

Dehydration of 1,5-Pentanediol over CeO₂-MeOx Catalysts

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The dehydration reaction of 1,5-pentanediol was performed over CeO₂ and modified CeO₂ (CeO₂—MnO_x, CeO₂—ZnO, CeO₂—MgO, CeO₂—CaO, CeO₂—Na₂O) catalysts in a fixed-bed tubular reactor at 350 °C and an atmospheric pressure. The undoped CeO₂ produced a mixture of the products containing mainly 4-penten-1-ol, 1-pentanol, cyclopentanol, cyclopentanone and tetrahydropyran-2-one from 1,5-pentanediol, while additions of MgO, MnO_x, or ZnO to CeO₂ was found to enhance the overall production rate of unsaturated alcohol. On the other

Introduction

Vapor phase dehydration of diols is catalyzed by various metal oxides that include rare earth oxides.^[1-4] Dehydration of diol is an important reaction that generate unsaturated alcohols, a raw material used in the polymer and fine chemicals industry.^[5-8] In the past, however, selective conversion of the diols into unsaturated alcohol was achieved with 1,3- and 1,4diols.^[9,10] Dehydration of 1,5-pentanediol often producing more cyclized products such as cyclopentanol, tetrahydropyran than the desired product, i.e., unsaturated alcohol using REO's. Sato^[5,11-15] has claimed that rare earth oxides (REO's) such as CeO₂, Tb₄O₇, ErO₂O₃, and Yb₂O₃ were effective on producing unsaturated alcohols from various terminal diols. Regarding 1,5pentanediol, Sc₂O₃^[13] Lu₂O₃, and Sc–Yb mixed oxides^[14] have shown a higher activity and more selective to 4-penten-1-ol. CeO₂ exhibits the lower activity for dehydration of 1,5pentanediol in comparison with other diols and moreover the selectivity to 4-penten-1-ol was achieved as high as 25% at 400 °C.^[5]

 CeO_2 is well-known as a redox catalyst due to its high oxygen storage capacity. The defect centers are produced upon O elimination from CeO_2 and re-oxidation by O_2 would happen even at room temperature as shown in Scheme 1. This oxygen deficiency can act as an adsorption site for reactants such as CO, H₂O and alcohols including diols. Earlier, Sato proposed that Ce cations exposed at an oxygen-defect site of CeO_2 (111) surface are the active center for the dehydration of diols.^[5] The conversion of diols increases with an increase in the CeO_2 particle size possibly due to more CeO_2 (111) facets on larger

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 E-mail: burtron.davis@uky.edu hand, more basic metals like CaO or Na₂O tend to decline the dehydration activity of CeO₂. The porous structure of CeO₂ did not change appreciably with the addition of metal oxides. Temperature programmed desorption of adsorbed CO₂ on an activated catalyst suggest more CO₂ remain on the catalyst surface, particularly CeO₂–CaO and CeO₂–Na₂O indicating that fewer defect sites are only available for reaction. The defect sites or oxygen vacancy on CeO₂ controls both activity and selectivity for the dehydration of 1,5-pentanediol.

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Scheme 1. Formation of oxygen defect center on CeO₂

particles.^[12] On the other hand, CeO₂ also catalyze side reactions such as dehydrogenation and/or cyclization producing cyclopentanol, cyclopentanone, and tetrahydropyran-2-one from 1,5-pentanediol.

In a recent study, we have investigated the effects of addition of Na on ceria for the conversion of 1,5-pentanediol and found that Na additions to CeO₂ enhanced 4-penten-1-ol formation from 1,5-pentanediol.^[16] The basicity of CeO₂ was found to increase with increasing Na content and this could eventually affect the formation of defect centers (i.e., oxygen vacancy and the associated bridged hydroxyl groups) on CeO₂ while activation in hydrogen. In the present work, CeO2 is modified by the addition of different metal oxides with the aim of altering the basic property and the defect sites of CeO₂ to control both activity and selectivity for dehydration of 1,5pentanediol. All catalysts were characterized by X-ray diffraction (XRD), BET surface area, temperature programmed reduction (H₂-TPR), temperature programmed desorption of CO₂ (CO₂-TPD) and attenuated total reflection Fourier transform infrared (ATR-FTIR) techniques. Our results indicate that the defect sites are responsible for both activity and the associated side reactions occur on CeO₂ during dehydration of 1,5-pentanediol.

