

The Role of Ceria in Hydrogenation of Carbon Monoxide and Dehydration of Bio-Ethanol

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Abstract—Ceria is the active catalyst for various chemical processes. The reactions of hydrogenation of carbon monoxide and dehydration of bioethanol using the cerium oxide as catalyst are considered. The role of cerium oxide in the investigated processes, which have a positive influence on the selectivity, the process conditions, the dispersion of catalysts are shown. Cerium oxide improves the dispersion of active component and has the own catalytic activity.

Index Terms—Ceria, catalyst, dehydration of ethanol, conversion of bio-ethanol.

I. INTRODUCTION

Cerium containing catalysts are an important subject of hundreds of scientific research works carried out in recent years in the field of chemistry. Such interest in these catalytic systems is due to a set of interesting properties [1]-[5].

In the chemical and petrochemical industry cerium oxide is used as catalyst. Usefulness of cerium catalysts explained by commercial availability of ceria, simple production technology and its significant advantages in comparison to commercial catalysts used, namely:

- High activity and selectivity;
- Duration lifetime;
- The ability to reduce the temperature and pressure process;
- Synergies effect in interaction with other components of the catalyst;
- Reduction or complete elimination of the use of precious metals.

Cerium catalyst plays several catalytic roles, it acts as a stabilizer of the surface area of alumina, as a basis for the shift reaction, as the oxygen storage component, as amplifier anoxic reducing activity of rhodium [6], [7].

This review shows the role of cerium oxide in the carbon monoxide hydrogenation and dehydration of ethanol as an

active catalyst component, as modifying additive and a carrier for the catalyst.

II. MATERIALS AND METHODS

Investigation of the catalytic activity of the catalysts during the conversion of ethanol and CO hydrogenation was carried out under high pressure on automated catalytic unit (PKU-2VD).

The installation includes the following blocks: block gas flow controller, the fluid pump, reactor, an evaporator, a switch, a separator and a control unit. The installation uses thermal mass gas flow controllers, into which the source gases are supplied from cylinders under pressure of 5.5 MPa. The outputs of the regulators are connected with each other and have a common outlet through which the gas or gas mixture supplied to the evaporator inlet. The apparatus uses a high-pressure pump. The output of the pump fluid enters the evaporator. The pump is controlled from the software. The reactor is made of stainless steel and is placed vertically. The incoming stream from the evaporator is fed from the bottom, passes between the outer container and the reactor tube with catalyst, is then passed through the catalyst bed and is also down. Located within the reactor vessel with the catalyst, wherein the catalyst bed is located after a stainless steel filter.

The reaction products were identified by chromatography on device "Chromos GC-1000" using an absolute calibration method and a thermal conductivity detector. Separation of components was carried out on two columns (length 2 m, internal diameter 3 mm) filled with NaX zeolite and porapak-T, carrier gas - helium and argon.

Temperature-programmed reduction (TPR) was performed in a laboratory setting, including the gas preparation system with a tubular reactor furnace and a thermal conductivity detector. Reducing was carried out by hydrogen passing the gas mixture (5% H₂ and 95% Ar) through a reactor at a rate of 30 ml / min. Linear heating rate was 10⁰C / min. The changing the concentration of hydrogen in the stream was monitored using a thermal conductivity detector. Quantitative determination of the absorbed hydrogen was performed by calibration, built on the basis of reduction of accurate batches of NiO.

Electron microscopy and diffraction characteristics of the catalysts were recorded on a microscope "Computers - 100AK" (increase 120 000) and diffractometer "DRON-0.5" in conjunction with X-ray diffraction analysis. When using the method suspensions, test material suspended in distilled water and dispersed on the device UZDN-2T. Then the sample was supported on a colloidal film substrate. The

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preparation should contain a sufficient amount of particles deposited uniformly with a small clearance between them and without overlap.

Catalysts were prepared by solution-combustion method, as well as joint capillary wetness impregnation of the support with solutions of nitrates and subsequent drying at 300°C (2 h) and calcination at 500°C for three hours.

III. RESULTS AND DISCUSSION

Due to its oxidation - reduction properties cerium is frequently used in the Fischer-Tropsch process [8]-[15].

