

Dehydration of 1,5-Pentanediol over Na-Doped CeO₂ Catalysts

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The effects of CeO₂ doped with Na on the dehydration of 1,5pentanediol were studied by using a fixed-bed reactor at two different temperatures (350 and 400 °C) and atmospheric pressure. For characterization, BET surface area, hydrogen temperature-programmed reduction, CO₂ temperature-programmed desorption, and diffuse reflectance infrared Fourier transform spectroscopy techniques were utilized. The conversion of the diol on CeO₂ was found to depend on Na loading. The selectivity to the desired product (i.e., unsaturated alcohol) increased and the selectivity to undesired products (i.e., tetrahydropyran, tetrahydropyran-2-one, cyclopentanol and cylopentanone) decreased with increasing Na content on CeO_2 . The basicity of hydroxyl groups or surface oxygen on CeO_2 was altered with the addition of Na, and controlled the dehydration reaction pathway.

selectivity to unsaturated alcohols was not defined. Igarashi

et al. have shown that the selectivity for unsaturated alcohol

from diol is influenced by the nature of the crystalline planes

present on the surface of ceria after calcination at various temperatures.^[15] In this regard, CeO₂ {111} facets become predomi-

nant on the larger particles and are active for the formation of

unsaturated alcohols, whereas CeO₂ {100} and {110} facets are

more exposed on the smaller ceria particles and catalyze side

ceria is the presence of defect sites. Diols are adsorbed on

defect sites on ceria; however, the defect sites are nonuniform

and sites located on different exposed planes have different re-

activity. In this regard, Wu et al. recently showed that rod-

shaped ceria has a greater number of defect sites than cubic

and octahedral geometries.^[20] Not only do defect sites change with the geometric structure of ceria, but the acid–base prop-

erties are altered as well. Kobune et al. observed that dehydration of 1,3- and 1,4-butanediol to unsaturated alcohol on ceria is a structure-sensitive reaction the activity of which increases with increasing particle size of ceria.^[4] Previously, we reported that Ga- and In-modified ceria displayed higher reactivity for dehydration of 1,5-pentanediol in comparison with ceria; moreover, the product spectrum shifted towards greater cyclization and cracking relative to dehydration. This was attributed to differences in the shape of ceria as well as the intrinsic activity of Ga and In.^[21] In the current contribution, the acid-base property of ceria was modified by the addition of Na. Temperature-programmed desorption (TPD) of CO₂ and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) techniques were employed to investigate the basic properties of the catalysts. The activity and selectivity for dehydration of 1,5pentanediol were correlated with the defect sites present on

Another factor to be considered regarding the catalysis of

reactions, such as cracking and cyclization.^[15]

Introduction

Cerium oxide (CeO₂, ceria) is known for its excellent redox property, and is useful for many applications, including the three-way catalyst for auto exhaust cleanup.^[1] The high oxygen storage capacity of ceria results from its rich density of oxygen vacancies. Likewise, the acid–base properties of ceria can catalyze transformations of a variety of organic molecules, including reactions such as dehydration, dehydrogenation, dimerization of alcohols, and condensation of aldehydes.^[2–10]

The conversion of pentanediol into value-added products is becoming increasingly important because of its abundance derived mainly from the biomass-based building block, furfural.^[11] One of the promising targets is the selective conversion of 1,5-pentanediol into 4-penten-1-ol, as it is one of the raw materials used to produce polymers.^[12] The Sato group^[13-19] has worked on the dehydration of diols over various rare earth oxides, and these authors found that the dehydration selectivity to unsaturated alcohol from 1,5-pentanediol on ceria remains lower in comparison with other diols, although the reason for such low

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the surface of ceria.