Results and Discussion

The XRD patterns of CeO_2 and modified CeO_2 are shown in Figure 1. All samples show a typical diffraction pattern of fluorite-like cubic structure of CeO_2 as identified using the

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Figure 1. XRD patterns of CeO₂ and modified CeO₂ catalysts after calcinations at 500 $^\circ$ C.

standard data JCPDS Card No. 81-0792. For a cubic structure, the lattice constant 'a' is evaluated using the relation [Eq. (1)],

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$
(1)

Where, (hkl) are the Miller indices and d is the interplanar spacing. The lattice parameter of CeO₂ was found to be 5.424 Å. The data agree well with those reported in the literature.^[17–19] The addition of MeO_x have decreased the lattice parameter of CeO₂ from 5.424 to 5.421 for MnO_x, 5.414 for ZnO, 5.408 for MgO, 5.421 for CaO and 5.417 for Na. This change in the lattice parameter could be interpreted due to differences in the ionic radius between CeO₂ and MeO_x. Here all additives containing metal cations are smaller in size relative to Ce⁴⁺ and thus the lattice parameter is expected to shrink with the addition of metal oxides (MnO_x, ZnO, MgO, CaO, and Na₂O) indicating the intrusion of metal cations into the lattice of CeO₂.

BET surface area and average pore size distributions for CeO_2 and modified CeO_2 are shown in Table 1 and Figure 2. Both BET surface area as well as the pore volume of CeO_2 were decreased with the addition of MeO_x . As seen in Table 1, the surface area for pure CeO_2 was $114 \text{ m}^2/\text{g}$ and it was dropped to 100 for CeO_2 — MnO_x , 95 for CeO_2 —ZnO, 93 for CeO_2 —MgO, 92 for CeO_2 —CaO and 83 for CeO_2 — Na_2O catalysts. The hysteresis corresponds to a type-IV isotherm which remains unaltered by



Figure 2. BJH adsorption-desorption isotherms (top) and corresponding BJH pore size distributions (bottom) of CeO_2 and modified CeO_2 catalysts calcined at 500 °C.

the addition of MeO_x and BJH pore size distributions for CeO_2 has been shifted slightly to lower pore diameter as shown in Figure 2 indicating that MeOx did not affect the porosity of CeO_2 .

The temperature programmed reduction profiles using hydrogen for various CeO_2 -based catalysts are shown in Figure 3. Pure CeO_2 shows a typical two peak reduction pattern. The maxima for the low temperature peak is 463 °C corresponding to partial reduction of surface cerium oxide from Ce^{4+} to Ce^{3+} and another peak at 787 °C related to the bulk reduction

Table 1. BET surface area and average pore size of CeO ₂ and modified CeO ₂ catalysts.										
Catalyst description	BET surface area [m²/g]	Single point pore volume ^(a) [cm ³ /g]	BJH pore volume ^[b] [cm³/g]	Pore diameter ^[c] [nm]	BJH pore diameter ^[d] [nm]					
CeO ₂	114	0.167	0.171	5.8	4.5					
CeO ₂ -MnO _x	100	0.149	0.153	5.9	4.6					
CeO ₂ -ZnO	95	0.149	0.152	6.3	4.8					
CeO ₂ –MgO	93	0.142	0.146	6.2	4.6					
CeO ₂ –CaO	92	0.130	0.133	5.6	4.4					
CeO ₂ -Na ₂ O	83	0.137	0.140	6.6	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 nm and 300 nm diameter; [c] Desorption average pore diameter by BET; [d] BJH desorption average pore diameter.

