microporous volumes were obtained by the t-plot method and the Dubinin-Radushkevich equation was used to calculate the mesoporosity.

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

XRD patterns of all catalysts were recorded over a Bruker D5005 diffractometer thanks to Diffrac+ software (XRD Wizard and XRD Commander) and interpreted with Eva and Topas softwares. The experimental conditions were as followed: λ = 1.542 Å, 10 °2θ to 75 °2θ, 0.02 °2θ and 4 seconds by step. Sherrer method was used to calculate the particle sizes for all samples [17].

Temperature-programmed reduction (TPR) measurements of the calcined samples (0.025 g) were performed with a H_2/N_2 mixture (10 mol % H_2), flow rate 50 ml/min and linear temperature increase 20 °C/min up to 1000 °C. A change in H_2 concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vakuum). Reduction of the grained CuO (0.16-0.315 mm) was repeatedly performed to calculate absolute values of the hydrogen consumed during reduction.

Temperature-programmed desorption (TPD) of NH_3 and CO_2 was carried out to examine acid and basic properties of the catalysts surface, respectively. The measurements were accomplished with 0.050 g of a sample in the temperature range 20 - 1000 °C, with helium as a carrier gas and CO_2 or NH_3 as adsorbing gases. The heating rate 20 °C/min was applied. During the experiments the following mass contributions m/z were collected: 2-H_2, 18-H_2O, 16-NH_3, and 44-CO_2. The spectrometer was calibrated by dosing an amount (840 μl) of CO_2 or NH_3 into the carrier gas (He) in every experiment. The TPR and TPD experiments were evaluated using OriginPro 7.5 software with an accuracy of ± 5 %.

The oxygen storage capacities, oxygen storage complete capacity (OSCC) and oxygen storage capacity in dynamic conditions (OSC) were calculated following the reduction reaction of the catalysts: $CO(g) + ½ O_2(s) \rightarrow CO_2(g) + \square (s)$. Prior the experiments, the samples were brought to 400 °C under flowing He (30 ml/min). Then, the catalysts were pre-treated under O_2, before undergoing CO pulses (0.267 ml) up to the catalysts maximal reduction. This permits to know the total amount of available oxygen in the samples (OSCC). After that, the samples were re-oxidized by O_2 pulses and underwent alternate pulses of CO and O_2 to calculate the O_2 amount immediately available in the samples. Oxygen storage capacities are expressed in $\mu mol_{CO2}/g$ from the CO_2 formation (after CO pulses) and transformed by calculation in $\mu mol_O/g$ stored in the samples.

2.3 Catalytic testing

The catalytic oxidation of *ethanol* was carried out *in Czech Republic* in a fixed-bed glass reactor (5 mm i.d.) in the temperature range from 100 to 400 °C (the temperature of the furnace was linearly increased by the rate of 3.5 °C/min). The catalyst (0.75 g of the sieved grains with the particle size of 0.16 – 0.315 mm) was examined at 10 m³/kg·h gas hourly space velocity (GHSV). The inlet concentration of VOC in the air was 1 g/m³. Reaction products were analysed using a gas chromatograph Hewlett-Packard 6890 equipped with a FID detector and a capillary column (HP-5 19091 J-413, 30 m × 0.32 mm × 0.25 mm with 5 % phenylmethyl silicone). The accuracy of the conversion and selectivity determination was ± 2 %. Temperature T_{50} (the temperature at which 50 % conversion of the examined VOC was observed) was chosen as a measure of the catalyst activity. Selectivity in ethanol conversion was evaluated as the GC peak area of by-products analysed at 95 % conversion of ethanol. Complete composition of the ethanol oxidation reaction mixtures were calculated on the basis of mass balance.