In [8] the structure, adsorption and catalytic properties of bimetallic Ru-Ce/Al₂O₃ catalysts for Fischer-Tropsch synthesis were studied. In hydrogenation of CO over Ru-Ce catalysts the reaction products are C₁-C₈ hydrocarbons. CO conversion and selectivity determined by the Ru / Ce ratio. It was shown that ruthenium and cerium interacts forming bimetallic Ru⁰-Ceⁿ⁺ clusters. Adsorption of CO, H₂ and CO + H₂ was studied with the use of microcalorimetry, TDS and IR spectroscopy. Based on the experimental data [9] it was determined that a decrease in the heat of CO and hydrogen adsorption on the bimetallic catalyst leads to a suppression of methanation and subsequent enhancement of polymerization processes.

In [10] the effects of different supports (e.g. Al₂O₃, SiO₂, TiO₂, zeolites and magnesium silicate) and different promoters such as Li, K, Rb and Mg on the structure and morphology of precipitated cobalt cerium catalyst for Fischer-Tropsch synthesis were investigated. The effect of several preparation variables including the precipitate ageing time, the [Co] / [Ce] ratio of the precipitation solution, and calcination temperature was also studied. Addition of 20% Ce in to the cobalt catalyst resulted in a decrease of selectivity to methane from 35 to 26 % and selectivity increase towards ethylene from 18 to 32 %. The catalyst containing 80 %Co - 20% Ce was found to be the optimum one for conversion of synthesis gas to light olefins (C₂-C₄) at H₂/CO = 4/1, GHSV=4050 h⁻¹, P=1 atm at 450°C.

The cobalt cerium catalysts were calcined at different conditions (T=500°C for 7 h, T=600°C for 6 h and T=700°C for 5 h) and tested in hydrogenation of CO with the catalyst calcined at 600°C showing better catalytic performance.

The 80%Co / 20%Ce catalyst was characterized by H₂-TPR revealing that the calcined catalyst had four distinct reduction peaks at 180, 300, 420 and 540°C. The peaks at 180 and 300°C correspond to the reduction of Co₃O₄, with a shift to low temperature by 50-90°C. A proper amount of Ce could improve the reduction ability of Co₃O₄ [11]. Addition of Ce into the Co₃O₄ oxide lowered the redox ability of Co³⁺ to Co²⁺. The peak at 420°C was due to the reduction of CeO₂ surface oxygen [12]. The reduction peak at 540°C was attributed to the bulk reduction of CeO₂ by elimination of O²⁻ anions from the lattice [13].

The authors [14] have applied ceria as an acid promoter for an iron-containing catalyst operating under at elevated pressures and temperatures. In fact cerium was introduced as a part of a mixture of neodymium and cerium silicates in a weight ratio of the acid component and the iron-containing catalyst from 1 to 6. The ratio of cerium silicate to neodymium counterpart varied from 1:9 to 9:1. Application

of this additive increased selectivity and productivity of the catalyst towards liquid hydrocarbons at the same time decreasing the content of aromatic hydrocarbons in the liquid products.

Co-ZrO₂ / Al₂O₃ and Co-ZrO₂-CeO₂ / Al₂O₃ catalysts were studied [15] for the production of aliphatic hydrocarbons from synthesis gas diluted with nitrogen. The authors have found that the promotion of cobalt by cerium and zirconium oxides leads to a substantial increase of its activity and C₅₊ hydrocarbon yield. Co-ZrO₂-CeO₂/Al₂O₃ catalyst exhibited high selectivity to CO₂ in the temperature range 473 K amounting up to 15% and 12% for the undiluted and diluted synthesis gas respectively. The authors suggested that this increase in carbon dioxide selectivity is due to the contribution of the Boudouard reaction enhanced because of CO dissociation on the surface of active oxygen centers present in CeO₂.

Similar results were obtained in our study [16] devoted to hydrogenation of carbon monoxide on cobalt containing catalysts modified by ceria - Co / Al₂O₃ and Co - CeO₂/Al₂O₃. The catalysts were prepared by incipient wetness impregnation of the support, reduced before experiments in a hydrogen stream at 573 K. Fig. 1 shows the influence of reaction temperature and the catalyst composition on carbon monoxide conversion at atmospheric pressure. Introduction of cerium oxide into Co/Al₂O₃ catalyst leads to an increase in carbon monoxide hydrogenation.