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Figure 3. H₂-TPR patterns of CeO₂ and modified CeO₂ catalysts.

of CeO₂. Doping of various metal oxides was found to shift the reduction temperatures of CeO_2 . The CeO_2 -MnO_x catalyst displayed a strong TCD response at 200 °C which can be assigned to the reduction of manganese oxide from MnOx to Mn_3O_4 and another peak at 329 °C corresponds to the partial reduction of surface cerium oxide along with the reduction of Mn₃O₄ to MnO. However, the high temperature reduction profile remains unaffected for CeO_2 by the addition of MnO_x indicating that the presence of manganese improves the reducibility of cerium oxide [20]. Similarly, CeO2-ZnO also seems to decrease the reduction temperature of CeO₂. The extent of reduction of CeO₂ in CeO₂–ZnO might be higher than CeO₂ alone as seen with increase in the intensity of reduction peaks. On the other hand, MgO has shifted the reduction peaks of CeO₂ from 463 to 502 °C. The intensity of high temperature peak for CeO₂ has been reduced significantly. The low temperature profile for CeO2-MgO appearing at 410°C can be attributed to CO₂ evolution from MgO. Likewise, CaO and Na₂O containing CeO₂ also show very strong TCD signals between 450-490 °C correspond to evolved CO₂. The H₂-TPR reveals that MnO_x and ZnO additions have a positive effect on the cerium oxide reduction while MgO, CaO and Na₂O tend to suppress it.

The CO₂-TPD profiles of CeO₂ and modified CeO₂ after activation in hydrogen at 500 °C are shown in Figure 4. The pure CeO₂ displayed two evident peaks, the first peak was centered at ~110 $^\circ\text{C}$ and another with maxima at about 150 $^\circ\text{C}$ and both are related to a weakly adsorbed CO₂ on CeO₂. After addition of MeO_x to CeO_2 , the intensity of both peaks dropped and at the same time the high-temperature shoulder at 175 °C has been shifted further to a higher value. This reveals that the addition of MeO_x could generate more medium strength basic sites. In addition, CeO_2 –MnO_x and CeO_2 –MgO were shown a broad peak between 300 to 500 °C and it could be attributed to the desorption of CO₂ from a separate MeO_x species. Similarly, CeO2-CaO exhibits multiple high temperature peaks between 130 to 300 °C. This high temperature peak can be attributed to desorption of the adsorbed CO₂ species from separate CaO phase.^[21] However, the amount of CO₂ desorbed from





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Figure 4. TPD of CO $_2$ on CeO $_2$ and modified CeO $_2$ catalysts after H $_2$ activation at 500 $^\circ\text{C}.$

CeO₂–Na₂O is relatively low compared to all other catalysts. Boaro et al.^[22] proposed a strong adsorption of CO₂ on the reduced Ce³⁺ sites. Therefore, one could correlate the amount of desorbed CO₂ to oxygen vacancy sites on a reduced CeO₂. In this case, the addition of more basic metal oxides such as MgO, CaO and Na₂O tend to suppress the oxygen vacancy sites on CeO₂ after activation due to CO₂ being desorbed.

ATR-FTIR technique was used to analyze adsorbed CO_2 on calcined samples from atmosphere. The spectrum collected at room temperature are shown in Figure 5. The pure CeO_2 and



Figure 5. ATR-FTIR spectrum of CeO₂ and modified CeO₂ catalysts.

modified CeO₂ catalysts exhibit carbonate bands between 1310 and 1600 cm⁻¹. A shoulder peak at 1630 cm⁻¹ δ (HOH) can be assigned to the bending vibrations of undissociated water molecule. The addition of MeOx tends to shift carbonate bands to a higher wavenumber indicating the increased stability of



carbonate species on modified CeO₂ catalysts compared to pure CeO₂. Based on the relative absorptivity, Na-modified CeO₂ possess more CO₂ meaning that more basic than CeO₂–CaO. The relative basicity of catalysts decrease in the following order: CeO₂–Na₂O > CeO₂–CaO > CeO₂–MgO > CeO₂=CeO₂–ZnO > CeO₂–MnO_x. Altogether, CeO₂–Na₂O is expected to release less CO₂ during activation with hydrogen and form oxygen vacancy sites on CeO₂. If this is the case, CeO₂–ZnO and CeO₂–MnO_x should have higher vacancy sites than pure CeO₂ after pretreatment and that should be reflected on dehydration activity.