The destruction of 1360 ppm of *isopropanol,* mixed in synthetic and wet air (80 % nitrogen, 20 % oxygen, 33 % relative humidity, 1.2 mol % water), was carried out *in France* in a fixed bed reactor (i.d. = 5 mm, length = 90 cm) at atmospheric pressure and followed as a function of time (for 5 hours) at constant temperature. The catalysts used (140 mg) were previously sieved (0.2-0.4 mm) and activated overnight in air at 450 °C in the same reactor, inserted into an oven and the temperature was measured by a thermocouple inserted near the catalyst bed. The gas hourly space velocity (GHSV) was kept constant and equal to 18000/h, calculated at room temperature and pressure. The apparatus was coupled with a gas phase chromatograph (Varian 3400) equipped with a packed column and a thermal conductivity detector (TCD) to analyse air and carbon dioxide and with a capillary column (30 m VF-5ms with 0.25 mm of internal diameter and 0.25 μm film thickness) and a flame ionization detector (FID) to analyse hydrocarbons, namely isopropanol and secondary products, basically acetone and propene.

3 Results and discussion

3.1 Characterization of prepared catalysts

The specific surface areas and pore volumes of all prepared catalysts are gathered in Table 1. BET surface areas of the metal mixed oxides are close to 100 m²/g. CeO_2 exhibits only a little bit lower S_{BET} value than the mixed oxides – 80 m²/g, while NaX

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

boasts with the high specific surface area – more than 700 m^2/g. The hybrid of those two compounds, NaX-CeO$_2$, keeps its value someplace in the middle (around 400 m^2/g). The volume of micropores follows the same order CeO$_2$ > Co$_4$MnAl ≥ NiMgMn > NaX-CeO$_2$ > NaX in the range 0.03-0.3 cm^3/g. V_{Me} shows rather opposite tendency.

Table 1

The specific surface areas S_{BET} and pores volumes of all catalysts

Catalyst	S_{BET} (m^2/g)	V_{Mi} (cm^3/g)	V_{Me} (cm^3/g)
Co4MnAl	94	0.04	0.33
NiMgMn	113	0.04	0.36
NaX	762	0.30	0.01
NaX-CeO$_2$	423	0.17	0.08
CeO$_2$	80	0.03	0.19

Powder XRD patterns of all samples are traced on Fig. 1. Concerning the metal mixed oxides, after calcination of the LDH precursors at 500 °C, spinel-type mixed oxides were formed ("S" on Fig. 1).
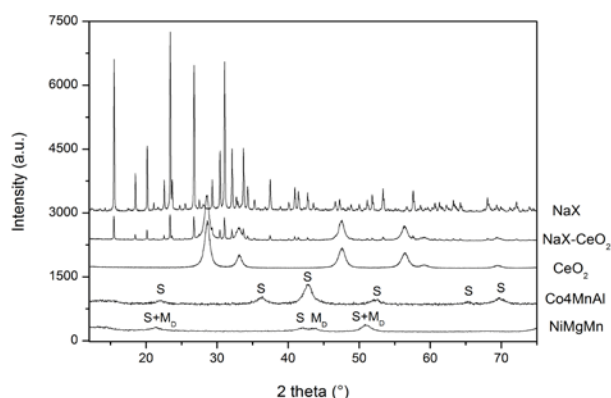

Fig. 1 powder XRD patterns of all prepared catalysts; "S" indicates spinel (Co-Mn-Al or Ni-Mg-Mn) and "M$_D$" disordered murdochite

Only spinel diffraction lines were found in the powder XRD pattern of Co4MnAl catalyst. Diffraction lines of non-stoichiometric mixed oxide with murdochite-type structure appear ("M$_D$" on Fig. 1) with the spinel lines in XRD pattern of NiMgMn. The average particle sizes are 0.8 nm for Co4MnAl and 0.3 nm for NiMgMn. The

crystallographic structures of NaX and CeO$_2$ do not seem to be affected by the hybrid catalyst preparation or thermal treatment since significant peaks of both compounds are visible in NaX-CeO$_2$ XRD spectrum. The average particle sizes are equal to 13 nm and 104 nm for respectively ceria and faujasite NaX, with almost no difference for hybrid catalyst.

