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Short Communication

Dehydrogenation and Diels–Alder reactions in a one-pot synthesis of benzaldehyde from n-butane over acid catalysts

José-Luis Sánchez-García [a], Ricardo García-Alamilla [b], Marco Martín González-Chávez [a], Brent E. Handy [a], María-Guadalupe Cárdenas-Galindo [a,]*

[a] *CIEP-Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr.Manuel Nava #6, San Luis Potosí, S.L.P. 78210, México*
[b] *División de Estudios de Posgrado e Investigación, ITCM, Juventino Rosas y Jesús Urueta S/N, Cd. Madero, Tamps. 89440, México*

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ABSTRACT

VOx/ZrO_2/SiO_2 catalysts were synthesized via grafting of vanadium and zirconium alkoxides over Aerosil 380. With these materials the formation of benzaldehyde from butane was possible in a one-pot synthesis, where oxidative dehydrogenation (ODH) for the formation of butadiene is coupled with a Diels–Alder reaction for the formation of benzaldehyde. Experiments performed with a catalyst where the support was modified with Ce instead of Zr, give a material that under the reaction conditions studied does not yield benzaldehyde, showing that acidity plays an important role in the formation of this compound.

1. Introduction

Benzaldehyde (BZ) is an aromatic aldehyde widely used in the food industry as a flavoring agent, and in the cosmetics and personal care products as a fragrance [1]. Even when it is extracted from natural sources, most of the benzaldehyde for industrial application stems from the chlorination and oxidation of toluene. These processes either require the use of organic solvents, which are not environmentally friendly, or may produce a chlorine contaminated benzaldehyde that is not acceptable in the pharmaceutical and food industries [2].

There is an ongoing search for alternative technologies with special emphasis in the partial oxidation of benzyl alcohol and styrene oxidation [3–5]. Nevertheless, there is not a process yet that can be industrially scaled to satisfy the requirements of the food and pharmaceutical industry.

In this work, we explore an alternative for the production of benzaldehyde based on the use of n-butane as starting material. Use of n-butane as a feedstock has been studied and used for several applications that involve partial oxidation and oxidative dehydrogenation reactions (ODH) [6,7]. The catalytic production of olefins from alkanes using ODH is a very attractive process that offers the possibility of reducing the energy consumption in the reactor, where the energy demands of the ODH are satisfied by the heat released in the alkane oxidation. With the right type of catalyst the selectivity to olefins could be favored over CO y CO_2 formation, making possible the conversion of n-butane to butadiene with high yield. Controlling the reaction conditions, it might be possible to produce also compounds that could act as a dienophile in a cycloaddition reaction, such as the Diels–Alder, with the butadiene as the conjugated diene, making possible the formation of compounds containing an unsaturated six-membered ring. If the catalyst shows selectivity to the formation of acrolein, the reaction product will be an aldehyde that via oxidative dehydrogenation produces benzaldehyde. A similar approach has been suggested by Izawa et al. [8] for the production of phenols using a catalyst for dehydrogenation, but starting with the Diels–Alder reaction. In this work we show that it is possible to start with the alkane and in one pot reaction to produce the aromatic molecule with the aid of a catalyst.

Acid properties as well as particle size of the catalyst play an important role on both catalytic activity and selectivity. In this regard, ZrO_2 is an interesting material because of its acidic properties, and if V is supported on it, the production of olefins from butane is observed [9,10]. However, bulk ZrO_2 has a low surface, but a non-acidic material such as SiO_2 can be used as a support to increase the surface area. For this work the catalysts were prepared with V supported on Zr grafted on SiO_2; for comparison purposes, non-acidic materials were prepared with Ce instead of Zr.

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* Corresponding author at: CIEP-Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava #6, Zona Universitaria, San Luis Potosí, S.L.P. 78210, México. Tel.: +52 444 826 2440; fax: +52 444 826 2372.
E-mail address: cardenas@uaslp.mx (M.-G. Cárdenas-Galindo).

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2. Experimental

2.1. Catalyst synthesis

Catalysts 10 VZrS and 20 VZrS: ZrO_2–SiO_2 mixed oxide supports were prepared by contacting an appropriate amount of Zirconium(IV) n-butoxide (Aldrich, 80%) with 473 K dried, pure silica (Degussa, Aerosil 380 m^2/g) to give surface Zr densities of 4 and 8 atom Zr/nm^2. During this procedure the solid powder was maintained 12 h continuously immersed and stirred under toluene reflux at room temperature. The solids were then dried and calcined in flowing oxygen at 673 K for 8 h, before contacting with vanadyl (V) triisopropoxide (Alfa Aesar, 98%) to achieve 4 wt % V loading. This procedure was analogous to that used with the Zr grafting procedure described, but using isopropanol as the solvent, maintaining reflux at 333 K for 12 h, and finally drying and calcining the solid at 823 K for 8 h.