Results and Discussion

The amount of Na present in ceria and Na-doped ceria was measured experimentally by using inductively coupled plasma optical emission spectroscopy (ICP–OES) and the data are shown in Table S1 in the Supporting Information. The estimated values are in close agreement with the theoretical values calculated for all catalysts based on molecular formulae of NaCeO₂ except 0.08Na0.92Ce and 0.10Na0.90Ce catalysts, for which both were on the low side. Notably, even undoped ceria has a slight percentage of Na (0.22 wt%). As expected, data presented in Table S1 clearly show an increasing trend of Na content in the ceria samples studied. The surface areas and pore-size distributions of ceria and Na-doped ceria catalysts are shown in Table 1. The surface area of the calcined ceria

Table 1. BET surface area and average pore size							
Catalyst description	BET S.A. [m ² g ⁻¹]	Pore volume Single-point ^(a) BJH ^(b) [cm ³ g ⁻¹] [cm ³ g ⁻¹]		Pore o BET ^[c] [nm]	liameter BJH ^[d] [nm]		
CeO ₂ 0.01Na0.99Ce 0.02Na0.98Ce 0.05Na0.95Ce 0.08Na0.92Ce 0.1Na0.9Ce	114 112 112 100 88 83	0.167 0.164 0.164 0.149 0.141 0.137	0.171 0.169 0.168 0.153 0.144 0.140	5.8 5.8 5.9 6.3 6.6	4.5 4.5 4.6 4.8 4.7		
[a] Single-point pore volume obtained from single-point desorption total volume of pores at $P/P_o = 0.99$. [b] BJH desorption cumulative volume of pores between 1.7 and 300 nm diameter. [c] Desorption average pore diameter by BET. [d] BJH desorption average pore diameter.							

was 114 m²g⁻¹, and Na addition did not introduce any noticeable changes up to a Na content of 0.02. A systematic decreasing trend in BET surface area and pore volume was observed with further increases in Na content up to 0.1. The N₂ adsorption-desorption isotherms for ceria and various Na-doped ceria catalysts were measured at the boiling temperature of liquid nitrogen (-196°C) and are shown in Figure S1 in the Supporting Information. All samples show a typical type IV isotherm with hysteresis, which is a characteristic of mesopores. The BJH analysis infers that ceria possesses a narrow pore size distribution and the pore sizes range from 2.5 to 7.0 nm. The addition of Na to ceria was found to decrease both singlepoint as well as the BJH pore volumes. The results suggest that partial blockage in the pores of ceria occurred upon addition of Na above a certain level, which may have occurred during calcination. The XRD patterns of ceria and Na-doped ceria catalysts calcined at 500 °C are shown in Figure S2. The patterns are indexed to the cubic fluorite structure of ceria. The estimated crystallite sizes for various catalysts are 9.0-9.3 nm. This indicates that there are no significant differences in the phases of ceria formed with addition of Na.

The hydrogen temperature-programmed reduction (H_2 -TPR) profiles of the calcined sample of ceria and Na-doped ceria catalysts are depicted in Figure 1. A typical two-peak reduction pattern is observed between 300 and 500 °C and 650 and

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Figure 1. TPR profiles of CeO_2 and Na-doped CeO_2 catalysts: (a) CeO_2 , (b) 0.01Na0.99Ce, (c) 0.02Na0.98Ce, (d) 0.05Na0.95Ce, (e) 0.08Na0.92Ce, (f) 0.1Na0.9Ce.

850 °C for all catalysts. The first reduction peak is generally associated with the partial reduction (e.g., surface shell reduction) of ceria from Ce⁴⁺ to Ce³⁺ and the second peak is attributed to bulk reduction of ceria from Ce^{4+} to Ce^{3+} .^[22] The former may involve removal of surface-capping oxygen atoms resulting in oxygen vacancy defects^[22] and/or the formation of bridging OH groups, either from dissociative adsorption of hydrogen or formation of water and subsequent dissociation of water at the oxygen vacancy; ample evidence for the latter viewpoint has been provided by infrared spectroscopy experiments.^[23, 24] Note that replacing two surface O atoms by OH groups is accompanied by a change in oxidation state of associated Ce atoms from Ce⁴⁺ to Ce³⁺. Addition of Na to ceria up to 0.02 caused a shift in the reduction peaks to higher temperature. Further addition of Na (i.e., >0.02) to ceria resulted in a sharpening of the reduction peak associated with surface shell reduction. A likely explanation is that Na increases the basicity of the catalyst, resulting in greater stability of carbonate, as observed with low-temperature water-gas shift catalysts containing alkali metals.^[25] From investigations of the reduction of ceria by using X-ray absorption near-edge spectroscopy (XANES) and DRIFTS, it is well known that upon surface shell reduction of ceria, decomposition of surface carbonate also occurs, with the formation of bridging OH groups.^[21,22,26-29] The shift in reduction peaks to higher temperature upon Na addition indicates that the reduction process associated with the ceria surface is hampered by the presence of Na. Possible explanations include (1) Na hindering the hydrogen dissociative adsorption mechanism, attributed to a decreasing probability for the formation of adjacent bridging OH groups because of the presence of Na on the surface, and (2) Na increasing the stability of surface carbonate because of the increased surface basicity.