Temperature program desorption (TPR) patterns of all catalysts are shown in Fig. 2. Temperature-programmed reduction (TPR) measurements of the calcined samples were performed up to 1000 °C, however, catalytic components reducible at temperatures higher than used reaction temperatures cannot likely contribute to the catalytic reaction. For that reason, we zoomed in on a lower temperature region (up to 350 °C) corresponding to our reaction temperature area. Up to selected temperature, CeO$_2$, NaX-CeO$_2$ and NaX catalysts showed very similar course of TPR patterns, with practically no reduction behaviour. The first reduction peak appeared at limit temperature 350 °C for NiMgMn as well as Co4MnAl. For both catalysts, the peak can be ascribed to the reduction of an easily reducible Mn^{IV} phase to Mn^{III} (during the reduction of free MnO$_x$, the peaks with maxima at 328 and 424 °C were reported [18]). Regarding Co4MnAl, the same peak can be also ascribed to reduction of Co^{III} to Co^{II} oxides. Observations of Arnoldy and Moulijn [19] explain its slight shift to higher temperatures (indicating worse reducibility of the arising components of Co4MnAl catalyst comparing to NiMgMn) by influence of Al^{3+} cations.
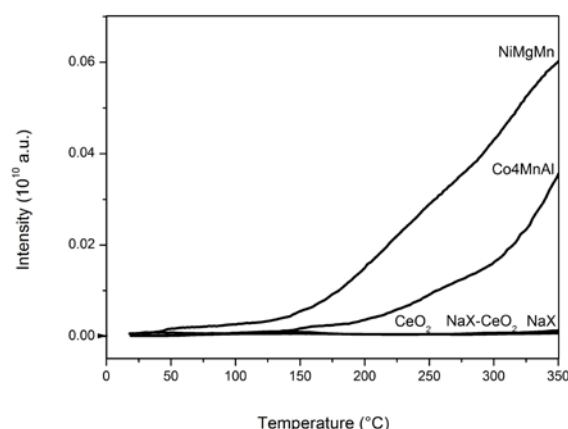

Fig. 2 TPR patterns of all catalysts

Temperature-programmed desorption (TPD) of NH$_3$ and CO$_2$ can be applied to determine the density and strength of acidic and basic sites in the samples [20]. *TPD of NH$_3$* visualized very

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

significant differences in surface acid properties associated to the catalysts. Desorption curves of NH_3 (TPD) from all catalysts are traced up to 350 °C in the Fig. 3. One main low-temperature desorption peak centred between 110-140 °C with a shoulder at between 180-230 °C, is characteristic for NH_3 desorption curves of all tested samples. The low-temperature peak corresponds to acid centres of moderate strength and the shoulder corresponds to stronger acidic sites. The amount of such centres for the temperature range of 25-350 °C (Table 2) decreased in order of corresponding catalysts as following:

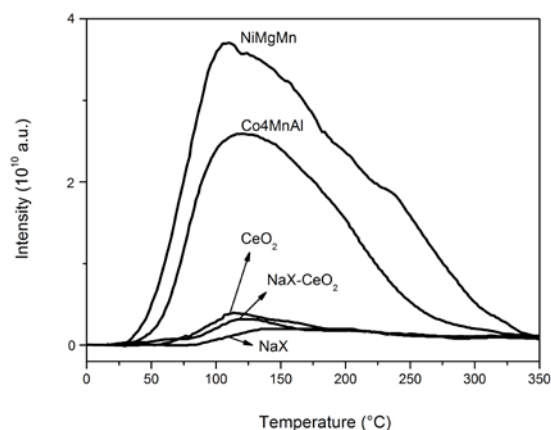NiMgMn (1.34 mmol/g) > Co4MnAl > CeO_2 ≥ NaX-CeO_2 ≥ NaX (0.22 mmol/g).