The conversion of 1,5-pentanediol on ${\rm CeO}_2$ and modified-CeO_2 catalysts are shown in Figure 6. Oure CeO_2 shows 40 \%



Figure 6. Conversion of 1,5-pentanediol over CeO₂ and modified CeO₂ catalysts. Reaction conditions: 350 °C, 1 atm, LHSV=0.6 ml/h, carrier gas= H_2 (50 sccm), 1.0 g catalyst.

conversion of diol that remained more or less the same, while CeO_2 -MnO_x and CeO_2 -ZnO both exhibited a higher conversion (CeO_2 -MnO_x: 48-50% and CeO_2 -ZnO: 60%) than CeO_2 and other modified CeO_2 catalysts. The conversion of 1,5-pentane-diol decreased in the following order: CeO_2 -ZnO> CeO_2 -MnO_x> CeO_2 CeO₂-MnO_x> CeO_2 -CaO> CeO_2 -Na₂O. The

selectivity to various products obtained for all catalysts are summarized in Table 2. The selectivity for 4-penten-1-ol on CeO_2 -MnO_x (17.4%) and CeO_2 -ZnO (18.3%) catalysts is similar as that of CeO_2 (18.1%) but MgO and Na additions tend to increase the unsaturated alcohol selectivity for CeO_2 . The production rate of 4-penten-1-ol as a function of time onstream for all catalysts are shown in Figure 7. The production



Figure 7. Rate of 4-penten-1-ol formation over CeO₂ and modified CeO₂ catalysts. Reaction conditions: 350 °C, 1 atm, LHSV = 0.6 ml/h, carrier gas = H_2 (50 sccm), 1.0 g catalyst.

rate of 4-penten-1-ol for CeO₂ was 0.28 mmol/h/g catalyst. Due to a higher conversion, both CeO₂–ZnO and CeO₂–MnO_x were shown a higher productivity compared to CeO₂ though the selectivity to 4-penten-1-ol for all three catalysts were very close. In this context, Na₂O and CaO modified CeO₂ was producing less unsaturated alcohol compared to CeO₂ under similar reaction conditions.

The activity and product selectivity of dehydration of 1,5pentanediol were compared for different catalysts using either H_2 or N_2 as a carrier gas. Figure 8 shows the ratio of linear alcohols to the cyclized product for different catalysts. The

Table 2. Dehydration of 1,5-pentanediol over CeO ₂ and modified CeO ₂ catalysts. ^[a]													
Catalyst	Carrier gas	<i>T</i> [°C]	Conv. [%]	Selectivity [4-P-1-ol	%] 1-P-ol	CyP-ol	CyP-one	THP-2-one	others				
CeO ₂	H ₂	350	44.2	18.1	15.3	5.3	20.7	26.8	13.8				
CeO ₂ –MnO _x	H ₂	350	50.7	17.4	13.2	0.0	30.0	23.8	15.6				
CeO ₂ –ZnO	H ₂	350	58.4	18.3	9.8	19.3	13.9	30.8	7.9				
CeO ₂ –MgO	H ₂	350	31.2	24.1	17.4	7.0	18.8	23.5	9.2				
CeO ₂ –CaO	H ₂	350	18.6	16.4	16.4	6.2	6.6	29.5	24.9				
CeO ₂ –Na ₂ O	H ₂	350	10.8	31.5	23.9	0.0	8.2	27.2	9.2				
CeO ₂	N ₂	350	44.9	16.0	12.4	6.3	26.6	22.8	15.9				
CeO ₂ –MnO _x	N ₂	350	37.9	3.8	6.7	7.6	20.1	12.0	49.8				
CeO ₂ –ZnO	N ₂	350	68.4	15.3	6.2	12.3	12.2	42.0	12.0				
CeO ₂ –MgO	N ₂	350	34.8	21.1	16.4	7.0	23.0	18.1	14.4				
CeO ₂ –CaO	N ₂	350	22.7	16.1	16.2	5.8	7.5	29.4	25.0				
CeO ₂ -Na ₂ O	N ₂	350	10.0	31.0	19.5	0.5	7.8	26.0	15.2				

[a] 4-P-1-ol=4-penten-1-ol; 1-P-ol=1-pentanol; CyP-ol=cyclopentanol; CyP-one=cyclopentanone; THP-2-one=tetrahydropyran-2-one; others=others included ethanol, 1-propanol, 3,4-dihydropyran, 2-methylcyclopentanone, cyclohexane methanol, 4-penten-1-ol propanoate, valeric acid pentenyl ester, cyclohexane carboxylic acid cyclohexyl ester, 2,2-dimethyl 3-octanol.