The CO₂-TPD profiles of ceria and Na-doped ceria (i.e., after reduction at 500 °C under flowing H₂ followed by the adsorption of CO₂ at 30 °C) are shown in Figure 2. Pure ceria displayed multiple peaks in the temperature range of 60–200 °C. The low-temperature peak at \approx 60 °C corresponds to the de-





Figure 2. TPD profiles of CO₂ of CeO₂ and Na-doped CeO₂ catalysts after reduction under flowing H_2 (50 cm³min⁻¹) at 500 °C for 2 h.

sorption of physically adsorbed CO₂ on ceria.^[30] The multiple peaks between 100 to 200 °C indicate the presence of basic sites of varying strengths on activated ceria. In general, the basic sites on ceria are attributed to the presence of hydroxyl groups and/or oxy anions associated with the partially reduced ceria sites (Ce–OH or Ce³⁺–O[–]). The addition of Na on ceria was found to suppress the overall intensity of the thermal conductivity detector (TCD) signal. This suggests that Na ions might undergo exchange with protons associated with hydroxyl groups on ceria and this could eventually have altered the adsorption property of CO₂. Gaillard found a single desorption peak between 130 and 180 °C from CO₂-TPD over ceria and the author attributed this to both mono- and bidentate carbonate species.^[31] In our case, the presence of Na has made the decomposition of carbonate become more difficult on ceria.

DRIFTS spectra of ceria and Na-doped ceria after pre-treatment conditions are shown in Figure 3. Ceria is known to adsorb CO₂ from the atmosphere and forms various carbonate species (e.g., bicarbonate, bridged carbonate, bidentate carbonate, monodentate carbonate) depending on the nature of the adsorption sites.^[20] The DRIFTS spectra, as shown in Figure 3 in the region between 1200 and 1600 cm⁻¹, are assigned to the vibrations of various carbonate species. The intensities of the peaks (1350 cm⁻¹ and 1450 cm⁻¹) increase with increasing Na content on ceria up to 0.05, with a further increase in Na causing the merging of the two peaks into a single peak with a relatively higher intensity. This shows that the amount of CO₂ left over on ceria after activation depends on the net Na content in the catalyst. Under the reducing environment, CO₂ was likely bound to hydroxyl groups as well as coordinatively unsaturated oxygen vacancy sites on ceria, and, therefore, the number of sites available on ceria for adsorption of diols was diminished. This is reflected in the DRIFTS results over the hydroxyl region for various reduced catalysts. There are at least two major types of OH groups present on the surface of reduced ceria. They are type I terminal OH groups (3700–3720 cm⁻¹) and lower wavenumber type II bridging OH



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Figure 3. DRIFTS images for the CeO_2 and Na-doped CeO_2 catalysts after reduced under flowing H₂/He at 500 °C. The difference spectra were made by using KBr as a background. (top, carbonate region; bottom, hydroxyl region).

groups (Scheme 1) with the main band associated with Ce^{3+} defects located in the 3630–3660 cm^{-1.[27,32]}

In our case, the peak intensity of type II bridging OH groups remained more or less the same with the addition of Na on ceria up to 0.05, and further addition resulted in a steep decrease in the intensity. This suggests that Na primarily targeted the negatively charged oxyanion species initially and then replaced the protons according with



OH (II-B)



placed the protons associated with hydroxyl groups on ceria.