Fig. 3 desorption curves of NH_3 (TPD) from all catalysts

In TPD experiments, carbon dioxide as a probe molecule manifests sufficient acidity to determine all basic sites in a catalyst [21]. *TPD patterns of CO_2* (Fig. 4) from two selected catalysts, Co4MnAl and NaX-CeO_2, are an example for two peaks identified for all catalysts: very weak (T_{max} around 80 °C) and stronger basic centres (T_{max} around 300 °C).
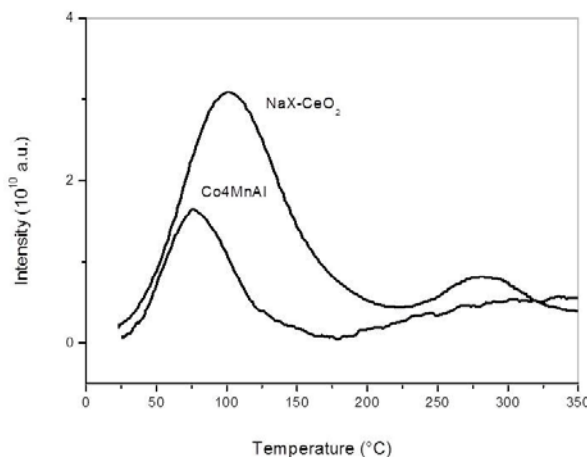

Fig. 4 desorption curves of CO_2 (TPD) from selected catalysts

In Table 2, the amount of basic centres for the temperature range of 25-350 °C is given.

Table 2

TPD characteristics of all catalysts

Catalyst	TPD NH_3 (mmol/g) [a]	TPD CO_2 (mmol/g) [a]
Co4MnAl	0.70	0.16
NiMgMn	1.34	0.09
NaX	0.22	0.20
NaX-CeO_2	0.23	0.20
CeO_2	0.25	0.19

[a] 25-350 °C.

The overall number of basic sites decreased in opposite order comparing to the amount of acid cites: NaX (0.20 mmol/g) ≥ NaX -CeO_2 ≥ CeO_2 > Co4MnAl > NiMgMn (0.09 mmol/g).

The TPD NH_3 and CO_2 experiments confirmed that Co4MnAl and NiMgMn systems are more acidic than basic while NaX, NaX-CeO_2, CeO_2 are more basic than acidic.

As a rule, two mechanisms can account for *oxygen storage* in oxide materials: (i) either there is diffusion of oxygen species from the bulk to the surface and the reaction with the reducer (CO) takes place at the surface or (ii) the reaction takes place in the bulk, which implies that there is bulk diffusion of the reducer and back-diffusion of the reaction products (CO_2). The second mechanism is quite unlikely for OSC using CO as a reducing agent and

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

such OSC mechanism is mainly controlled by oxygen mobility.

The total amount of available oxygen in the samples (OSCC) and the O_2 amount immediately available in the samples (OSC), expressed in $\mu mol_O/g$ stored in the samples, are presented in Table 3.

Table 3

OSC and OSCC of all catalysts

Catalyst	OSCC ($\mu mol_O/g$)	OSC ($\mu mol_O/g$)
Co4MnAl	2661	1867
NiMgMn	3640	1350
NaX	98	1
NaX-CeO$_2$	113	45
CeO$_2$	326	80

There are visible differences between OSCC as well as OSC values of measured samples. The metal mixed oxides exhibit extremely high oxygen storage values: OSCC around 3000 $\mu mol_O/g$ and OSC about 1500 $\mu mol_O/g$. The total amount of available oxygen in NiMgMn is the highest comparing to all other samples, 3640 $\mu mol_O/g$. On the other hand, among all catalysts, in Co4MnAl is the highest O_2 amount immediately available, 1867 $\mu mol_O/g$. As expected, $CeO_2 > NaX\text{-}CeO_2 > NaX$ is decreasing order of OSCC and OSC values respectively. The presence of CeO_2 in NaX structure increased the oxygen storage capacity of a hybrid in comparison to bare NaX, which is able to exchange the oxygen atoms above 600 °C [22]. The increase of oxygen exchange by the introduction of a metal cation can be done via a multiple exchange [23]; a rapid exchange of the oxygen of the ceria surface and a slower exchange of the oxygen atoms from the zeolite lattice is proposed explanation for the hybrid sample [24].

3.2 Catalytic testing

The samples were tested as catalysts in total *oxidation of ethanol and isopropanol*. The main results of catalytic tests are summarized in Table 4. The temperatures T_{50} and T_{90} – at which 50 and 90 % conversion of ethanol and isopropanol was achieved – were chosen as a measure of catalytic activity of the prepared catalysts in oxidation processes.