Catalysts VCeGS and VCeIS: In both preparations, CeO_2-SiO_2 supports were synthesized such that the Ce surface density corresponded to 5 atom/nm^2. In the first preparation, an appropriate amount of Cerium (IV) isopropoxide (Alfa Aesar) was contacted with the dried Aerosil silica immersed in isopropanol under continuous stirring and reflux at 343 K for 24 h, left to dry overnight, and calcined at 823 K under flowing oxygen for 8 h. In the VCeIS preparation, the silica powder was wet to incipient wetness with an appropriate concentration of aqueous cerium ammonium nitrate solution (Mallincrodt Baker), dried overnight at 373 K, and calcined at 823 K. In a second step, the vanadium grafting procedure described above with the Zr catalysts was applied to obtain the VCeGS and VCeIS catalysts.

2.2. Catalyst characterization techniques

Specific surface area and micropore volumes were determined with nitrogen isotherms at 77 K using a homemade volumetric adsorption apparatus equipped with precision capacitance manometers and capable of achieving 10^{-6} Torr under dynamic pumping. Prior to obtaining adsorption isotherms, samples were degassed (10^{-3} torr) at 473 K for 2 h. BET and t-plot analysis were conducted on at least ten points obtained in the 0.01–0.40 p/p_o range. X-ray diffraction (XRD) patterns were obtained using a X'pert PRO (PANalytical) automated diffractometer system, using Cu Kα radiation ($\lambda = 0.15405$ nm, 35 kV, 30 mA) and collecting data in the $5° < 2\theta < 80°$ range. Ammonia adsorption microcalorimetry was conducted at 473 K on a homemade Tian–Calvet calorimeter whose design and operation have been described elsewhere [11]. In brief, 0.2 g sample sizes were previously degassed under vacuum (10^{-5} torr) at 623 K to achieve a leak rate no greater than 10^{-4} torr/min at that temperature, before inserting the cells in the calorimeter and stabilizing the heat flow baseline. Ammonia gas doses of 10 μmol/g were admitted in succession onto the sample, allowing sufficient time (ca. 30 min) for each dose to achieve thermal equilibrium before proceeding with the next dose. This procedure was continued up to a saturation pressure of at least 3 torr NH_3, obtaining both isotherm and differential heat of adsorption data. For acidity comparison purposes, important NH_3 adsorption site densities are those that correspond to adsorption heats greater than 60 kJ/mol.

2.3. Catalytic activity

The catalytic activity for the conversion of n-butane to ODH, partial oxidation and cycloaddition products was evaluated in a continuous flow quartz reactor at ambient pressure. Reactant and product concentrations were measured on-line with gas chromatography (Chromepak MicroGC, TCD detector, CPSil-5 and Hayesep-A columns). Product gases were also collected via a sampling bulb and analyzed with a Selective Mass Detector 5973 Network coupled with a 6890 N GC system (Agilent Technologies). The catalyst charge of 100 mg was pretreated at 823 K in flowing oxygen for 60 min, followed by cooling to 673 K. The feedstock composition was kept at 10 vol % of n-butane and 90 vol % of O_2/He (molar ratio of 5/95) and a total flow rate of 100 cm^3 NTP/min using mass flow controllers. Butane conversion was determined according to:

$$\%X_{nC4} = (\text{moles } nC_4 \text{ consumed}/\text{moles } nC_4 \text{ in feed})\cdot 100$$

while the selectivity to reaction products was calculated as follows:

$$\%Si = (v_{nC4}/v_i).(\text{moles product I}/\text{moles } nC_4 \text{ consumed})\cdot 100$$

where v_{nC4} and v_i are, respectively, the stoichiometric factors of nC_4 and the product I, in the reaction $nC_4 \rightarrow I$.

With mass spectroscopy, traces of other compounds were detected, which included acrolein, benzene, 2-propenoic acid, formic acid, and acetic acid.