The dehydration of 1,5-pentanediol was compared for various catalysts at two different temperatures (350 and 400 °C). The effect of Na addition to ceria for the conversion of 1,5-pentanediol at 350 °C is shown in Figure 4. All catalysts exhibited a relatively stable conversion. A systematic decrease in conversion of diol was observed with the addition of Na on ceria. Both CeO₂ and 0.01Na0.99Ce catalyst samples displayed similar conversions (\approx 45–48%), whereas the 0.02Na0.98Ce sample had a lower conversion of \approx 32%. The samples having higher Na content (i.e., 0.05Na0.95Ce, 0.08Na0.92Ce, and 0.1Na0.90Ce)





Figure 4. Conversion of 1,5-pentanediol over CeO₂ and Na-doped CeO₂ catalysts. Reaction conditions: 350 $^{\circ}$ C, 1 atm, 0.6 mL h⁻¹ of 1,5-pentanediol, $H_2 = 50 \text{ cm}^3 \text{min}^{-1}$.

exhibited much lower conversion. The selectivity to 4-penten-1-ol and 1-pentanol plotted against Na content are shown in Figure 5. The selectivity to the desired product (i.e., 4-penten-1-ol) increased with Na content and, at the same time, increasing Na content tended to decrease the conversion of diols for ceria. The CO₂-TPD and DRIFTS studies indicate that Na altered the acid-base characteristics of ceria, which could play an important role in the activity and the selectivity of the dehydration reaction. The selectivities of CeO₂ and various Na-doped CeO₂ catalysts were compared at similar conversion levels so that the effect of conversion on selectivity could be ruled out. In this regard, the data in Figure 6 and Table 2 reveal an increasing trend of selectivity to 4-penten-1-ol and 1-pentanol from 12.2 and 22.2% for ceria to 34.5 and 28.2% for 0.1Na0.9Ce, respectively. In contrast, selectivity to the cyclized products such as tetrahydropyran (THP) derivatives, cyclopentanol, and cyclopentanone decreased. This suggests that Na addition to ceria influences the reaction pathways for 1,5-pentanediol.

The adsorption of 1,5-pentanediol may take place on the surface of reduced ceria. Depending upon the nature of sites, as shown in Scheme 2, the reactant undergoes dehydration and forms unsaturated alcohols or it might be involved in cyc-



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Figure 5. Effect of Na content in CeO₂ on the conversion and the product selectivity for the dehydration reaction of 1,5-pentanediol. Reaction conditions: 350 °C, 1 atm, 0.6 mL h⁻¹ of 1,5-pentanediol, $H_2 = 50 \text{ cm}^3 \text{min}^{-1}$.



Figure 6. Effect of Na content in CeO₂ on the product distribution for the dehydration of 1,5-pentanediol at similar conversion levels. Reaction conditions: 400 °C, 1 atm, 0.6–1.8 mL h^{-1} of 1,5-pentanediol, $H_2 = 50 \text{ cm}^3 \text{min}^{-1}$. CyP-ol, cyclopentanol; CyP-one, cyclopentanone; THP, tetrahydropyran.

lization that leads to tetrahydropyran (THP), tetrahydropyran-2one (THP-2-one), cyclopentanol, or cyclopentanone formation. It is reported that either the acid-base property or the surface

Table 2. Dehydration of 1,5-pentanediol on CeO ₂ and Na-doped CeO ₂ catalysts.								
Description	Calcination temp. [°C]	Conversion of 1,5-pentanediol [%] ^[a]	Product distributions [%] 4-penten-1-ol 1-pentanol Cyclopentanol Cyclopentanone THP derivatives ^(b) Ot					Others ^[c]
CeO ₂	500	65.6	12.2	22.2	3.8	31.5	8.9	21.4
0.01Na0.99Ce	500	48	22.2	16.5	0	31.3	26	4
0.02Na0.98Ce	500	51.7	18.7	20.2	16.2	14.7	21.1	9.1
0.05Na0.95Ce	500	51.3	28.2	24.1	0	24.7	20.2	2.8
0.08Na0.92Ce	500	48.5	31.3	27.0	1.4	20	16.2	4.1
0.1Na0.9Ce	500	49.4	34.5	28.2	1.5	20	12.6	3.2
[a] Reaction conditions: 400 °C, 1 atm, 0.6–1.8 mLh ⁻¹ of 1,5-pentanediol, H ₂ =50 cm ³ min ⁻¹ ; [b] THP derivatives include tetrahydropyran, tetrahydropyran-2- one: [c] others include ethanol, acetone, 1-propanol, pentanal, cyclohexanone, cyclohexanemethanol, 4-penten-1-ol propanoate, valeric, acid, pentenyl								

ester.