Table 4

Temperatures of 50 and 90 % conversion of ethanol and isopropanol achieved with all catalysts

Catalyst	Ethanol[a]		Isopropanol[a]	
	T_{50}	T_{90}	T_{50}	T_{90}
Co4MnAl	132	150	205	240
NiMgMn	129	198	210	234
NaX	309	319	300	325
NaX-CeO$_2$	300	316	190	210
CeO$_2$	160	178	<120	180

[a] GHSV = 18000/h

The catalytic oxidation of *ethanol*, carried out *in Czech Republic*, reveals the best performance for mixed oxides catalysts: NiMgMn and Co4MnAl. The presence of those catalysts assures the values of T_{50} close to 130 °C (129 °C for NiMgMn and 132 °C for Co$_4$MnAl). Other very active catalyst was oxide of ceria, which is able to catalyse the half of ethanol oxidation already at 160 °C. The highest values of T_{50}, 300 and 309 °C, are linked to zeolite NaX-CeO$_2$ and pure NaX respectively. The positive effect of CeO_2 addition to NaX is visible on slightly lower value of T_{50} for NaX-CeO$_2$ comparing to pure NaX, anyhow, these catalysts are the less suitable for catalytic oxidation of ethanol from all tested compounds. For better understanding of the differences in catalytic activity, the properties and the characteristics of the catalysts need to be taken in account. Several connections were found, presented in Fig. 5.
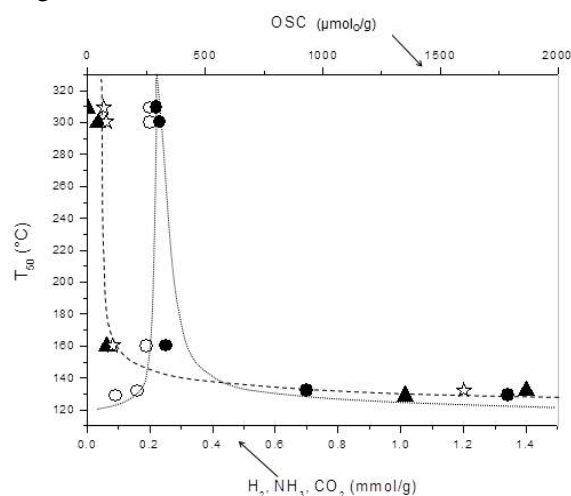

Fig. 5 dependence of catalytic activity in total oxidation of ethanol over tested samples on their OSC (▲), the amount of hydrogen consumed during

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

TPR (∗) and acidic (●) or basic (○) properties in the temperature range (25-350 °C)

The dashed exponential curve joins the values of T_{50} in dependence of the ones for OSC (▲ in Fig. 5) and at the same time the amount of hydrogen consumed during TPR (∗ in Fig. 5) for all catalysts. The curve describes a growing advantage for catalytic performance in ethanol oxidation with increasing amount of immediately available oxygen in the sample (OSC). Concurrently, it declares that the enhancement of reducibility of the catalyst is reflected in higher activity in ethanol oxidation. Cerium-based heterogeneous catalysts have been widely studied, used, and developed due to their well-known oxygen storage capacity (OSC) and high oxygen mobility, especially in the case of gas-phase reactions [25]. However, a higher oxygen storage and reducibility of metal mixed oxide Co4MnAl and NiMgMn, comparing to CeO_2, assured the highest activity in ethanol oxidation. The results of catalytic activity in dependence of TPD measurements in the temperature range (25-350 °C) leaded to tracing of two dotted curves – one for acidic (● in Fig. 5) and one for basic ◌ in Fig. 5) properties of the compounds. The curves describe the following tendency: more the catalysts are acidic, resp. less basic, higher is the activity in ethanol oxidation. The authors suggest that redox and acid-base parameters are the key factors for ethanol oxidation. Furthermore, the authors interpret the fact that dashed and dotted curves (Fig. 5) has an exponential character by their "mutual influence" on catalytic activity.