Figure 8. Effect of carrier gas on the ratio of linear-to-cyclization products formed from 1,5-pentanediol over CeO_2 and modified CeO_2 catalysts.

carrier gas was found to influence the product selectivity obtained using both CeO_2 —MnO_x and CeO_2 —ZnO catalysts. Overall, hydrogen seems to be a better carrier gas than nitrogen from the selectivity point of view (Table 2). It is noticed that the ratio of linear/cyclized products formed during the dehydration reaction on CeO_2 —MgO, CeO_2 —CaO and CeO_2 —Na₂O were well above pure CeO_2 . The positive effect from H₂ on product selectivity could be due to the preference of cerium oxide from oxidation and keeping the cerium in partially reduced state so as to interact with diols.

 CeO_2 is known to have oxygen vacancy with reduced Ce^{3+} sites after the reduction at higher temperatures.^[20] This vacancy site is claimed to be responsible for the activity of dehydration of alcohols. Many suggest that the dissociative adsorption of alcohol is the primary reaction occurs on a vacant site of surface CeO_2 . As shown in Scheme 2, diol tend to undergo cyclization on CeO_2 and form many other side products such as cycloCHEMCATCHEM Full Papers

pentanone, cyclopentanol, tetrahydropyran, tetrahydropyran-2one as all these products are thermodynamically favorable under our reaction conditions. The cyclization of 1,5-pentanediol to tetrahydropyran was accompanied by a loss of water and tetrahydropyran-2-one through H₂ elimination. On the other hand, cyclopentanone could be formed from 1,5pentanediol through 4-peneten-ol or 5-hydroxypentanal intermediate as shown in Scheme 2. It is also possible that cyclopentanone could be formed directly from 1,5-petanediol on ceria. Addition of basic metals on CeO₂ have changed its reduction and oxygen vacancy sites as inferred from H₂-TPR and CO2-TPD. The vacancy sites on CeO2 decreased with addition of MgO, CaO or Na₂O; on the other hand MnO_x and ZnO promote more oxygen vacancy. Therefore, the dehydration activity of 1,5-pentanediol for CeO2-MnOx and CeO2-ZnO catalysts are higher than CeO₂. Also, irrespective of conversion levels these catalysts promote not only the dehydration but also the cyclization route equally. This suggest that addition of MnO_x and ZnO had a positive impact on the activity for dehydration of 1,5-pentanediol whereas MgO, CaO and Na₂O could potentially impact the adsorption sites of CeO₂ for diol.

Conclusions

The addition of MeO_x was found to affect both activity and selectivity of CeO_2 for dehydration of 1,5-pentanediol. BET surface area and pore volume of CeO_2 decreased with addition of MeOx but increased the pore diameter slightly. H₂-TPR reveals that the partial surface reduction of CeO_2 enhanced with addition of ZnO, MnO_{xv} or MgO while CaO and Na₂O additions tend to suppress the conversion. The CO_2 -TPD infers that MeO_x additions to CeO_2 increased the catalyst basicity. The undoped CeO_2 shows dehydration as well as cyclization activity,



Scheme 2. Formation of products from dehydration of 1,5-pentanediol on CeO₂-based catalysts.

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while MgO, MnO_x and ZnO modified CeO₂ increase the productivity of unsaturated alcohol (i.e., 4-penten-1-ol) from 1,5-pentanediol. The oxygen vacancy was generated on CeO₂ by ejecting the adsorbed CO₂ from the reduced Ce³⁺ sites are potentially the adsorption sites for 1,5-pentanediol. The reactivity of 1,5-pentanediol toward the selective formation of unsaturated alcohol depend mostly on the neighboring sites associated with an oxygen vacancy.

Experimental

Catalyst Preparation

The CeO₂ (HSA-10) was obtained commercially from Rhodia. The material was calcined in a static air flow at 500 °C for 4 h. All metal nitrates were purchased from Sigma Aldrich (99.9%). An appropriate amount of metal nitrate (90Ce:10Me) was dissolved in deionized water and further added on to the calcined ceria samples by following the incipient wetness impregnation (IWI) procedure. The catalysts were dried in an oven at 100 °C for 24 h and further calcined in a muffle furnace at 500 °C for 4 h.