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Tetrahydropyran-2-one

Scheme 2. Formation of various products from the dehydration of 1,5-pentanediol over CeO₂ and Na-doped CeO₂ catalysts.

geometry of rare earth oxides affects the formation of cyclic ethers from the dehydration of 1,4-butanediol.^[33] A recent report suggests that a strong adsorptive interaction between the catalyst and reactant would be favorable for the formation of unsaturated alcohols from the corresponding diols.^[34] In our study, Na addition appears to increase the surface basicity of ceria resulting in a decrease in the dehydration activity owing to a loss in active sites (both oxygen vacancy sites as well as basic hydroxyl groups) and a change in the selectivity from cyclized product to the desired product (i.e., unsaturated alcohol). This is manifested by the nature of the neighboring sites associated with oxygen vacancy sites on ceria. Thus, the addition of Na provides ceria with a controlled environment that prevents THP formation from 1,5-pentanediol. A study on the effect of other alkali and alkali earth metals added to ceria for the dehydration of 1,5-pentanediol is in progress. This further enhances the understanding of the mechanisms of various products formed from 1,5-penetanediol over ceria and its interrelation to acid-base properties.

The effect of calcination temperature on ceria and Na-doped ceria catalysts was investigated for the dehydration of 1,5-pentanediol, and the data collected after 3 h of time on-stream are shown in Table 3. The dehydration reaction was performed at

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400 °C and atmospheric pressure either by flowing H_2 or N_2 (50 sccm) along with 1,5-pentanediol. For CeO₂, higher calcination temperature (800 °C) resulted in a positive effect on the conversion of 1,5-pentanediol whereas the selectivity for 4-penten-1-ol and 1-pentanol did not vary significantly with calcination temperature. However, THP formation decreased but cyclopentanone content increased with increasing calcination temperature. On the other hand, the 0.1Na0.9Ce catalyst exhibited decreasing conversion of 1,5-pentanediol with increasing calcination temperature from 500 to 800°C. Moreover, the selectivity to 4-penten-1-ol was diminished in the presence of flowing H₂ from 34.5 to 20.8% with increasing calcination temperature, and, consequently, 1-pentanol selectivity increased from 28.2 to 34.9%. A similar trend was observed using 0.1Na0.9Ce catalyst in N₂ atmosphere. The results indicate that lower calcination temperature favors the

formation of desired product (i.e., 4-penten-ol) from 1,5-pentanediol using 0.1Na0.9Ce. The higher activity has been reported with increasing calcination temperature of CeO₂ for dehydration of 1,3- and 1,4-butanediols.^[4,35] In the present study, the use of H₂ instead of N₂ along with reactant provided a positive effect both on conversion as well as selectivity towards unsaturated alcohol.

Conclusions

Vapor-phase catalytic dehydration of 1,5-pentanediol was investigated over ceria and Na-modified ceria catalysts. The addition of Na to ceria was found to enhance the selectivity to unsaturated alcohol (i.e., 4-penten-1-ol) at similar conversion levels and to suppress the selectivity to cyclized products such as tetrahydropyran, tetrahydropyran-2-one, cyclopentanol, and cyclopentanone from 1,5-pentanediol. Temperature-programmed reduction profiles indicate that the partial reduction of surface ceria was hampered with addition of Na. Diffuse reflectance infrared Fourier transform spectra and CO₂ temperature-programmed desorption profiles of the activated catalysts revealed that the basicity of Na-doped ceria was higher than that of the undoped catalyst. The addition of Na on ceria re-