The further comparisons, analysing also T_{90} for ethanol oxidation, displays the different order of catalytic performance of the samples evaluated by T_{50} and T_{90}. The most active catalyst NiMgMn according to T_{50} values appears at the third place pursuant to T_{90} evaluation. NiMgMn is able to catalyse 90 % of ethanol oxidation at 198 °C, which is later than sample Co4MnAl (T_{90} = 150 °C) or CeO_2 (T_{90} = 178 °C). The possible explanation of a slower catalytic oxidation of NiMgMn than Co4MnAl and CeO_2 can be the different preparation process. Co4MnAl and CeO_2 were prepared from nitrates but for synthesis of NiMgMn the sulphate precursors were used. The activity of such catalyst can be inhibited during oxidation process by formation of sulphates on its surface.

Ethanol is a primary alcohol, so the product of its oxidation is first an aldehyde (acetaldehyde) and with further oxidation a carboxylic acid (acetic acid). Oxidation of acetic acid gives the final product of total oxidation of ethanol: CO_2 and H_2O.

Depending on the reagents and conditions, different by-products can be detected during ethanol oxidation. Conversion of ethanol as well as selectivity to CO_2 thus may be evaluated. The major path appears to be the direct oxidation of acetaldehyde to CO_2, while its oxidation via the acetic acid should be a minor path, because no acetic acid is detected in the products [26].

The catalytic oxidation of **isopropanol** was carried out *in France*. The main results of the tests are gathered in Table 4 and temperature dependence of isopropanol conversion over the catalysts can be seen on Fig. 6.
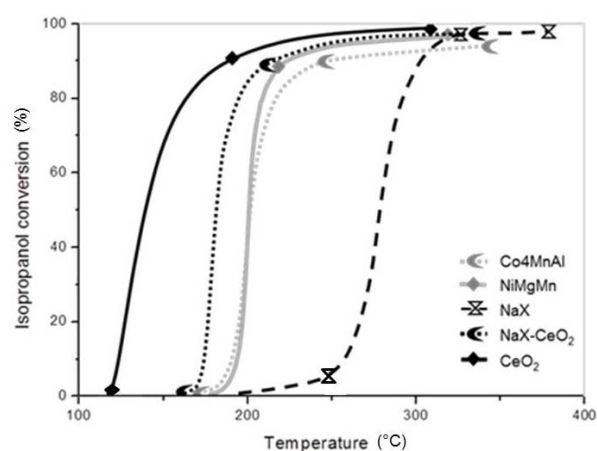

Fig. 6 temperature dependence of isopropanol conversion over all tested catalysts

All catalysts – hybrid zeolite, the metal mixed oxides and cerium oxide – except NaX showed dissimilar activity order in oxidation of isopropanol and ethanol. Different laboratory setup or experimental conditions may move the values if T_{50} or T_{90} to the higher or lower temperature range, but the order of catalytic performance for the tested samples should remain the same. Anyhow, the results between two laboratories will not be compared, but the elementary difference between two tested alcohols simply might be noted. Ethanol is a primary alcohol, which can be oxidised to aldehydes or further to carboxylic acids. Isopropanol is a secondary alcohol and secondary alcohols can be oxidised to ketones but no further. Based on the data from French laboratory for all tested catalysts, isopropanol is quickly and easily transformed into carbon dioxide and for certain samples to one intermediate product – propene. Other possible intermediate product – acetone, which is corresponding ketone – was not observed. Regarding the fact that reagents useful for the

Jana Gaálová, Květuše Jirátová, Jan Klempa,
Olga Šolcová, Irene Maupin, Jerome Mijoin,
Patrick Magnoux, Jacques Barbier, Jr.