3. Results and discussion

3.1. Catalyst and support characterization

Table 1 summarizes the composition of each catalyst and the BET surface areas calculated from the N_2 physisorption data. After grafting/impregnation, all the surface areas experienced an area reduction (up to 55%) from the original Aerosil (380 m^2/g). For the Zr materials, the X-ray diffraction pattern shows only the amorphous nature of pure silica in the 10 VZrS material, suggesting that with the grafting method, high dispersions of zirconium and vanadium species on the surface were achieved (Fig. 1). In contrast, the 20 VZrS diffraction pattern shows peaks at 30°, 50° and 60° that are characteristic of tetragonal zirconia crystals, however there is no evidence of a vanadium oxide crystalline phase present, implying that vanadium is well dispersed over the modified support. The literature shows that at the calcination temperature used for this work, the formation of a stable vanadium oxide monolayer is expected over the ZrO_2, and since the affinity of V for Zr is higher than for Si, most of the vanadium oxide must be confined to the ZrO_2 in the mixed oxide [12]. For the Ce materials, VCeGS and VCeIS, X-ray diffraction shows the presence of CeO_2 crystals. Additionally, in the VCeGS it shows also the presence of $CeVO_4$. This compound is the product of a solid state reaction that can occur between highly dispersed vanadium and cerium at temperatures above 500 °C [13]. The $CeVO_4$ formed during calcination (550 °C) and it was favored by the grafting method. As in the zirconium catalysts, vanadium oxide crystals were not detected. It is expected that the vanadium that is not part of $CeVO_4$ must be interacting mainly with the CeO_2, since the vanadia–silica interactions are very weak [13,14].

The microcalorimetry data at 200 °C show differential heat values ≤100 kJ/mol for all the materials (Fig. 2). These values are lower than those reported by other researchers for ammonia adsorption over pure ZrO_2, which typically are as high as 180 kJ/mol [15]. The heat values for V/SiO_2 are usually lower and dependent on the vanadium loading, with the highest values (100 kJ/mol) determined for materials with crystalline V_2O_5. For highly dispersed vanadium, as in the materials studied here, the differential heat of adsorption is below 60 kJ/mol [15]. Since the values measured in this work are between those of pure ZrO_2 and those for highly dispersed V/SiO_2, the V must be moderating the acidity of Zr, resulting in a less acidic material

Table 1
Synthesized catalysts and BET surface area of zirconium and cerium catalysts.

Catalyst	Zr (nm^{-2})	Ce (nm^{-2})	BET area (m^2/g)	V micro (cm^3/g)
10 VZrS	4	0	239	0.011
20 VZrS	8	0	266	0.014
VCeGS	0	5	168	0
VCeIS	0	5	230	0

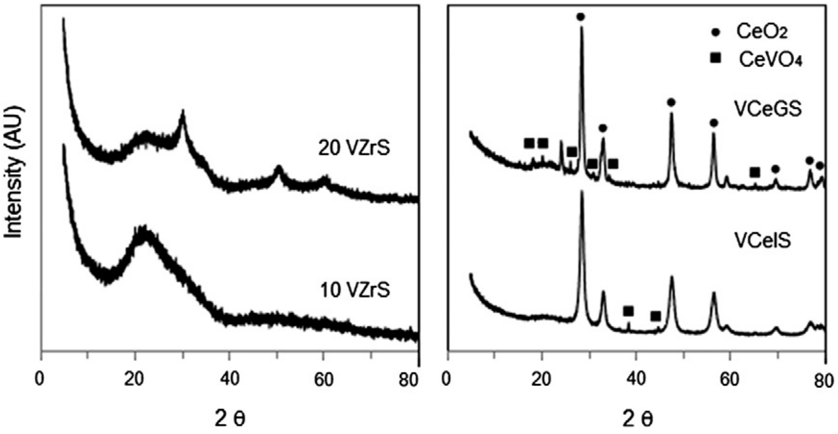


Fig. 1. X-ray diffraction patterns of silica modified with V and Zr (left), and V and Ce (right).

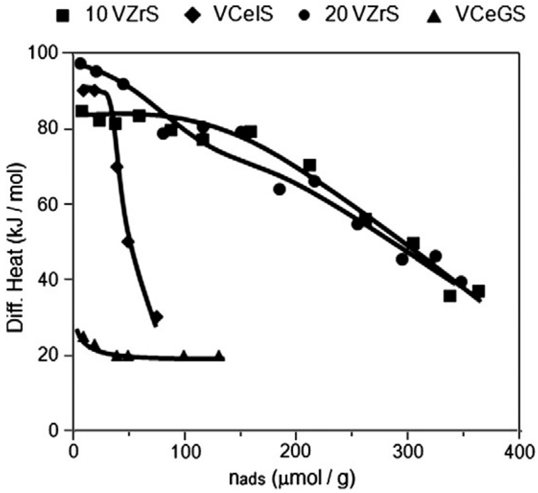


Fig. 2. Differential heat of ammonia adsorption in all catalysts.

than pure ZrO_2. However, the moderating effect diminishes as the V/Zr ratio decreases, resulting in more sites with stronger acidity (100 kJ/mol for 20 VZrS vs 80 kJ/mol for 10 VZrS), but still weaker than for pure ZrO_2.