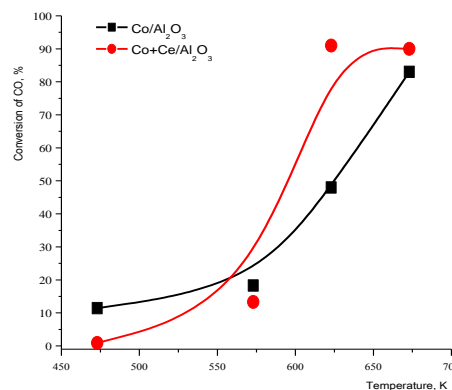


Fig. 1. Effect of reaction temperature and catalyst composition on the conversion of carbon monoxide.

For instance, at 623K conversion of carbon monoxide over Co / Al₂O₃ catalyst was 48%, while over Co+Ce/Al₂O₃ it reached 91%. Unfortunately, after introduction of cerium oxide the selectivity to carbon dioxide increased.

A number of studies [17]-[20] investigated electrochemical and catalytic oxidation of alcohols using cerium oxide.

In [17] CuO-CeO₂ compounds with different ratios of copper oxide to cerium oxide were synthesized by the citrate method and used in total oxidation of ethanol. The most active was 0.25 CuO – 0.75 CeO₂ catalyst, affording complete conversion of ethanol to CO₂ at 493K. At low temperature acetaldehyde (5%) was also formed in small amounts. Interestingly enough on the individual oxides the yield of acetaldehyde was much higher being 15% over CeO₂, and 45% over CuO.

Ce-containing catalysts supported on alumina [20] and

zeolite 5A were synthesized in [20] by wetness impregnation of the support followed by drying at room temperature and 573 K and further calcination at 773 K for three hours. Before the experiment the catalysts were reduced in a hydrogen stream for 1 hour at 773 K and atmospheric pressure. Cerium catalysts on alumina ($\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ and $\text{CeLa} / \gamma\text{-Al}_2\text{O}_3$) were thereafter tested in dehydration of ethanol to ethylene in a fixed bed reactor in an inert gas in the temperature range 523–723 K and space velocity 1500 - 13000 h^{-1} .

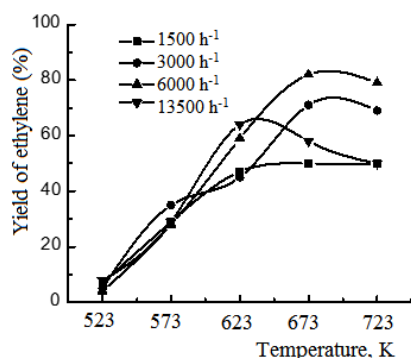
Table I shows the effect of the reaction temperature on the catalytic activity of $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$. It can be seen that at 523K, the yield of ethylene is 39% with selectivity 95%.

TABLE I: EFFECT OF REACTION TEMPERATURE ON THE YIELD OF ETHANOL CONVERSION PRODUCTS OVER CERIA CATALYST

T,K	Conversion of ethanol,%	Product yield,%				Selectivity,%			
		CH_4	C_2H_4	C_2H_6	C_3H_6	CH_4	C_2H_4	C_2H_6	C_3H_6
523	42	-	39	-	-	-	95	-	-
573	59	-	56	-	0.70	-	95	-	1.2
623	75	-	67	-	4.5	-	89	-	0.6
673	87	-	80	0.38	3.8	-	91	0.4	4.4
723	90	1.0	75	0.62	3.3	1.11	83	0.7	3.7

Ceria supported on alumina allows conducting ethanol dehydration at lower temperatures (673 K) compared with other catalysts. For example, in [22] $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst prepared by mixing commercial $\gamma\text{-Al}_2\text{O}_3$ powder with Na_2CO_3 solution with subsequent addition Ti (SO_4)₂ and Na_2CO_3 solutions was investigated. SO_4^{2-} was eliminated by washing and centrifugation. Thereafter, the material was dried and calcined giving $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$. Catalytic tests resulted in up to 99.4 % ethylene selectivity at 773 K.