transformation of primary alcohols to aldehydes are normally also suitable for the oxidation of secondary alcohols to ketones, missing acetone in isopropanol oxidation can be coherent with missing aldehyde presence in ethanol oxidation for tested catalysts. Intermediate product propene was observed for more basic catalysts, where isopropanol can be transformed via a basic mechanism into propene before complete oxidation in CO_2. The advantage of more basic catalysts in isopropanol oxidation might be a stronger adsorption of VOC molecule on the cations and framework oxygen of the zeolite. When isopropanol is adsorbed on a zeolite with alkali cations, it is probable that the OH group of isopropanol will adsorb on the cation (acting as a Lewis acid site), and that hydrogen of molecule will adsorb on the basic framework oxygen. From Table 4 and Fig. 6 is noticeable that the most active catalysts among those tested in isopropanol oxidation are CeO_2 and hybrid zeolite NaX-CeO_2 (T_{50} = 120 °C for CeO_2 and T_{50} = 190 °C for the hybrid). TPR and TPD indicated them to be more basic than acidic. On the other hand, the zeolite NaX is the most basic from all the catalysts, however, is the less active in isopropanol oxidation. Here should be repeated that NaX is not able to exchange the oxygen atoms under 600 °C and oxygen mobility is minimal in the temperature range of the oxidation process. That might be a handicap for NaX. Also, the mixed oxides NiMgMn and Co4MnAl were evaluated as acidic; still, their great oxygen storage capacity and the good reducibility permit them to perform isopropanol oxidation rather actively.
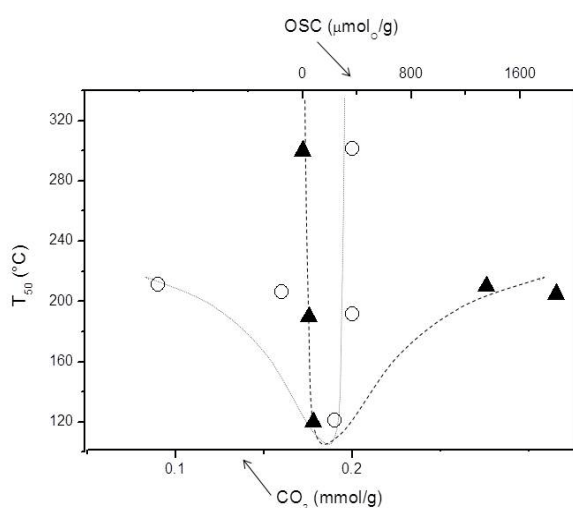

Fig. 7 dependence of catalytic activity in total oxidation of isopropanol over tested samples on their OSC (▲) and basic (○) properties in the temperature range (25-350 °C).

A combination of basicity and oxygen mobility is proposed as advantageous characteristics for isopropanol oxidation. Yet, basicity and OSC values of the catalysts follow the opposite order (Table 2 and 3). Fig. 7 shows the dependence of catalytic activity in total oxidation of isopropanol over tested samples on their OSC (▲) and basic (○) properties in the temperature range (25-350 °C). OSC values are linked by dashed line and basicity representing points are linked by dotted line. The intersection of the curves illustrates a "compromise" of two key parameters. Closer the values of OSC and basicity for a catalyst are to the intersection, higher activity reveals in isopropanol oxidation.

4 Conclusion

Zeolite NaX, hybrid NaX-CeO_2, cerium oxide and the mixed oxides – Co4MnAl and NiMgMn – were tested and compared in catalytic oxidation of ethanol and isopropanol respectively. The basic zeolite NaX, converted 50 % of ethanol as well as isopropanol at around 300 °C. All other catalysts were more active. The comparison revealed that CeO_2 and zeolite NaX-CeO_2 are the most suitable for oxidation of isopropanol while oxidation of ethanol is the fastest in a presence of the metal mixed oxides, Co4MnAl and NiMgMn. Basicity/acidity appears to be one of the crucial parameter for alcohol oxidation. However, it seems to lead hand by hand with oxygen mobility to a higher performance of the catalysts. The results of ethanol (the primary alcohol) oxidation indicate growing performance with increasing acidity and OSC of the catalysts. Authors suggest, that exponential curve of activity amelioration illustrates a "mutual work" of these two key characteristics. The importance of both parameters was visible also in isopropanol oxidation, though, this secondary alcohol prefers higher basicity. Basicity and OSC values of the catalysts follow the opposite order. Therefore, in this case, the main parameters go "against each other", ending by the compromise for the best activity: CeO_2, relatively basic catalyst with rather sufficient OSC.

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WSEAS TRANSACTIONS on ENVIRONMENT and DEVELOPMENT

Jana Gaálová, Květuše Jirátová, Jan Klempa,
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