According to the literature pure ceria is an amphoteric material, with differential heats of ammonia adsorption in the vicinity of 200 kJ/mol [16]. As with the Zr materials, inspection of Fig. 2 shows that the addition of V has a strong influence in the acidity of the support, with a stronger effect when V is grafted on the mixed oxide, causing the disappearance of its acid character. The formation of the $CeVO_4$ is partially responsible for this, while the overlayer of V on the CeO_2 modifies the characteristics of this phase hampering its acidity. In contrast, stronger acid sites are observed on VCeIS, and since no crystalline V_2O_5 is observed with XRD, they may not be related to V/SiO_2 sites [16,17], but to the CeO_2 phase formed after impregnation that, unlike with the grafting preparation, in this case shows acid character. It has been documented that well dispersed vanadia on CeO_2 materials prepared with wetness impregnation shows significant acidity, but the strength is a function of calcination temperature, with a tendency to lower surface acidity as the temperature increases [18] and with values similar to those reported here. The interaction between vanadia–silica is generally considered to be weaker than vanadia–zirconia or vanadia–ceria interactions [19,20].

3.2. Catalytic activity results

All the catalysts modified with V exhibited activity for dehydrogenation and oxidation reactions, with their selectivity shown in Fig. 3. Gas chromatography detected important quantities of c-2-butene, t-2-butene, CO, and CO_2. The concentrations of these products, combined with those of 1,3-butadiene and benzaldehyde, correspond to more than 95% of the total carbon balance (see Table 2). Trace amounts of acrolein and other compounds (benzene, toluene, 2-butenal, 2-propenoic acid, formic acid and acetic acid) were detected with mass spectrometry. Butane dehydrogenation products were formed over all

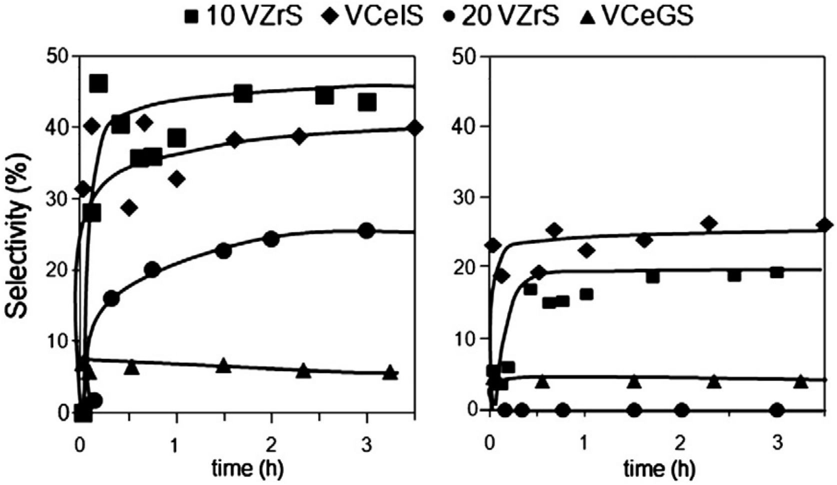


Fig. 3. Catalytic activity results for all catalysts on the ODH of n-butane: a) selectivity to 1,3 butadiene and b) selectivity to benzaldehyde.

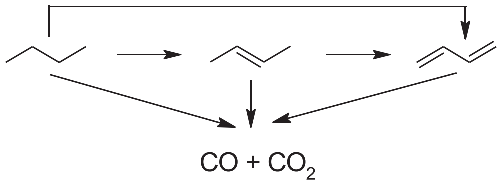
Table 2
Conversion and selectivity to dehydrogenation products and COx.

Catalyst	X $_{Butane}$ (%)	S $_{Butadiene}$ (%)	S $_{Benzaldehyde}$ (%)	S $_{Butenes}$ (%)	S $_{CO}$ (%)	S $_{CO2}$ (%)
V/SiO$_2$	4.2	3.2	0	0	23	71
V/ZrO$_2$	11	7	0	66.4	8.2	14.3
10 ZrS	16.8	0	0	0	62	22
10 VZrS	15	44	20	6	6	7
20 VZrS	5	25	0	17.5	30	21.5
VCeGS	11	6	4	0	29	35
VCeIS	7	40	27	12	10	1.4
	5	10	0	48	33	8
	3.6	7.4	0	26.2	53	11

the catalysts with exception of the vanadium-free catalyst, 10 ZrS, where the activity was higher but only with production of CO and CO$_2$. V/SiO$_2$ and VCeGS showed activity for the formation of butadiene but the butenes were not detected, suggesting that butadiene can be formed directly from butane. Benzaldehyde production was observed only over 10 VZrS and VCeIS, which were the catalysts maintaining the highest selectivity to butadiene and lowest selectivity to CO and CO$_2$. For the catalyst that showed the highest selectivity to benzaldehyde, VCeIS, the effect of conversion on selectivity was studied at lower conversion levels by using smaller amounts of catalyst. Benzaldehyde was not observed at the lower conversion levels, with butadiene selectivity decreasing and the butenes selectivity increased.