Lanthanum modification of $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ catalyst was reported by authors [20], [23] to improve catalytic ability at low temperatures.

Fig. 2. Effect of temperature and space velocity on the yield of ethylene over ceria-lanthanum supported on $\gamma\text{-Al}_2\text{O}_3$ catalyst.

The effect of lanthanum oxide [20] addition on activity of $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ catalyst was investigated in the temperature range 523-723K and space velocity 1500-13500 h^{-1} (Fig. 2). As seen from Fig. 2 at 523 and 573K the effect of space velocity on the activity is minor at all flow rates.

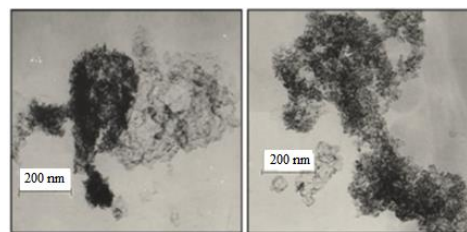
With increasing the reaction temperature to 623K the highest yield of ethylene of 62% was observed at WSHV of 13500 h^{-1} . At 673K with introduction of lanthanum into $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ catalyst the optimal space velocity is shifted to a higher region from 3000 to 6000 h^{-1} , where there maximum yield of ethylene reached 82%.

Addition of lanthanum oxide in ceria catalyst increases dispersity [20], [21]. The phase composition of the catalysts ($\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ and $\text{CeLa} / \gamma\text{-Al}_2\text{O}_3$) was determined by

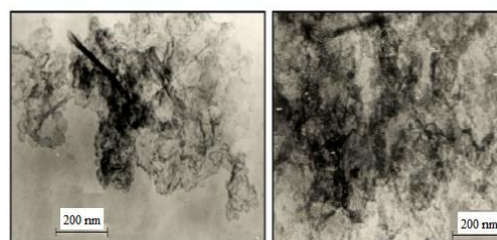
With increase of conversion of ethanol is elevated to 59%, giving the yield of the main product - ethylene 56%. The reaction products besides ethylene contain small amounts of propylene (0.70%). Propylene can be formed by metathesis of ethylene and butene-2 [21]. The highest yield of ethylene (80%) was observed at 673 K when selectivity to ethylene was still high exceeding 90%.

Above 673 K, besides ethylene and propylene, ethane was formed in small amounts (0.38%). Further increase in the reaction temperature to 723 K leads to a decrease in the desired product yield. These data indicate that the optimal temperature of $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst for ethanol dehydration is 673K.

electron microscopy [20]. Results for $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ catalyst are shown in Fig. 3 illustrating accumulation of particles with a size of 5-10 nm, which can be attributed to a mixture of Ce_6O_4 (JCPDS, 32-196) and AlCe_3 (JCPDS, 9-260) phases.

Fig. 3. The microphotographs of the sample $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$.

Modification of $\text{Ce} / \gamma\text{-Al}_2\text{O}_3$ by lanthanum increases a catalyst dispersion (Fig. 4), giving aggregation of mainly small particle with the size of 2 nm, although clusters of the size 10 nm are also present. Micro diffraction pattern shows a small set of rings and can be attributed to a mixture of phases - $\alpha\text{-La}$ (JCPDS, 2-618), Ce_2O_3 (JCPDS, 23-1048), La_2O_3 (JCPDS, 22-269), La_2O_3 (JCPDS, 24-554), as well as to the metal clusters - Al_3La (JCPDS, 19-25), AlCe_3 (JCPDS, 9-269), AlLa_3 (JCPDS, 25-1131).

Fig. 4. The microphotographs of the sample $\text{CeLa} / \gamma\text{-Al}_2\text{O}_3$.

Ethanol dehydration process is an acid catalyzed process with involvement of Brønsted and Lewis acid sites [24]. According to [25] the Brønsted acid sites can be formed in ceria modified zeolites by first treatment of for example NaY zeolite with solutions of the rare-earth elements and subsequent hydrolysis.