Table 3. Effect of the carrier gas on the dehydration of 1,5-pentanediol over CeO ₂ and 0.1Na0.99Ce at different calcination temperatures.										
Description	Carrier gas	Calcination temp. [°C]	Time on stream [h]	Conversion of Product distributions [%] 1,5-pentanediol [%] ^[a] 4-penten-1-ol 1-pentanol Cyclopentanol Cyclopentanone THP derivatives ^[b] O			Others ^[c]			
CeO ₂	H ₂	500	3	65.6	12.2	22.2	3.8	31.5	8.9	21.4
	H ₂	800	3.5	74.4	12	22.1	0.2	41.2	4.7	19.8
	N ₂	500	3	62.4	11	21.4	3.6	35.4	8.9	19.7
	N_2	800	3	72.4	9	21	0.7	43.4	2.8	23.1
0.1Na0.9Ce	H₂	500	2.5	49.4	34.5	28.2	1.5	20	12.6	3.2
	H ₂	800	3	26.4	20.8	34.9	3.5	14.1	13.2	13.5
	N ₂	500	2	39	29	26.9	2	17.9	8.1	16.1
	N ₂	800	3	25.7	16.5	30.3	3.8	17.6	11.1	20.7
[a] Reaction conditions: 400°C, 1 atm, feed rate of 1,5-pentanediol (1.2 mLh ⁻¹ for CeO ₂ and 0.6 mLh ⁻¹ for 0.1Na0.9Ce), H ₂ or N ₂ =50 cm ³ min ⁻¹); [b] THP derivatives include tetrahydropyran, tetrahydropyran-2-one; [c] others include ethanol, acetone, 1-propanol, pentanal, cyclohexanone, cyclohexanemetha-										

nol, 4-penten-1-ol propanoate, valeric acid pentenyl ester.

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duces both the density of reduced defect centers (i.e., oxygen vacancies and associated bridging hydroxyl groups) which adversely affects the activity of ceria for the dehydration of 1,5-pentanediol but, on the other hand, promotes the selectivity to desired products. The higher calcination temperature of CeO₂ favors higher activity for the dehydration of 1,5-pentanediol whereas low calcination temperature shifts the selectivity for 0.1Na0.9Ce catalyst more towards unsaturated alcohols.

Experimental Section

Catalyst preparation

The ceria utilized in this study was HSA-10 Rhodia CeO₂. The material was calcined in static air at 500 °C for 4 h and further used for loading Na to different levels. An appropriate amount of Na (atomic fractions, 0.01Na0.99Ce, 0.02Na0.98Ce, 0.05Na0.95Ce, 0.08Na0.92Ce, 0.1Na0.9Ce) was introduced into ceria in the form of aqueous sodium nitrate (99.999% Sigma Aldrich) solution by following the incipient wetness impregnation (IWI) procedure. The resulting solid was then dried in an oven at 100 °C for 24 h and further calcined in a muffle furnace at 500 or 800 °C for 4 h.

Characterization

Elemental analysis of Na present in all catalyst samples was determined by ICP-OES using a Varian 720-ES analyzer. The materials were dissolved in a perchloric/nitric acid mixture and the emission spectra of dissolved species were compared to those of a series of standard solutions of known concentrations. Specific surface areas of calcined catalysts were measured by the BET method using a Micromeritics 3-Flex system. Before performing the test, the temperature was gradually increased to 160°C, and the sample was evacuated at the same temperature for 12 h to a pressure of 6.67 Pa. The BET surface area, single-point pore volume, and singlepoint average pore diameter were obtained. The Barrett-Joyner-Halenda (BJH) method was used to estimate pore volume, pore diameter, and pore-size distribution as a function of pore radius. Powder X-ray diffractograms of the calcined catalysts were recorded using a Philips X'Pert diffractometer with monochromatic $Cu_{K\alpha}$ radiation (λ = 1.5418). XRD scans were taken over the range of 2hetafrom 10-90°. The scanning step was 0.01, the scan speed was 0.0025 s⁻¹, and the scan time was 4 s. The crystallite sizes of ceria were determined using the Scherrer equation, $B = K\lambda/L\cos\theta$ (in which B stands for peak width, K is a constant (0.94), λ equals to 0.154 Å, and L is the mean size of ordered crystalline domains. TPR profiles for catalyst samples were recorded using a Zeton-Altamira AMI-200 unit, which makes use of a thermal conductivity detector (TCD). Typically, a 200 mg quantitiy of the sample was first subjected to a heat treatment at 350 °C in a flow of pure Ar (30 cm³min⁻¹) to remove residual water from the sample. The sample temperature was then cooled to 50°C before the start of the TPR experiment. TPR was performed by using a 10%H₂/Ar mixture referenced to Ar at a flow rate of 30 cm³min⁻¹. The sample was heated to 800 °C at a ramp rate of 10 °C min⁻¹. The TPD of adsorbed CO₂ was examined by using an in-house system consisting of a furnace capable of operating at temperatures of up to 1200°C, along with a TCD. Prior to TPD, the samples were pretreated at 500 °C in flowing H_2 (50 cm³min⁻¹) for 2 h. The samples were then saturated with pure CO₂ at 30 °C for 1 h and subsequently flushed with He to remove the physisorbed CO2. The CO2-TPD was performed by using He and the temperature was increased to 850 °C at a ramp rate of 6.8 °C min⁻¹. DRIFTS spectra of samples were recorded using a Nicolet Nexus 870 spectrometer equipped with a deuterated triglycine sulfate and thermoelectrically cooled (DTGS–TEC) detector. A thermo spectra–tech cell capable of high-pressure/high-temperature operation and fitted with ZnSe windows served as the chamber for in situ reduction treatments. Scans were taken before and after reduction in 100 cm³ min⁻¹ of H₂/He at 500 °C at a resolution of 4 cm⁻¹ to give a data spacing of 1.928 cm⁻¹. The difference spectra were made using KBr as the background.