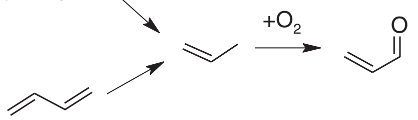
3.3. Mechanistic considerations

The activity/selectivity results suggest that n-butane over these catalysts is dehydrogenated to butadiene in consecutive reactions. At the reduced conversion levels an increment in the selectivity to CO and CO$_2$ was also observed. This can be explained if two competitive reactions occur, one being a dehydrogenation path, the second a path for oxidation products. All these results are consistent with the following reaction scheme,

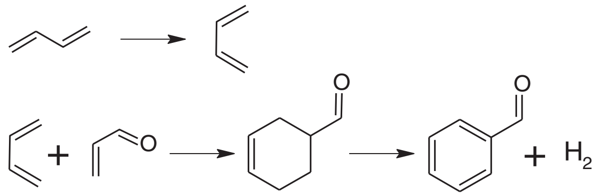


This network has been suggested to explain the oxidative dehydrogenation of n-butane over acid catalysts without strong acid sites [21]. Acidic sites are also required for formation of butadiene, explaining the lower yield of this product over VCeGS, which the microcalorimetry results have shown to be an essentially non-acidic material. For the reaction conditions used in this work, dehydrogenation activity is apparent as long as catalytic material shows some degree of acidity.

The presence of formic acid, acetic acid, and acrolein makes evident that some degree of cracking occurred as well as partial oxidation reactions. The cracking of 1,3-butadiene and of butane isomers to propylene has been reported over vanadium based catalysts [22], and the formation of acrolein from propylene has been observed over vanadium based catalysts [23]. This suggests the following reaction network:



Upon formation, the acrolein immediately reacts with the butadiene in a Diels–Alder reaction



I

The selectivity to butadiene is higher than for acrolein, the latter becoming the limiting reactant in the Diels–Alder reaction. All the 3-cyclohexene-1-carboxaldehyde (I) formed in this reaction is dehydrogenated to benzaldehyde since no traces of this compound are detected with the experimental setup. On VCeGS, the low selectivity to benzaldehyde (4%) is the result of a high selectivity for the formation of COx with this material (64%). The lack of acidity precludes appreciable butane dehydrogenation; however, total oxidation reactions lead to an overall conversion that is larger than with VCeIS, implying a stronger oxidative ability of the Ce species in the VCeGS than in the VCeIS. On the other hand, small differences in number and strength of acid sites may explain the lack of selectivity to benzaldehyde observed with the 20 VZrS: compared with 10 VZrS, there are about 50 mmol/g sites of higher differential heats of adsorption (>80 kJ/mol) that may favor the formation of COx over partial oxidation products such as acrolein (see Table 2). Since the formation of butenes is not observed with VCeGS, and butadiene is formed in very small quantities (≅5% selectivity), the oxidative dehydrogenation reactions on this material are reduced to total oxidation reactions

The selectivity to benzaldehyde is higher with 10 VZrS and VCeIS, catalysts where the presence of acid sites of moderate strength favors the dehydrogenation reactions, and does not favor total oxidation reactions over the formation of acrolein.

4. Conclusions

This work shows the feasibility of having a process for the production of benzaldehyde from a chlorine free feedstock, coupling a Diels–Alder reaction with the ODH of n-butane. This one-pot synthesis is possible over catalysts that favor the formation of dehydrogenation products of butane to produce butadiene, and partial oxidation products to form acrolein. The butadiene acts as a diene in a Diels–Alder reaction with the acrolein, the dienophile, to form 3-cyclohexene-1-carboxaldehyde that goes through a consecutive dehydrogenation to form benzaldehyde. The use of an acid catalyst is essential for this reaction to produce butadiene and acrolein, but strong acidity prevents the formation of benzaldehyde as a result of the production of COx instead of acrolein.

Experimental results indicated that grafted vanadium over modified silica with Ce and Zr were active catalysts for benzaldehyde synthesis from n-butane.

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