Formation of the acidic sites on the surface of cerium-containing catalysts was investigated using temperature-programmed desorption of ammonia (TPD).

The desorption of ammonia from the catalyst surface Ce / γ -Al₂O₃ (Fig. 5) takes place in three temperature domains with corresponding temperature maxima of 433, 753 and 943K [26]. In the temperature range 323-638 K ammonia desorbs probably from weak acid sites with the amount equal of 9.32×10^{-4} mol / g cat. In the interval 638-853K ammonia is desorbed (7.21×10^{-4} mol / g cat) from medium strength centers of, while desorption from strong acid sites occurs in the temperature range 853-1163 K with the respective amount of ammonia being 6.04×10^{-4} mol / g cat [27].

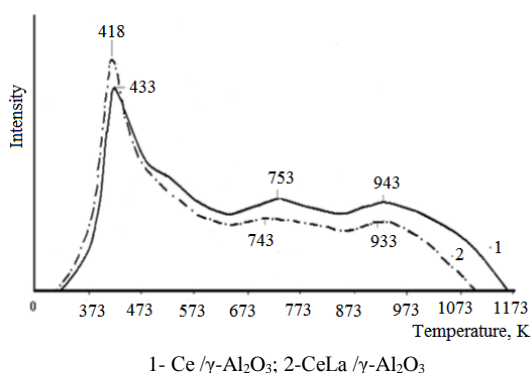


Fig. 5. TPD of ammonia from Ce containing catalysts.

With the introduction of the lanthanum into the cerium catalyst ammonia desorbed from the catalyst surface in three temperature ranges, with the peaks at 418, 743 and 933K (Table II).

TABLE II: THERMAL PROGRAMMED DESORPTION OF NH₃ FROM CERIA CATALYSTS

Sample	T max, K	The amount of desorbed ammonia		
		ml/ g cat	mol/g cat	Total volume (mol/g cat)
Ce / γ -Al ₂ O ₃	433	20.9	$9.32 \cdot 10^{-4}$	$22.57 \cdot 10^{-4}$
	753	16.2	$7.21 \cdot 10^{-4}$	
	943	13.5	$6.04 \cdot 10^{-4}$	
Ce La / γ -Al ₂ O ₃	418	27.5	$12.29 \cdot 10^{-4}$	$23.38 \cdot 10^{-4}$
	743	11.9	$5.3 \cdot 10^{-4}$	
	933	12.9	$5.79 \cdot 10^{-4}$	

Ce containing catalysts supported on zeolite CaA were prepared by wetness impregnation of the carrier and by «solution combustion» method [28]. The latter method being one of the options of self-propagating high-temperature synthesis involves the use of a reactive aqueous solution of various oxidizing agents (metal nitrates) and fuels (e.g. glycine, urea, hydrazine, etc.). As a result of high temperature combustion the desired composition of the particles can be achieved.

The content of cerium oxide on the carrier was varied in the range of 0.1-3.0 wt.%. As the feedstock bioethanol of the following composition: ethyl alcohol (92%), t-butylcarbinol (5.6%), cyclohexane (0.64%), acetal (0.61%), isopropyl alcohol (0.47%), toluene (0.39%) was investigated.

Fig. 6 displays the results of bioethanol transformations to ethylene on catalysts with different content of cerium oxide. As can be seen from the figure incorporation of ceria into

the zeolite with a concentration of 0.1 wt. % leads to a minor increase in ethylene concentration in the products from 61 to 63 vol. %. With a further increase in the concentration of ceria to 0.5 wt. %, ethylene concentration increases from 63 to 67 vol. %. Subsequent increase in the content of ceria to 3.0 wt. % results in a decrease of catalytic activity.

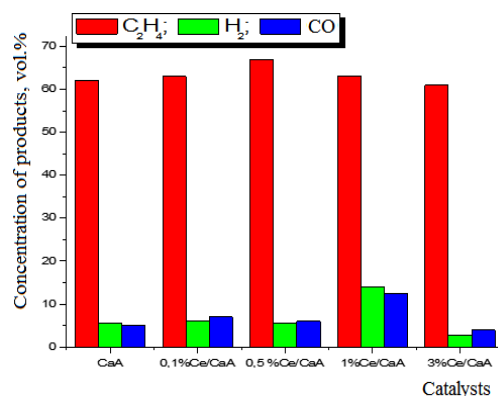


Fig. 6. Effect of ceria in zeolite A on ethylene concentration during bioethanol dehydration at WHSC = 60 h⁻¹ and reaction temperature 623K.