Dehydration activity

The dehydration reaction was performed by using a fixed-bed reactor in the temperature range between 350 and 400 °C and atmospheric pressure. Typically, the calcined catalyst (1.0 g) in a powder form (40-100 µm) was loaded into the reactor. The reactor was a stainless-steel tube having a length of 35.6 cm with an internal diameter of 0.9 cm. The toal catalyst bed length was approximately 2.54 cm. The catalyst was pretreated under flowing H₂ (50 cm³min⁻¹) at 500 $^{\circ}$ C for 2 h. The catalyst-bed temperature was monitored by a movable thermocouple (K-type) housed in a thermowell. The catalyst-bed temperature was decreased to the desired reaction temperature (350-400 °C) and 1,5-pentanediol (99.9% Sigma Aldrich) was fed at the desired flow rate by using a syringe pump and combined with flowing H_2 or N_2 (50 cm³min⁻¹). The products were collected in a trap maintained at room temperature. The effluent gases were collected in a Tedlar gas bag during various time intervals and analyzed using a micro GC (HP quad series gas analyzer) to identify the formation, if any, of lower hydrocarbons. The liquid products condensed at room temperature were analyzed by using an Agilent 7890 gas chromatograph equipped with a DB-5 capillary column and a flame ionization detector (FID). An appropriate FID response correction factor as published in the open literature was applied for each component found in the reaction mixture.[36]

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Conflict of interest

The authors declare no conflict of interest.

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- [1] A. Trovarelli, Catal. Rev. Sci. Eng. **1996**, 38, 439–520.
- [2] S. Sato, F. Sato, H. Totoh, Y. Yamada, ACS Catal. 2013, 3, 721-734.
- [3] D. Haffad, A. Chambellan, J. C. Lavalley, J. Mol. Catal. A 2001, 168, 153– 164.
- [4] M. Kobune, S. Sato, R. Takahashi, J. Mol. Catal. A 2008, 279, 10-19.
- [5] S. Sato, R. Takahashi, N. Yamamoto, E. Kaneko, H. Inoue, Appl. Catal. A 2008, 334, 84–91.
- [6] B. M. Reddy, G. K. Reddy, L. Katta, J. Mol. Catal. A 2010, 319, 52-57.
- [7] B. M. Reddy, P. Lakshmanan, P. Bharali, P. Saikia, J. Mol. Catal. A 2006, 258, 355–360.
- [8] M. G. Cutrufello, I. Ferino, E. Rombi, V. Solinas, G. Colon, J. A. Navio, *React. Kinet. Catal. Lett.* 2003, 79, 93–99.
- [9] A. K. P. Mann, Z. Wu, F. C. Calaza, S. H. Overbury, ACS Catal. 2014, 4, 2437–2448.