Characterization

Powder X-ray diffractograms of CeO₂ and modified CeO₂ catalysts after calcinations were recorded using a Philips X'Pert diffractometer with monochromatic Cu K α radiation (λ =1.5418). XRD scans were taken over the range of 2 θ from 5 to 90°. The scanning step was 0.017°, and the scan speed was 0.042 s⁻¹.

BET surface area and porosity characteristics of the calcined catalysts were measured using a Micromeritics 3-Flex system. Before performing the test, the temperature was gradually ramped to 160 °C from room temperature and the sample was evacuated at this temperature for 12 h to approximately 50 mTorr. The BET surface area, single point pore volume, and single point average pore diameter were obtained for each sample. The Barrett-Joyner-Halenda (BJH) method was also used to estimate pore volume and average pore diameter, as well as to provide pore size distribution as a function of pore radius.

Both H₂-TPR and CO₂-TPD was performed using an in-house system consisting of a furnace capable of operating at temperatures of up to 1200 °C, along with a thermal conductivity detector (TCD, SRI-GC). For H₂-TPR, 10%H₂/Ar at a flow rate of 50 sccm (volume of a gas in cm³/min at 0 °C and 1 atmospheric pressure) was used as a reducing gas mixture and 0.2 g of catalyst sample was heated from 30 to 950 °C at a rate of 5.1 °C/min. In the case of CO₂-TPD, the samples were pretreated at 500 °C in flowing H₂ (50 sccm) for 2 h. The samples were then saturated with pure CO₂ at 30 °C for 1 h and subsequently flushed under He flow to remove the physisorbed CO₂. The CO₂-TPD was performed using He and the temperature was increased from 30 °C to 850 °C at a ramp rate of 6.8 °C/min.

ATR-FTIR spectra were obtained using a Thermo Scientific Nicolet iS-10 FT-IR spectrometer equipped with Attenuated Total Reflection (ATR) element of Smart iTX AR Diamond and an Omnic 5.1 software. Each spectrum averaged from 240 scans collected from 400 to 4000 cm^{-1} at 2 cm⁻¹ resolutions. The experiments run with air as the background and baseline corrections were applied.

Dehydration Activity

The dehydration reaction was carried out using a fixed-bed reactor at 350 °C and atmospheric pressure. Typically, 1.0 g of calcined catalyst in a powder form (40-100 microns) was loaded into the reactor. The reactor is a stainless steel tube having a length of 35.6 cm with an internal diameter of 0.9 cm. The total catalyst bed length is approximately 2.54 cm. The catalyst was pretreated under flowing H_2 (50sccm) at 500 °C for 2 h. The catalyst bed temperature was monitored by a K-type thermocouple (K-type) placed in the middle of a catalyst bed. The catalyst bed temperature was decreased to 350 °C and 1,5-pentanediol (99.9% Sigma Aldrich) was fed at the desired flow rate (0.6 ml/h) using a syringe pump and combined with flowing H_2 or N_2 (50 sccm). The products were collected in a trap maintained at 5°C. 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 in a trap (~5°C) were analyzed using an Agilent 7890 gas chromatograph equipped with a DB-5 capillary column and an FID detector. An appropriate FID response correction factor as published in the open literature was applied for each component found in the reaction mixture.[23

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: $CeO_2 \cdot metal \text{ oxides } \cdot \text{ basicity } \cdot \text{ dehydration } \cdot 1,5-$ pentanediol

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What a site! The defect sites on CeO_2 catalyze both dehydration and cyclization reactions for 1,5-pentanediol. The addition of MeOx was found to affect the defect sites formation over CeO_2 which greatly impact the activity and selectivity of dehydration of 1,5-pentanediol. The CO_2 -TPD and FTIR analyses indicate more CO_2 would remain on the surfaces of ceria after MeOx additions. Moderate basicity is needed for the selective conversion of 1,5-pentanediol to unsaturated alcohol on ceria. Dr. M. K. Gnanamani, Dr. M. Martinelli, Dr. S. Badoga, S. D. Hopps, Dr. B. H. Davis*

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Dehydration of 1,5-Pentanediol over CeO₂-MeOx Catalysts