0.5 wt. % Ce₂O₃ / CaA which was active in transformations of bio-ethanol to ethylene was prepared also by the "solution combustion" method.

The results showed that at the transformation of ethanol over 0.5 wt. % Ce₂O₃ / CaA catalyst prepared by wetness impregnation concentration of ethylene in the reaction products was 67 vol. %, while for the catalyst synthesizing by «solution - combustion» method an increase of catalyst activity was noticeable since ethylene concentration reached 89 vol. %.

Influence of the preparation method was also investigated by thermal programmed reduction (TPR).

Fig. 7 shows TPR spectra of 0.5 Ce / CaA catalyst prepared by wetness impregnation (№ 1) and "solution-combustion" (№ 2).

In the TPR spectrum of catalyst 1 four peaks are observed with maxima at $T_{\max}^1 = 903\text{K}$, $T_{\max}^2 = 973\text{K}$, and $T_{\max}^3 = 1083\text{K}$ and $T_{\max}^4 = 1173\text{K}$. According to the literature [29], reduction of ceria takes place on the surface in the range 653-903K, while reduction in the bulk occurs at 903-1273 K.

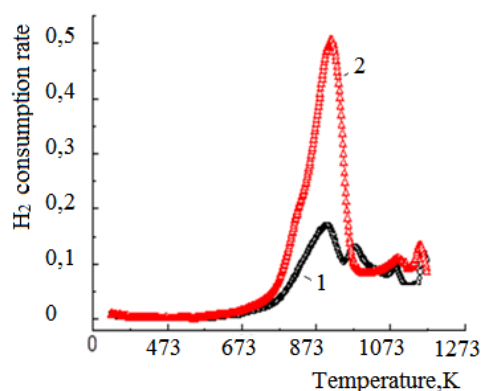


Fig. 7. TPR spectra of 0.5 Ce / CaA catalyst synthesized by: 1-wetness impregnation; 2-solution-combustion.

Synthesis of the catalyst by "solution-combustion" methods leads to an increase in the intensity of the peak at

$T_{\max}^I = 903$ K increasing ceria concentration on the surface and improving accessibility of bioethanol to the surface active sites.

IV. CONCLUSION

Summarizing the literature and our own data, it should be noted a significant role ceria in the hydrogenation and dehydration processes, characterized by multifunctionality, a positive influence on the selectivity, the process conditions, dispersion of the catalyst systems. Ceria improves the dispersion of the active component and also has its own catalytic activity.

Ceria is active catalyst for dehydration ethanol to ethylene. Electron microscopy showed that doping $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$ with lanthanum increases its dispersion, and some aggregates of fine (2 nm) particles could be observed. Temperature programmed desorption revealed that doping $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst with lanthanum raised the total number of acid sites from 22.57×10^{-4} to 23.38×10^{-4} mol / (g cat). The synthesized catalysts exhibited high activity and productivity in the catalytic conversion of ethanol. The highest activity was observed on the $\text{CeLa}/\gamma\text{-Al}_2\text{O}_3$ catalyst. At the optimum process parameters (reaction temperature, 623 K; 6000 h⁻¹), the yield of ethylene reached 82% at an ethanol conversion of 94% with a selectivity of 87.2%.

Preparation of 0.5 Ce/CaA catalyst by solution-combustion method leads to increasing concentration of ceria on the surface of carrier thereby interaction of bioethanol with surface active sites is facilitated.

A considerable amount of research and extremely interesting results of the study the use of cerium oxide in catalysis show the promise of this research area. The review covers only a few types of reactions catalyzed by ceria (dehydration, hydrogenation), although there are many more publications on application of ceria in other reactions including electrochemical oxidation, hydrogenation and dehydrogenation to name a few emphasizing importance of ceria as a catalytic material.

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