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- [10] H. Idriss, C. Diagne, J. P. Hindermann, A. Kiennemann, M. A. Barteau, J. Catal. 1995, 155, 219–237.
- [11] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M. L. Granados, Energy Environ. Sci. 2016, 9, 1144–1189.
- [12] W. Wang, L. Hou, S. Luo, G. Zheng, H. Wang, Macromol. Chem. Phys. 2013, 214, 2245–2249.
- [13] M. Segawa, S. Sato, M. Kobune, T. Sodesawa, T. Kojima, S. Nishiyama, N. Ishizawa, J. Mol. Catal. A 2009, 310, 166–173.
- [14] H. Gotoh, Y. Yamada, S. Sato, Appl. Catal. A 2010, 377, 92-98.
- [15] A. Igarashi, N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa, Appl. Catal. A 2006, 300, 50-57.
- [16] S. Sato, R. Takahashi, M. Kobune, H. Inoue, Y. Izawa, H. Ohno, K. Takahashi, Appl. Catal. A 2009, 356, 64–71.
- [17] N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa, H. Fujita, T. Atoguchi, A. Shiga, J. Catal. 2006, 239, 13–22.
- [18] F. Sato, H. Okazaki, S. Sato, Appl. Catal. A 2012, 419-420, 41-48.
- [19] F. Sato, S. Sato, Catal. Commun. 2012, 27, 129-133.
- [20] Z. Wu, A. K. P. Mann, M. Li, S. H. Overbury, J. Phys. Chem. C 2015, 119, 7340-7350.
- [21] M. K. Gnanamani, G. Jacobs, W. D. Shafer, S. D. Hopps, B. H. Davis, *ChemistrySelect* 2017, 2, 4150-4156.
- [22] H. C. Yao, Y. F. Y. Yao, J. Catal. 1984, 86, 254-265.
- [23] C. Binet, M. Daturi, J. C. Lavalley, Catal. Today 1999, 50, 207-225.
- [24] G. Jacobs, U. M. Graham, E. Chenu, P. M. Patterson, A. Dozier, B. H. Davis, J. Catal. 2005, 229, 499–512.

- [25] H. N. Evin, G. Jacobs, J. Ruiz-Martinez, G. A. Thomas, B. H. Davis, Catal. Lett. 2008, 120, 166–178.
- [26] J. El Fallah, S. Boujani, H. Dexpert, A. Kiennemann, J. Majerus, O. Touret, F. Villain, F. Le Normand, J. Phys. Chem. 1994, 98, 5522-5533.
- [27] A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J. C. Lavalley, J. El Fallah, L. Hilaire, F. Le Normand, E. Quemere, G. N. Sauvion, O. Touret, J. Chem. Soc. Faraday Trans. 1991, 87, 1601.
- [28] G. Jacobs, S. Ricote, P. M. Patterson, U. M. Graham, A. Dozier, S. Khalid, E. Rhodus, B. H. Davis, *Appl. Catal. A* 2005, 292, 229-243.
- [29] G. Jacobs, L. Williams, U. Graham, D. Sparks, B. H. Davis, J. Phys. Chem. B 2003, 107, 10398-10404.
- [30] X. Jiao, L. Li, N. Zhao, F. Xiao, W. Wei, Energy Fuels 2013, 27, 5407-5415.
- [31] F. Gaillard, Catal. Lett. 2004, 95, 23-29.
- [32] A. Badri, C. Binet, J. C. Lavalley, J. Chem. Soc. Faraday Trans. 1996, 92, 4669-4673.
- [33] S. Sato, R. Takahashi, T. Sodesawa, A. Igarashi, H. Inoue, Appl. Catal. A 2007, 328, 109-116.
- [34] H. Duan, M. Unno, Y. Yamada, S. Sato, Appl. Catal. A 2017, 546, 96-102.
- [35] S. Sato, R. Takahashi, T. Sodesawa, N. Honda, H. Shimizu, *Catal. Commun.* 2003, *4*, 77–81.
- [36] W. A. Dietz, J. Gas Chromatogr. 1967, 5, 68-71.

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FULL PAPERS

M. K. Gnanamani, G. Jacobs, M. Martinelli, W. D. Shafer, S. D. Hopps, G. A. Thomas, B. H. Davis*

Dehydration of 1,5-Pentanediol over Na-Doped CeO₂ Catalysts H = 0 H =

On a sodium basis: Na-doped ceria converts 1.5-pentanediol more selectively to unsaturated alcohol than undoped ceria. The basicity of catalysts determines the reaction pathway. Oxygen vacancies on the surface of ceria are the primary adsorption sites for alcohols.